Can Organometallic Noble Gas Compounds Be Observed in Solution at Room Temperature? A Time-Resolved Infrared (TRIR) and UV Spectroscopic Study of the Photochemistry of $M(CO)_6$ (M = Cr, Mo, and W) in Supercritical Noble Gas and CO_2 Solution

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Abstract: The first systematic TRIR study of the photolysis of $M(CO)_6$ in supercritical Ar, Kr, Xe, and CO_2 permits the observation of $M(CO)_5L$ (M = Cr, Mo, and W; L = Ar (W only), Kr, Xe, and CO_2). The second-order rate constants for the reaction of $M(CO)_5L$ with CO have been evaluated and the reactivity for each metal is Kr > Xe ≈ CO_2. For $M(CO)_5Kr$, $M(CO)_5Xe$, or $M(CO)_5(CO_2)$ the reactivity is Cr ≈ Mo > W. In supercritical Kr doped with either Xe or CO_2, the $M(CO)_5$ moiety interacts with Xe or CO_2 in preference to Kr. The effect of solvent density on the rate of the reaction of $W(CO)_5(CO_2)$ with CO has been investigated. This is the first time that the density dependence of any dissociative reaction has been followed in this way in supercritical solution. Our observations demonstrate that the reaction of $W(CO)_5(CO_2)$ with CO in $scCO_2$ is predominantly a dissociative process. The activation energies for the reaction of $W(CO)_5Xe$ and $W(CO)_5(CO_2)$ with CO and the relative wavelength of the visible absorption maxima for $Cr(CO)_5Xe$ and $Cr(CO)_5(CO_2)$ all indicate a similar strength of interaction for Xe and CO_2 with the $M(CO)_5$ moiety.

Introduction

Sixteen-electron coordinatively unsaturated metal carbonyl intermediates are highly reactive even toward seemingly inert molecules.[1] In low-temperature matrices, Perutz and Turner showed[2] that $M(CO)_5$, generated by photolysis of the group 6 hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, and W), could interact with ligands normally considered to be inert, including CF_4, SF_6, CH_4, Ar, Kr, and Xe. These interactions were deduced from blue shifts in λ_{max} of the visible absorption band of $M(CO)_5L$; the greater the shift, the stronger the interaction. Subsequently, Downs and co-workers[3] characterized $M(CO)_5(CO_2)$ for Cr and W in Ar matrices doped with CO_2 at 10 K. In solution, $Cr(CO)_5$(cyclohexane) was found to be formed within 50 ns of UV flash photolysis of $Cr(CO)_6$ in room temperature cyclohexane solution,[4] and subsequently picosecond UV/visible spectroscopy has shown that the solvation process for $Cr(CO)_5$ occurs *within the first picosecond* following irradiation.[5]

The coordination of a solvent molecule to photochemically generated metal carbonyl 16-electron intermediates[6] has now been observed for almost all of the metal carbonyl compounds studied by flash photolysis and the coordinated solvent has been termed the “token ligand”.[6,7] Nevertheless, solvated 16-electron intermediates have lifetimes which can vary considerably; for example, $CpV(CO)_3$(*n*-heptane)[8] has a lifetime ($1/k_{obs}$) of ca. 300 ns in *n*-heptane at room temperature while the lifetime of $CpRe(CO)_2$(*n*-heptane)[9] is ca. 1.5 × 10^7 ns (15 ms) under similar conditions. Thus, the coordination of even more weakly interacting ligands, such as Xe, cannot be studied in alkane solution, since the alkane interacts more strongly with the metal center than does the Xe. However, the coordination of Kr and Xe has been probed experimentally in two different environments: in the gas phase, where there are no solvent molecules to interact with the metal, or in liquefied noble gases (lKr or lXe), where the coordinating ligand is also the solvent. Thus, Simpson *et al*. observed[10] $Cr(CO)_5Xe$ using FTIR spectroscopy in lXe (−98 °C) and in |Kr doped with Xe (−122 °C) providing the first evidence for the formation of rare-gas complexes with significant lifetime in solution. Weiller[11] was able to detect $M(CO)_5L$ (M = Cr, W; L = Xe, Kr) in lXe and lKr using rapid-scan FTIR. Similarly, Bergman and co-workers identified $CpRh(CO)L$ (L = Kr, Xe)[12] in liquefied noble gas solution at cryogenic temperatures. Using the Arrhenius parameters for the reaction of $W(CO)_5Xe$ with CO, Weiller estimated the

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(1) Perutz, R. N. *Chem. Soc. Rev.* **1993**, *22*, 361.

(2) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

(3) Almond, M. J.; Downs, A. J.; Perutz, R. N. *Inorg. Chem.* **1985**, *24*, 275.

(4) Bonneau, R.; Kelly, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 1221.

(5) Simon, J. D.; Xie, X. J. *J. Phys. Chem.* **1986**, *90*, 6751. Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876.

(6) Dobson, G. R.; Hodges, P. M.; Healy, M. A.; Poliakoff, M.; Turner, J. J.; Firth, S.; Asali, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 4218.

(7) Bengali, A. A.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1995**, *117*, 3879.

(8) 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.

(9) George, M. W.; Nikiforov, S. M. *J. Chem. Soc.*, Dalton *Trans.* Submitted for publication.

(10) Simpson, M. B. Poliakoff, M.; Turner, J. J.; Maier, W. B.; McLaughlin, J. G. *J. Chem. Soc., Chem. Commun.* **1983**, 1355.

(11) Weiller, B. H. *J. Am. Chem. Soc.* **1992**, *114*, 10910.

(12) Schultz, R. H.; Bengali, A. A.; Tauber, M. J.; Weiller, B. H.; Wasserman, E. P.; Kyle, K. R.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 7369. Bengali, A. A.; Schultz, R. H.; Bergman, R. G.; Moore, C. B. *J. Am. Chem. Soc.* **1994**, *116*, 9585.

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W−Xe bond strength to be 8.2 ± 0.2 kcal/mol, in excellent agreement with Weitz's[13] estimate of the W−Xe bond strength from fast time-resolved infrared (TRIR) measurements in the gas phase (8.4 ± 1.0 kcal/mol), where reaction of $W(CO)_5Xe$ is necessarily dissociative.

The application of TRIR studies in the gas phase has been limited mainly to group 6 hexacarbonyl compounds, largely because the compound under study must have a relatively high vapor pressure; a range of $M(CO)_5L$ complexes have been identified by this method: M = Cr, L = H_2,[14] C_2H_4,[14,15] C_6F_6,[14] CH_4;[14] M = Mo, L = Xe;[13] M = W, L = Xe,[13] Kr,[13] Ar,[13] CF_2Cl_2,[16] N_2O,[17] CH_4,[18] CF_4,[18] CH_3F,[18] CH_2F_2,[18] CHF_3,[18], C_2H_5F,[18] H_2,[19] CO_2.[20] The $W-CO_2$ bond energy is of particular relevance to this paper. It has been estimated[20] by Fu and co-workers as 8.0 ± 1.0 kcal/mol, a value identical to that estimated by Weitz and co-workers[13] for the *W−Xe* bond strength.

In this paper we report the use of TRIR in supercritical fluids, a new technique, which offers a general route to studying the interaction of weakly coordinating ligands in solution at, or above, ambient temperature. Supercritical fluids exhibit properties which are a curious hybrid of those of gases and liquids and, like liquids, they can dissolve a wide range of compounds.[21] Many gases have a critical temperature, T_c, close to ambient, particularly Xe (T_c = 16.8 °C, critical pressure (P_c) = 58 atm) and CO_2 (T_c = 31.6 °C, P_c = 73 atm). Furthermore, supercritical nobles gases are ideal solvents for TRIR since they are completely transparent throughout the IR region. Supercritical CO_2 ($scCO_2$) is an excellent solvent to study the interaction of CO_2 with metal centers, because it offers the highest possible concentration of CO_2. More generally, supercritical fluids are attractive media for chemical reactions because the density of the solvent can be varied over a wider range than is possible with more conventional solvents. Other properties (e.g. viscosity, dielectric constant, diffusivity, mass transport) vary with density, which is a strong function of temperature and pressure near the critical region. Recently there has been considerable interest in changing chemical selectivity and reaction kinetics in supercritical fluids.[22] In this paper, we report the TRIR observation and stability of $W(CO)_5Ar$, $M(CO)_5Kr$, $M(CO)_5Xe$, and $M(CO)_5(CO_2)$ (M = Cr, Mo, and W), at, or above, ambient temperature in supercritical Ar, Kr, Xe, and CO_2 respectively. In addition, we used fast UV/visible spectroscopy to relate our results to previous matrix isolation data.

Experimental Section

The Nottingham TRIR apparatus has been described in detail elsewhere.[23] Briefly it consists of a pulsed UV source, either an Excimer laser (Lumonics HyperEx 440, 308 nm) or a Nd:YAG laser (Quanta-Ray GCR-11; 355 nm, 7 ns pulse), to initiate photochemical reactions, and cw IR lasers, Mütek IR diode laser (Model MDS 1100), to monitor the transient IR absorptions. The change in IR transmission at one particular IR frequency is measured following excitation and IR spectra are build up on a "point-by-point" basis by repeating this measurement at different IR frequencies. The TRIR spectrometer has an effective resolution of ±1 cm^{-1}. Each data point is recorded following a single laser pulse. The stainless steel cell used for supercritical TRIR measurements is identical to that described previously for conventional spectroscopic monitoring.[24] For TRIR experiments, the cells were used with CaF_2 windows, sealed with indium gaskets rather than epoxy cement, and with an RDP Electronics pressure transducer. Heating was achieved with an external aluminium jacket containing cartridge heaters. Changes in UV/visible absorption were measured in a "point-by-point" fashion, following irradiation (308 nm), using an Applied Photophysics Xe arc Lamp, monochromator, and photomultiplier. For these UV/visible experiments, the UV laser beam entered the cell through the CaF_2 windows and the solution was probed at 90° through two silica light guides, ca. 1.6 mm diameter. $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$ (Aldrich), Ar, Kr, and Xe (BOC Research Grade) were used as supplied. CO_2 (Air Products, SFC Grade) was dried over molecular sieve prior to use. Where a mixture of gases was used, the individual gases were added into the cell sequentially. The pressures quoted for each gas in the text refer to the *total* pressure in the cell after the addition of that gas.

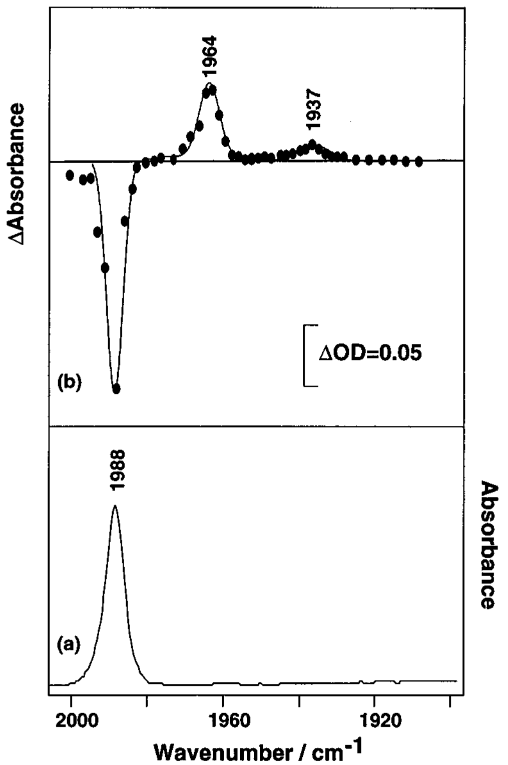

Figure 1. (a) FTIR spectrum of $W(CO)_6$ in scXe (1050 psi, 24 °C) in the presence of CO (30 psi). (b) TRIR *difference* spectrum obtained 100 ns after photolysis (355 nm) of the same solution. The positive peaks are assigned to $W(CO)_5Xe$, see text.

Results and Discussion

(a) Identification and Reactivity of $W(CO)_5Xe$ in scXe Solution. Figure 1a shows $W(CO)_6$ dissolved in scXe in the presence of 30 psi of CO. Figure 1b shows the TRIR spectrum obtained 100 ns following 355-nm excitation of this solution; the parent absorption is bleached and two new absorptions are produced which can be readily assigned to $W(CO)_5Xe$ by comparison with matrix isolation results,[2] data from liquefied

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(13) Wells, J. R.; Weitz, E. *J. Am. Chem.* **1992**, *114*, 2783.

(14) Wells, J. R.; House, P.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 8343.

(15) McNamara, B.; Becher, D. M.; Towns, M. H.; Grant, E. R. *J. Phys. Chem.* **1994**, *98*, 4622.

(16) Bogdan, P. L.; Wells, J. R.; Ryther, R. J.; Weitz, E. *J. Am. Chem. Soc.* **1991**, *113*, 1294.

(17) Weitz, E.; Wells, J. R.; Ryther, R. J.; House, P. *ACS Symp Ser.* **1993**, *530*, 147.

(18) Ishikawa, Y.; Brown, C.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1988**, *150*, 506. Brown, C.; Ishikawa, Y.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 2530.

(19) Ishikawa, Y.; Weersink, R. A.; Hackett, P. A.; Rayner, D. M. *Chem. Phys. Lett.* **1987**, *142*, 271.

(20) Zheng, Y.; Wang, W.; Lin, J.; She, Y.; Fu, K. J. *Chem. Phys. Lett.* **1993**, *202*, 148.

(21) Poliakoff, M.; Howdle, S. M.; Kazarian, S. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1275.

(22) Roberts, C. B.; Zhang, J.; Chateauneuf, J. E.; Brennecke, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 6553 and references therein.

(23) George, M. W.; Poliakoff, M.; Turner, J. J. *Analyst* **1994**, *119*, 551.

(24) Howdle, S. M.; Poliakoff, M. In *Supercritical Fluids—Fundamentals for Applications*; Kiran, E., Levelt Sengers, J. M., Eds.; Kluwar Academic Publishers: Dordrecht, The Netherlands, 1993; 273, p 527.

Table 1. Wavenumbers (cm^{-1}) of M(CO)$_5$L Species (M = W, L = Ar, Kr, Xe; M = Cr, L = H$_2$O) in Supercritical Fluid (sc), Gas Phase (g), Liquid (l), and Cryogenic Matrices (mx)

M(CO)$_5$L		wavenumber (cm^{-1})		condition	ref
Cr(CO)$_6$		1995		scKr	this work
Cr(CO)$_6$		1991		scXe	this work
Cr(CO)$_6$		1988		scCO$_2$	this work
Cr(CO)$_5$Kr		1969	1945	scKr	this work
Cr(CO)$_5$Xe		1956	1929	Ar/Xe (Mx)20 K	34
		1964	1938	scXe	this work
		1979		(g) 298 K	14
Cr(CO)$_5$(CO$_2$)		1955	1922	scCO$_2$	this work
Cr(CO)$_5$(H$_2$O)		1946	1916	cyclohexane 298 K	35
Cr(CO)$_5$(*n*-heptane)		1960	1938	*n*-heptane 298 K	25
Mo(CO)$_6$		1996		scKr	this work
Mo(CO)$_6$		1993		scXe	this work
Mo(CO)$_6$		1990		scCO$_2$	this work
Mo(CO)$_5$Kr		1977	1938	scKr	this work
Mo(CO)$_5$Xe		1962	1928	Ar/Xe (Mx)	34
		1972	1939	scXe	this work
		1982		(g) 298 K	14
Mo(CO)$_5$(CO$_2$)		1965		scCO$_2$	this work
Mo(CO)$_5$(*n*-heptane)		1969	1931	*n*-heptane 298 K	25
W(CO)$_6$		1992		scAr	this work
W(CO)$_6$		1990		scKr	this work
W(CO)$_6$		1988		scXe	this work
W(CO)$_6$		1985		scCO$_2$	this work
W(CO)$_5$(Ar)		1970	1935	Ar (Mx) 20 K	3
		1972	1941	scAr 298 K	this work
W(CO)$_5$Kr		1983		(g) 298 K	13
		1962	1933	lKr 150 K	13
		1969	1939	scKr 298 K	this work
W(CO)$_5$Xe		1975		(g) 298 K	13
		1953	1927	Xe/Ar (Mx) 20 K	34
2090	2090	1958	1930	lXe 170 K	11
		1963	1936	lKr 183 K	11
		1964	1937	scXe 298 K	this work
W(CO)$_5$(CO$_2$)		1970	1942	(g) 298 K	20
		1956	1926	Ar/CO$_2$ (Mx) 20 K	3
		1957	1930	lKr/CO$_2$ 198 K	36
		1954	1924	scCO$_2$ 308 K	this work
W(CO)$_5$(*n*-heptane)		1958	1929	*n*-heptane 298 K	25

noble gas,[10,11] and gas-phase TRIR experiments[13] (see Table 1). The formation of W(CO)$_5$Xe is reversible; the two bands decay fully to reform W(CO)$_6$ with no observable secondary photoproducts. The regeneration of W(CO)$_6$ is demonstrated more clearly in Figure 2 which shows the relevant TRIR kinetic decay traces; W(CO)$_6$ is reformed within 40 μs at a rate (k_{obs} = 1.6 ($\pm$0.4) $\times$ 10^5 s^{-1}) which is identical within experimental error to the rate of decay of W(CO)$_5$Xe (k_{obs} = 1.8 ($\pm$0.4) $\times$ 10^5 s^{-1}).

(b) Activation Parameter for the Decay of W(CO)$_5$Xe in scXe. Under these conditions, CO and scXe are completely miscible over quite a wide temperature range, which greatly simplifies variable-temperature studies. Figure 3a shows the temperature dependence of the rate of decay of W(CO)$_5$Xe in scXe in the presence of 30 psi of CO and the corresponding Arrhenius plot is shown in Figure 3b. The activation energy obtained, 8.2 ($\pm$0.2) kcal/mol, is identical to the W−Xe bond strength obtained by Weitz and co-workers[13] from TRIR measurements in the gas phase (8.4 kcal/mol) and to that found by Weiller[11] from Arrhenius data for the reaction of W(CO)$_5$Xe with CO at low temperature in lXe (8.2 kcal/mol). This agreement suggests that the reaction between W(CO)$_5$Xe and CO in scXe occurs mainly through a dissociative mechanism.

Thus, we are in a position to compare directly the reactivity toward CO of W(CO)$_5$Xe and W(CO)$_5$(*n*-heptane) in fluid solution at room temperature. Surprisingly, W(CO)$_5$Xe is less than twice as reactive as W(CO)$_5$(*n*-heptane); the second-order rate constant (k_2) for reaction with CO is 2.0 ($\pm$0.6) $\times$ 10^6 mol^{-1} dm^3 s^{-1} for W(CO)$_5$Xe in scXe and 1.2 ($\pm$0.1) $\times$ 10^6 mol^{-1} dm^3 s^{-1} for W(CO)$_5$(*n*-heptane) in heptane.[25] By contrast, the W−Xe bond dissociation energy (8.2 kcal/mol) is nearly 7 kcal/mol lower than the value of the W−heptane bond dissociation energy (15 kcal/mol) as measured by photoacoustic calorimetry.[26] Ignoring entropy, a difference in activation energy of 7 kcal/mol should lead to a reduction in the rate of a dissociative process by a factor greater than 1000. The discrepancy between reactivity and bond energies could be rationalized if W(CO)$_5$(*n*-heptane) were reacting with CO in *n*-heptane via a process which is not purely dissociative. Work by Long and co-workers[27] has provided experimental results consistent with this suggestion.

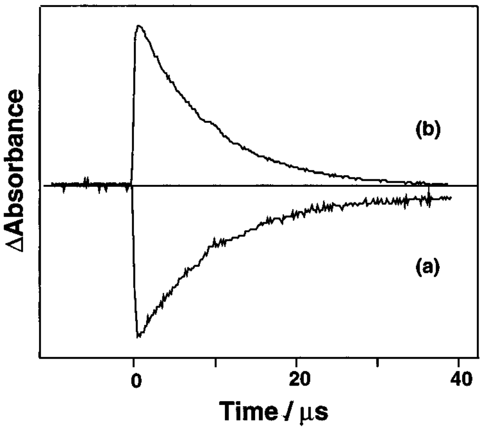

Figure 2. TRIR trace recorded following irradiation (355 nm) of W(CO)$_6$ in scXe (1050 psi, 24 °C) in the presence of CO (30 psi) (a) at 1988 and (b) 1964 cm^{-1} (similar behavior is observed for the band at 1973 cm^{-1}). The two traces have been normalized in intensity.

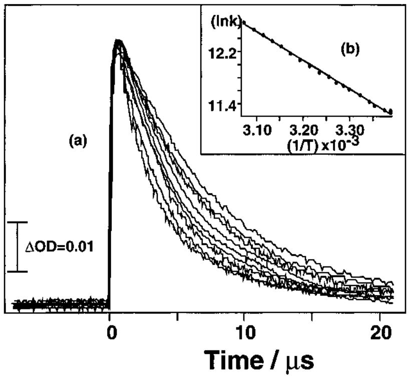

Figure 3. (a) TRIR traces recorded following irradiation (355 nm) of W(CO)$_6$ in scXe (1050 psi, 24 °C) in the presence of CO (30 psi); traces were monitored at 1988 cm^{-1} over the temperature range (35−50 °C) and (b) Arrhenius plot obtained from the data shown in part a.

(c) Identification and Reactivity of W(CO)$_5$Kr in scKr. Figure 4a shows the FTIR spectrum of W(CO)$_6$ dissolved in scKr in the presence of CO; the t$_{1u}$ ν(CO) absorption of W(CO)$_6$ (1990 cm^{-1}) is shifted +2 cm^{-1} relative to the same band in scXe. Figure 4b shows the TRIR spectrum obtained 100 ns following 355-nm excitation of W(CO)$_6$ in this solution. Again,

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(25) Hodges, P. M.; Jackson, S. A.; Jacke, J.; Poliakoff, M.; Turner, J. J.; Grevels, F-W. *J. Am. Chem. Soc.* **1990**, *112*, 1234.

(26) Burney, D. P.; Burkey, T. J. *Abstracts of the 207th ACS National Meeting, San Diego*; American Chemical Society: Washington, DC, 1994; Inor 19.

(27) Long and co-workers found[28] that the activation energy for the reaction of W(CO)$_5$(*n*-heptane) with CO in *n*-heptane solution appears to be significantly lower than the W−heptane bond dissociation energy (15 kcal/mol).

(28) Breheny, C. J.; Grevels, F.-W.; Kelly, J. M.; Klotzbücher, W. E.; Long, C.; Russell, G.; Pryce, M. T.; Walsh, M. Submitted for publication.

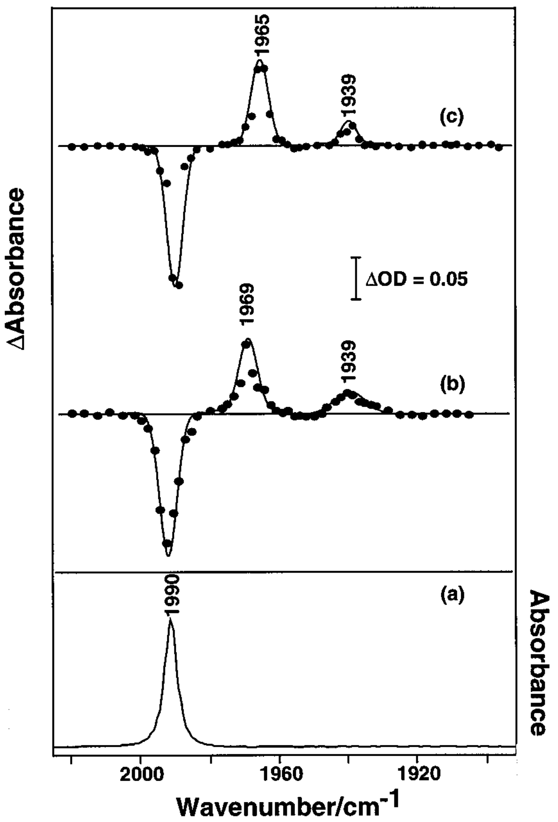

Figure 4. (a) FTIR spectrum of $W(CO)_6$ in scKr (3400 psi, 25 °C) in the presence of CO (9 psi), (b) TRIR spectrum obtained 100 ns after photolysis (355 nm) of $W(CO)_6$ in this solution, and (c) TRIR spectrum obtained 100 ns after photolysis (355 nm) of $W(CO)_6$ in scKr (3680 psi, 25 °C) in the presence of CO (9 psi) and Xe (260 psi).

it is clear that the band of $W(CO)_6$ is bleached and two new absorptions are produced, which can be assigned to $W(CO)_5Kr$. The system is fully reversible as monitored by FTIR spectroscopy but the regeneration of $W(CO)_6$ involves a secondary product also detected by TRIR.

The ν(C−O) bands of $W(CO)_5Kr$ are shifted to higher wavenumber relative to those assigned to $W(CO)_5Xe$ in scXe. This shift does not prove in itself that Kr is coordinating to the metal center because the ν(C−O) band of $W(CO)_6$ is also shifted relative to scXe. However, addition of Xe to scKr allows the coordination of *Xe* to the metal center to be investigated further, since Xe should coordinate to $W(CO)_5$ more strongly than does Kr.

Figure 4c shows the TRIR spectrum obtained 100 ns following photolysis of $W(CO)_6$ dissolved in scKr doped with Xe and a small amount of CO. It is clear that the absorption of $W(CO)_6$ at 1990 cm^{-1} is *not* significantly changed when the scKr is doped with Xe but the stronger of the new absorption bands is shifted relative to the TRIR experiment performed in pure scKr, Figure 4b. The wavenumbers of these transient ν(CO) absorptions (1965 and 1939 cm^{-1}) are identical, within the experimental error of the TRIR spectrometer, to those observed for $W(CO)_5Xe$ in scXe and are therefore assigned to $W(CO)_5Xe$ in scKr. The coordination of Xe is supported further by the kinetic behavior of $W(CO)_5L$ (L = Kr and Xe). Figure 5 compares the TRIR decay traces in pure and doped scKr. It can be seen that the presence of a modest quantity of Xe increases the lifetime of $W(CO)_5$ by almost one order of magnitude.

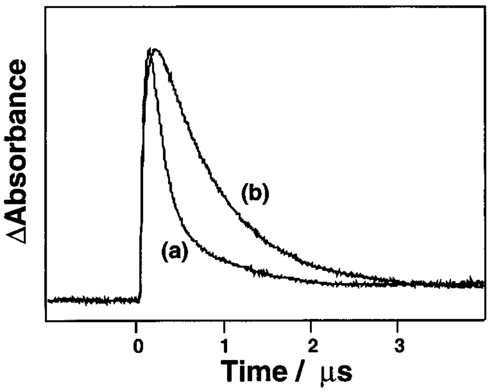

Figure 5. TRIR trace recorded (a) at 1969 cm^{-1} following irradiation (355 nm) of $W(CO)_6$ in scKr (3400 psi, 25 °C) in the presence of CO (9 psi) ($k_{obs} = 4.5 (\pm 0.5) \times 10^6\ s^{-1}$) and (b) at 1965 cm^{-1} following irradiation (355 nm) of $W(CO)_6$ in scKr (3680 psi, 25 °C) in the presence of Xe (260 psi) and CO (9 psi) ($k_{obs} = 6.6 (\pm 0.4) \times 10^5\ s^{-1}$).

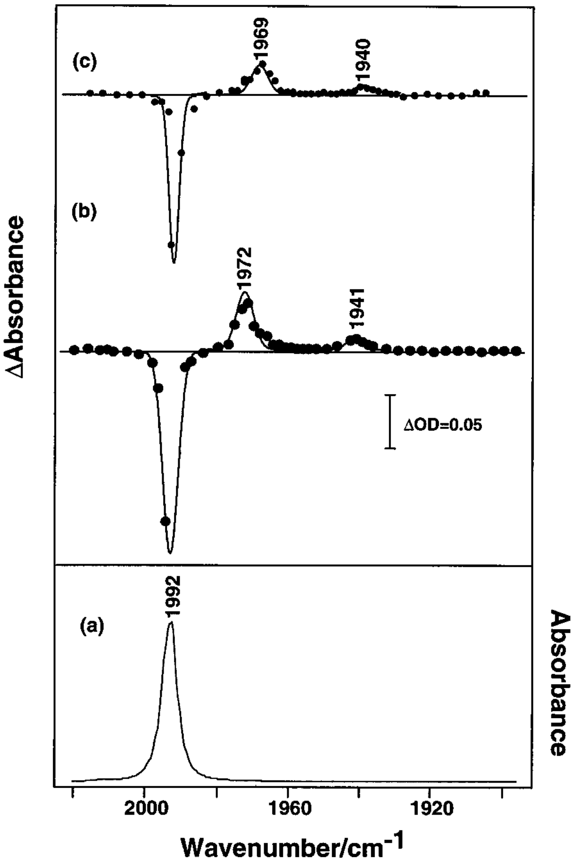

Figure 6. (a) FTIR spectrum of $W(CO)_6$ in scAr (5100 psi, 21 °C) in the presence of CO (3 psi), (b) TRIR spectrum obtained 100 ns after photolysis (355 nm) of $W(CO)_6$ in this solution, and (c) TRIR spectrum obtained 100 ns after photolysis (355 nm) of $W(CO)_6$ in scAr (5580 psi, 21 °C) in the presence of CO (3 psi) and Kr (200 psi).

(d) Identification and Reactivity of $W(CO)_5Ar$ in scAr. The experiments described above provide good evidence that Xe is interacting with the vacant site of $W(CO)_5$ but the coordination of Kr to the metal center is more speculative since our observations would also be consistent with unsolvated "naked" $W(CO)_5$. To pursue this further, we have investigated the reactivity of $W(CO)_5$ in scAr. Figure 6a shows the FTIR spectrum of $W(CO)_6$ dissolved in scAr (5100 psi, 21 °C) in the presence of CO (3 psi). The ν(CO) absorption of $W(CO)_6$ is shifted +2 cm^{-1} relative to the band in scKr. Figure 6b shows the corresponding TRIR spectrum; two new absorptions appear at 1972 and 1941 cm^{-1}, shifted relative to the TRIR experiment performed in pure scKr, and are tentatively assigned to $W(CO)_5(Ar)$. At longer delay times, the absorptions due to $W(CO)_5(Ar)$ decay and $W(CO)_6$ is reformed (ca. >80%). Figure 6c

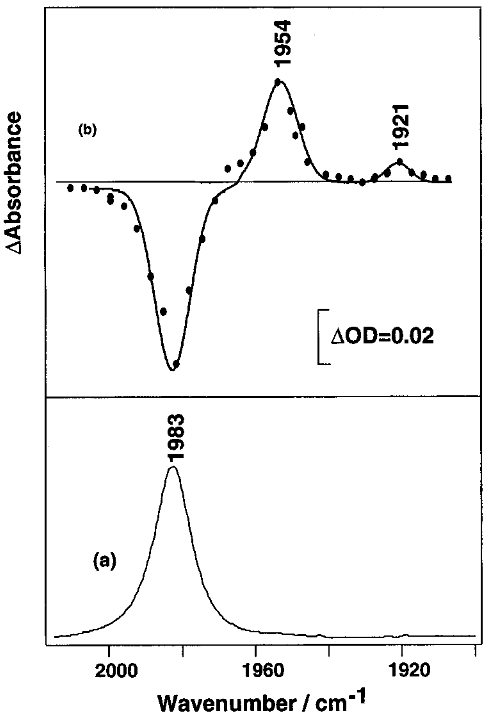

Figure 7. (a) FTIR spectrum of W(CO)$_6$ in scCO$_2$ and (b) TRIR spectrum obtained 100 ns after photolysis (355 nm) of W(CO)$_6$ in scCO$_2$ (1400 psi, 35 °C) in the presence of CO (30 psi).

shows the TRIR spectrum obtained 100 ns following photolysis of W(CO)$_6$ dissolved in scAr doped with Kr and CO (3 psi). The spectrum is superficially identical to that in Figure 6b but more careful inspection shows that the new bands are both shifted (-3 and -1 cm^{-1}) relative to the TRIR experiment performed in scAr without Kr, Figure 6b. By analogy with W(CO)$_5$Xe, these new bands are assigned to W(CO)$_5$Kr in scAr. The lifetime of W(CO)$_5$ is significantly shorter in undoped scAr ($k_{obs} = 1.2\ (\pm 0.6) \times 10^7\ s^{-1}$) than in scAr doped with Kr ($k_{obs} = 5.2\ (\pm 0.5) \times 10^6\ s^{-1}$), again supporting coordination of Kr to W(CO)$_5$. We have estimated the rate constant for the reaction of W(CO)$_5$Kr with CO to be 7.5 (±0.5) × 10^7 mol^{-1} dm^3 s^{-1}, by monitoring the partial reformation of W(CO)$_6$. This rate constant indicates that, as might be expected, the reactivity of these noble gas complexes is in the order W(CO)$_5$(Ar) > W(CO)$_5$Kr > W(CO)$_5$Xe. Finally, it should be stressed that an important difference between gas-phase TRIR, where the IR bands are broad, and supercritical fluid TRIR is that the density of the fluid leads to IR bands which are nearly as narrow as in conventional solvents.

(e) TRIR of W(CO)$_6$ in scCO$_2$. As noted earlier, the bond energies for W$-$Xe and W$-$CO$_2$ have been estimated from gas-phase TRIR measurements to be almost identical. We have used TRIR to monitor the photochemistry of W(CO)$_6$ in scCO$_2$ to investigate the interaction of CO$_2$ with the W metal center, in fluid solution at ambient temperature. Figure 7a shows the FTIR spectrum of W(CO)$_6$ dissolved in scCO$_2$ in the presence of CO and Figure 7b shows the TRIR spectrum obtained 100 ns after 355-nm excitation. Two new absorptions are produced which are assigned to W(CO)$_5$(CO$_2$) by comparison with previous data from low-temperature matrices[3] and gas-phase TRIR[20] (see Table 1). The TRIR kinetic traces (see supporting information) show that W(CO)$_6$ is reformed at the same rate ($k_{obs} = 3.4\ (\pm 0.3) \times 10^5\ s^{-1}$) as W(CO)$_5$(CO$_2$) decays ($k_{obs} = 3.6\ (\pm 0.4) \times 10^5\ s^{-1}$).

We have measured the temperature dependence of the rate of decay of W(CO)$_5$(CO$_2$) in scCO$_2$ in the presence of 30 psi of CO. The Arrhenius plots for these data were repeated with five different mixtures, and the values of E_a were found to vary by less than ±0.5 kcal/mol. The mean value, $E_a = 8.1 \pm 0.5$ kcal/mol, is in complete agreement with Fu's estimate[20] of the W$-$CO$_2$ bond strength (8.2 ± 1.0 kcal/mol) obtained by gas-phase TRIR measurements. Thus, the activation energies for the reactions of W(CO)$_5$Xe in scXe and W(CO)$_5$(CO$_2$) in scCO$_2$ with CO are identical within experimental error and we conclude that W(CO)$_5$Xe and W(CO)$_5$(CO$_2$) have similar thermal stability in supercritical solution. Furthermore, comparison of the second-order rate constants for W(CO)$_5$(CO$_2$) and W(CO)$_5$Xe indicates that the two compounds have similar reactivities toward CO at 35 °C: W(CO)$_5$(CO$_2$) (4.1 (±0.5) × 10^6 mol^{-1} dm^3 s^{-1}) and W(CO)$_5$Xe (3.2 (±0.7) × 10^6 mol^{-1} dm^3 s^{-1}). Although previous work[11] has provided evidence that the decay of W(CO)$_5$Xe is dissociative in lXe, this TRIR study is the first evidence that the decay of W(CO)$_5$(CO$_2$) is probably dissociative in *condensed* phases. This conclusion can be strengthened further by measuring the dependence of the lifetime of W(CO)$_5$(CO$_2$) on the density of scCO$_2$.

(f) Effect of the Density of scCO$_2$ on the Lifetime of W(CO)$_5$(CO$_2$). The density of a supercritical fluid can be varied substantially and continuously by relatively modest changes in the applied pressure. This tunability allows the effects of solvent density to be investigated in a way which would be virtually impossible in a conventional solvent. The reaction of W(CO)$_5$(CO$_2$) with CO in scCO$_2$ can be described by eqs 1$-$3 which cover both dissociative (eqs 1 and 2) and associative (eq 3) pathways.

$$\mathrm{W(CO)_5(CO_2)} \underset{k_s}{\overset{k_{-s}}{\rightleftharpoons}} \mathrm{W(CO)_5} + \mathrm{CO_2} \qquad (1)$$

$$\mathrm{W(CO)_5} + \mathrm{CO} \xrightarrow{k_d} \mathrm{W(CO)_6} \qquad (2)$$

$$\mathrm{W(CO)_5(CO_2)} + \mathrm{CO} \xrightarrow{k_a} \mathrm{W(CO)_6} + \mathrm{CO_2} \qquad (3)$$

Applying the steady state approximation, we obtain the rate law shown in eq 4 for the decay of W(CO)$_5$(CO$_2$).

$$k_{obs} = \frac{k_{-s}}{\gamma} + k_a[\mathrm{CO}], \qquad \text{where } \gamma = 1 + \frac{k_s}{k_d}\frac{[\mathrm{CO_2}]}{[\mathrm{CO}]} \qquad (4)$$

Thus, the lifetime of W(CO)$_5$(CO$_2$) should depend on the concentration of scCO$_2$ and hence on the density of the CO$_2$ solvent. The first term in eq 4 represents the dissociative pathway while the term k_2[CO] is a possible associative pathway. We have used the tunable density of CO$_2$ to distinguish between a purely dissociative pathway and a combination of dissociative and associative processes. This involved two experiments in which the lifetime of W(CO)$_5$(CO$_2$) was measured as a function of applied pressure, and hence of the density of scCO$_2$. In the first experiment, we used a mixture of CO$_2$ and CO, so that the density of scCO$_2$ could be decreased from 0.85 to 0.47 g/mL while the ratio of [CO$_2$]:[CO] was held constant (109:1). Under these conditions, the values of k_{obs} would only decrease with decreasing density if the reaction of W(CO)$_5$(CO$_2$) with CO were partially associative. However, even though the concentration of CO was decreased to 55% of its original value we found that k_{obs} *increased* reproducibly (from 5.8 → 6.4 × 10^5 s^{-1}), implying that associative processes are not significant in this reaction, i.e. $k_a \approx 0$. Our second experiment involved increasing the pressure of CO$_2$ *without altering* [CO] so that, from eq 4, $1/k_{obs} \propto [\mathrm{CO_2}]$. The data in Figure 8 show that the lifetime of W(CO)$_5$(CO$_2$) ($1/k_{obs}$) does indeed increase with

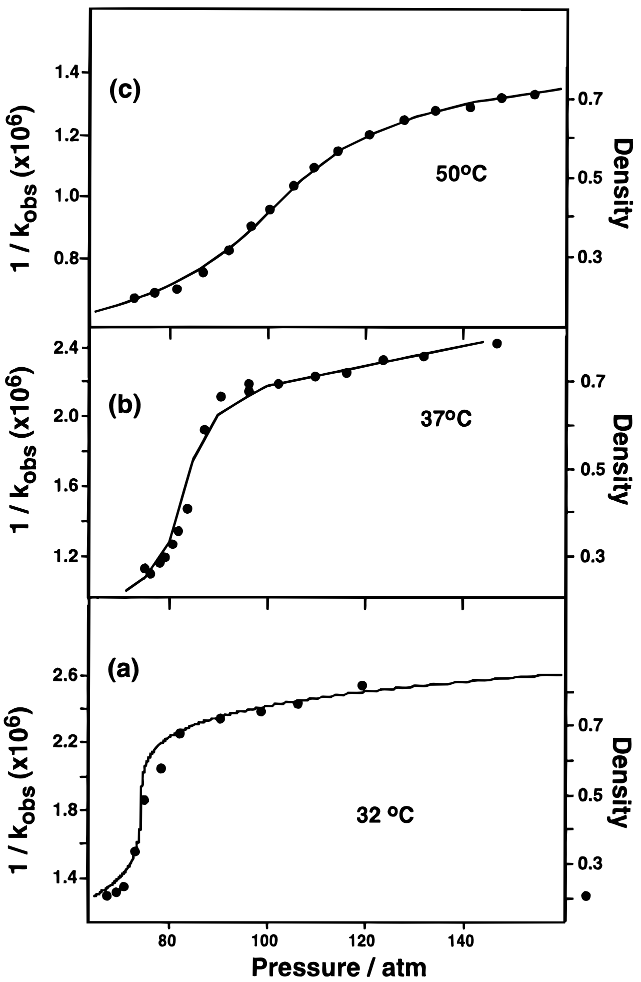

Figure 8. Plot of the lifetime ($1/k_{obs}$) (●) of $W(CO)_5(CO_2)$, obtained following photolysis of $W(CO)_6$ in $scCO_2$, as a function of pressure, at (a) 32, (b) 37, and (c) 50 °C. Note that the variation in lifetime follows almost exactly the variation in density of CO_2 with pressure (solid line, right-hand axis). Under these conditions, close to the critical point, the compressibility of CO_2 shows a substantial temperature dependence so that the relationship between density and pressure changes significantly between 32 and 50 °C. The density of CO_2 was calculated using the methods outlined in ref 38.

increasing pressure of CO_2, just as predicted by eq 4. The variation of density with applied pressure in $scCO_2$ is highly temperature dependent and Figure 8 shows that the lifetime of $W(CO)_5(CO_2)$ accurately follows the density of CO_2 at three different temperatures close to T_c. As far as we are aware, this is the first time that the density dependence of any *dissociative* reaction has been followed in this way in supercritical solution and complements the elegant study[29] of ring closure by Eyring and co-workers. Our observations demonstrate that the reaction of $W(CO)_5(CO_2)$ with CO in $scCO_2$ is predominantly a dissociative process.[30]

(g) TRIR Observation of $Cr(CO)_5L$ and $Mo(CO)_5L$ (L = Kr, Xe, and CO_2). We have repeated these TRIR experiments with $Cr(CO)_6$ and $Mo(CO)_6$ in scKr, scXe, and $scCO_2$. The spectroscopic data for $M(CO)_5L$ (M = Cr and Mo; L = Kr, Xe, and CO_2) are collected in Table 1 and the corresponding second-order rate constants for the reaction of $M(CO)_5L$ with CO are summarized in Table 2. Certain conclusions can be drawn from these data. For each complex, $M(CO)_5Kr$, $M(CO)_5Xe$, or $M(CO)_5(CO_2)$, the order of reactivity is Cr ≈ Mo > W. For each metal, the reactivity of the $M(CO)_5L$ complexes follows the order Kr > Xe ≈ CO_2 and the values of the rate constants for $M(CO)_5Xe$ and $M(CO)_5(CO_2)$ are very close, consistent with similar strengths for the M−Xe and M−CO_2 interactions in these complexes. This is in agreement with the near-identical activation energies for the reaction of $W(CO)_5Xe$ and $W(CO)_5(CO_2)$ with CO described above.

Table 2. Kinetic Data for the Reaction of $M(CO)_5L$ with CO in scL (M = Cr, Mo, and W; L = Ar, Kr, and Xe)

$M(CO)_5L$	[CO]	temp/°C	k_{obs}/s^{-1}	k_2/mol^{-1} dm^3 s^{-1}
$Cr(CO)_5(CO_2)^a$	0.085	35	1.1×10^6	1.2×10^7
$Cr(CO)_5(CO_2)^b$	0.085	35	1.0×10^6	1.2×10^7
$Cr(CO)_5Xe^a$	0.085	25	7.1×10^5	8.4×10^6
$Cr(CO)_5Xe^b$	0.085	20	1.1×10^6	1.2×10^7
$Cr(CO)_5Kr^a$	0.028	32	1.3×10^7	4.7×10^8
$Cr(CO)_5Kr^b$	0.085	20	3.2×10^7	3.8×10^8
$Mo(CO)_5(CO_2)^a$	0.085	35	6.4×10^5	7.6×10^6
$Mo(CO)_5Xe^a$	0.085	25	9.3×10^5	1.1×10^7
$Mo(CO)_5Kr^a$		30	1.3×10^7	4.3×10^8
$W(CO)_5CO_2^a$	0.085	35	3.6×10^5	4.1×10^6
$W(CO)_5Xe^a$	0.085	25	1.7×10^5	2.0×10^6
$W(CO)_5Kr^a$	0.028	25	2.1×10^6	7.5×10^7
$W(CO)_5(Ar)^a$	0.008	21	1.2×10^7	1.4×10^9

[a] TRIR. [b] UV/vis.

The interactions of $Cr(CO)_5$ with Xe and with CO_2 have been studied in low-temperature matrices.[2,3] Perutz and Turner pioneered the use of λ_{max} measurements in the UV/vis spectrum of $Cr(CO)_5L$ complexes as a sensitive probe of Cr−(Noble gas) interactions[2] and Downs and co-workers extended[3] the work to Cr−CO_2. The conclusion which could be drawn from these studies was that *the Cr−CO_2 interaction was considerably stronger than Cr−Xe* because λ_{max} for $Cr(CO)_5(CO_2)$ (370 nm) was substantially blue-shifted relative to $Cr(CO)_5Xe$ (503 nm). The effect for W−CO_2 and W−Xe appeared to be similar but the spectroscopic shifts were somewhat smaller. Our TRIR results are at variance with these conclusions. Although our TRIR spectra are in good agreement with the matrix spectra, the M−Xe and M−CO_2 interactions appear to have similar strengths in supercritical solution. Thus, we have investigated the UV/visible absorption maxima of $Cr(CO)_5L$ (L = Kr, Xe, and CO_2) in supercritical solution in order to resolve these differences.

(h) Visible Spectra of $Cr(CO)_5L$ (L = Kr, Xe, and CO_2). Figure 9a shows the transient visible spectrum of $Cr(CO)_5Xe$ (λ_{max} = 508 ± 10 nm), recorded in scXe. The rate constant for the decay of this band is identical, within experimental error, to the value obtained from TRIR for reaction of $Cr(CO)_5Xe$ with CO (see Table 2). Therefore, this visible band and the ν(C−O) IR bands can be assigned to the same species. Moreover, the value of λ_{max} is in reasonable agreement with the value for matrix-isolated $Cr(CO)_5Xe$, 492 nm. Figure 9c shows the corresponding absorption band of $Cr(CO)_5Kr$ (λ_{max} = 538 ± 10 nm) in scKr and, again, the decay kinetics are in excellent agreement with those obtained by TRIR (see Table 2). Although the S/N ratios of our spectra are not particularly high, it is clear that the band of $Cr(CO)_5Kr$ is at least slightly red-shifted relative to that of $Cr(CO)_5Xe$. Furthermore, if the experiment is repeated in scKr doped with Xe, λ_{max} shifts back to the position observed in pure scXe, a result consistent with Perutz and Turner's original observations in noble gas matrices.[2] Figure 9b shows the transient visible band of $Cr(CO)_5(CO_2)$ in $scCO_2$. The maximum (λ_{max} = 505 ± 10 nm) is indistinguishable from that of $Cr(CO)_5Xe$ (λ_{max} = 508 ± 10 nm), Figure 9a.

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(29) Jin, Q.; Eyring, E. M.; van Eldik, R.; Johnston, K. P.; Goates, S. R.; Lee, M. L. *J. Phys. Chem.* **1995**, *99*, 13461.

(30) The sign of $\Delta S^‡$ is indicative of the nature of a particular reaction mechanism. We obtain a value for $\Delta S^‡$ from the Eyring plot of +22.4 (±10.0) J K^{-1} mol^{-1}.

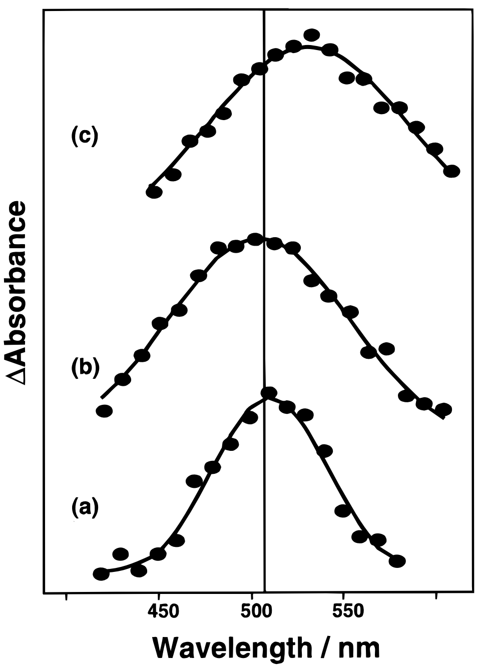
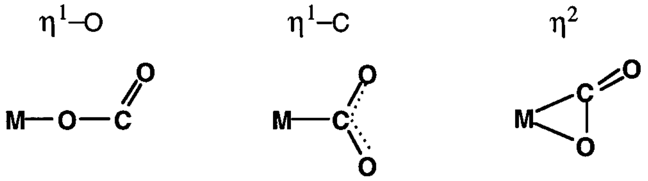


Figure 9. Visible absorbance spectrum recorded 100 ns after flash photolysis of $W(CO)_6$ in (a) scXe (1150 psi, 20 °C), (b) $scCO_2$ (2500 psi, 40 °C), and (c) scKr (2990 psi, 20 °C).

Chart 1



An identical visible absorption spectrum is obtained following flash photolysis of $Cr(CO)_6$ in scKr doped with CO_2. This is surprisingly different from matrix isolation[3] where a blue-shift >120 nm (492 → 370 nm) was observed between the λ_{max} of $Cr(CO)_5Xe$ and $Cr(CO)_5(CO_2)$. We found no evidence for a strong absorption band of $Cr(CO)_5(CO_2)$ at 370 nm. There is a further difference between supercritical and matrix experiments. In $scCO_2$, formation of $Cr(CO)_5(CO_2)$ is reversible, even after quite prolonged UV irradiation, and there is no overall loss of $Cr(CO)_6$ starting material. By contrast, UV photolysis of $Cr(CO)_5(CO_2)$ in CO_2-doped Ar matrices[3] leads to oxidation of the metal center with formation of metal oxide species.

There seems to be little reason to doubt that the $Cr(CO)_5Xe$ species observed in scXe and Xe matrices are the same. However, CO_2 has at least three possible coordination modes to metal centers (Chart 1) and, therefore, different isomers of $Cr(CO)_5(CO_2)$ could be involved in the matrix and supercritical experiments, particularly because ν(CO) bands of $M(CO)_5L$ species are often relatively insensitive to the precise coordination of L.

The η^1-C and η^2-coordination types have been observed and there are structurally characterized examples of both types of binding.[31] However, there are no structurally characterized examples of η^1-O complexes, although theoretical and spectroscopic measurements in low-temperature matrices have provided evidence for such coordination.[31] It is surprising that CO_2 does not appear to interact any more strongly with the metal center than does Xe in the complexes studied here and this may indicate that we have η^1-O coordination since η^1-C and η^2-CO_2 complexes have been isolated. Although Downs and co-workers[3] were unable to identify any vibrations due to coordinated CO_2 in matrix-isolated $Cr(CO)_5(CO_2)$, they suggested η^1-O coordination of the CO_2. This is in agreement with recent calculations by Pidum and Frenking,[32] which support η^1-O coordination of the CO_2 ligand to a $W(CO)_5$ moiety. Although the precise nature of the binding of CO_2 to the $Cr(CO)_5$ moiety is still unclear to our experiments, it appears that CO_2 may have a different mode of bonding in $scCO_2$ from that observed by Downs and co-workers in low-temperature matrices[3] since we have significant shifts in the λ_{max} of the visible absorption band. It is possible that we are observing η^1-O coordination in solution at room temperature and some other coordination mode was observed in low-temperature matrices. There is clearly much to learn about organometallic noble gas and CO_2 complexes and TRIR will prove increasingly useful for this purpose.

Conclusions

The use of TRIR to study organometallic reactions in supercritical fluids provides a new method for studying the interaction of metal centers with weakly coordinating ligands in solution at ambient temperatures. The combination of TRIR and supercritical fluids not only allows highly reactive organometallic species to be generated at room temperature but also offers the possibilty of probing the photophysical effects of the supercritical fluid environment on chemical reactions. In our experiments, a series of organometallic noble gas compounds, $W(CO)_5(Ar)$, $M(CO)_5Kr$, $M(CO)_5Xe$ (M = Cr, Mo, and W), have been detected for the first time in fluid solution at room temperature. We have shown that $M(CO)_5Xe$ species are surprisingly stable and have reactivity similar to $M(CO)_5(CO_2)$ and to the corresponding heptane complexes, $M(CO)_5$(*n*-heptane).

The supercritical TRIR technique is quite general. Preliminary studies[33] indicate that $CpRe(CO)_2L$ (L = Xe and Kr) is significantly less reactive toward CO than $M(CO)_5L$ and this stability may allow us to follow the displacement of Kr by Xe on a nanosecond time scale in scKr doped with Xe. Recent TRIR experiments[34] with *trans*-$[CpMo(CO)_3]_2$ in $scCO_2$ have shown that reactivity of the 17-electron radical is greatly enhanced near the critical point. Moreover, the formation of *gauche*-$[CpMo(CO)_3]_2$ allows the cage-effect in supercritical fluids to be directly probed.

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(31) For reviews see: (a) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37. (b) Mascetti, J.; Tranquille, M. *J. Phys. Chem.* **1988**, *92*, 2177.

(32) Pidum, U.; Frenking, G. *Organometllics* **1995**, *14*, 5325. Note that the structure shown in Chart 1 is just one of several possible geometries for η^1-O coordination.

(33) Sun, X.-Z.; George, M. W.; Grills, D. C.; Nikforov, S. M.; Poliakoff, M. To be submitted for publication.

(34) Sun, X.-Z.; George, M. W.; Poliakoff, M. To be submitted for publication.

(35) Perutz, R. N. Ph.D. Thesis, University of Cambridge, 1974.

(36) Church, S. P.; Grevels, F-W.; Herman, H.; Schafftner, K. *Inorg. Chem.* **1985**, *24*, 418.

(37) Wieller, B. H. *ACS Symp. Ser.* **1993**, *530*, 164.

(38) *International Thermodynamics Tables of the Fluid State, Carbon Dioxide*; Angus, S., et al., Eds.; Pergamon Press: Oxford 1976.

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Supporting Information Available: A figure showing TRIR traces recorded following irradiation (355 nm) of $W(CO)_6$ in $scCO_2$ (1400 psi; 35 °C) in the presence of CO (30 psi) (a) at 1983 and (b) 1954 cm^{-1} (1 page). See any current masthead page for ordering and Internet access instructions.

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