agrees with that reported earlier.[14]

Preparation of 3a,4,4a,8-Tetrahydro-4,4,8,8-tetramethyl-4-sila-*s*-indacene (3). To a solution of 47 g (0.27 mol) of dicyclopentadienyldimethylmethane in 500 mL of THF at −20 °C, 27 mL of 2.0 N hexane solution of *n*-butyllithium (0.54 mol) was added under stirring at −20 °C. The mixture was allowed to warm to room temperature, TMEDA (62.6 g, 0.54 mol) was added, and the mixture was cooled to −50 °C. A solution of 34.9 g (0.27 mol) of dichlorodimethylsilane in 200 mL of THF was added dropwise within 3 h. Stirring was continued for another 1 h at −50 °C. After warming to room temperature, the mixture was decanted from the solid residue, the solvents were removed in vacuo, and the resulting oil was distilled. The fraction at 80–82 °C (0.1 Torr) was collected (the yield of resultant **3**, **6**, and minor isomers was up to 52%). The major isomer **3** was isolated after recrystallization from pentane (17 g, 25%). ^{1}H NMR (toluene-d_8, 26 °C): δ −1.06 (s, 3 H, CH_3Si), 0.25 (s, 3 H, CH_3Si), 1.37 (s, 3 H, CH_3C), 1.57 (s, 3 H, CH_3C), 3.40 (m, 2 H, H–C(3a),C(4a)), 6.19–6.21 (m, 2 H, Cp), 6.22–6.25 (m, 2 H, Cp), 6.32–6.36 (m, 2 H, Cp); $^{13}C\{^1H\}$ NMR (dioxane-d_8), 26 °C, see Table I. Anal. Calcd for $C_{15}H_{20}Si$: C, 78.91; H, 8.83. Found: C, 79.01; H, 9.46.

Thermolysis of 3. The solution of **3** in toluene-d_8 was heated at 100 °C for 2 h in an NMR tube. The additional signals of **6** appeared in the NMR spectrum. When the resulting solution was heated some time more, the ratio of **3** and **6** (about 3:2) remained the same. The fraction of isomers different from **3** and **6** is less than 5% of the total amount of substance. Compound **6**: ^{1}H NMR (toluene-d_8, 26 °C) δ −0.43 (s, 3 H, CH_3Si), 0.26 (s, 3 H, CH_3Si), 1.32 (s, 3 H, CH_3C), 1.50 (s, 3 H, CH_3C), 2.72–2.89 (AB part of ABXY spin system, $J_{AB} = 23.8$ Hz, $J_{AX} \approx J_{AY} \approx J_{BX} \approx J_{BY} \approx 1.2$–1.5 Hz, 2 H, $H_2C(3)$), 3.50 (m, 1 H, HC(4a)), 6.37–6.39 (m, 1 H, Cp), 6.43–6.46 (m, 1 H, Cp), 6.55–6.63 (3 overlapping mult, 3 H, Cp); $^{13}C\{^1H\}$ NMR (dioxane-d_8, 26 °C), see Table I.

Preparation of 4-Germa-3a,4,4a,8-tetrahydro-4,4,8,8-tetramethyl-*s*-indacene (4). The synthesis is analogous to that described above for **3**. From 23 g (0.13 mol) of dicyclopentadienyldimethylmethane, 27 g (0.09 mol) of **4** was obtained (bp 86–91 °C (0.1 Torr), yield 71%). ^{1}H NMR (toluene-d_8, 26 °C): isomer **4a** δ −0.97 (s, 3 H, CH_3Ge), 0.43 (s, 3 H, CH_3Ge), 1.35 (s, 3 H, CH_3C), 1.57 (s, 3 H, CH_3C), 3.54 (m, 2 H, H–C(3a),C(4a)), 6.18–6.23 (2 overlapping m, 4 H, Cp), 6.28–6.32 (m, 2 H, Cp); isomer **4b** δ −0.08 (s, 6 H, $(CH_3)_2Ge$), 1.42 (s, 6 H, $(CH_3)_2C$), 3.08 (m, 2 H, H–C(3a),C(4a)), 6.1–6.5 (3 m overlapping with signals of **4a**, 6 H, Cp). $^{13}C\{^1H\}$ NMR (THF-d_8, 26 °C), see Table I. Anal. Calcd for $C_{15}H_{20}Ge$: C, 66.04; H, 7.38. Found: C, 65.92; H, 7.31.

Preparation of 3a,4,4a,8-Tetrahydro-4,4,8,8-tetramethyl-4-stanna-*s*-indacene (5). The synthesis is analogous to that described above for **3**. From 47 g (0.27 mol) of dicyclopentadienyldimethylmethane, 47 g (0.15 mol) of **5** was obtained (bp 100–105 °C (0.1 Torr), yield 57%). ^{1}H NMR (THF-d_8, 26 °C) δ −0.1 (br s, 6 H), 1.52 (s, 6 H), 5.2 (br m, 4 H), 6.21 (t, J = 1.2 Hz, 4 H). ^{1}H NMR (THF-d_8, −90 °C): isomer **5a** δ −1.26 (s, 3 H, CH_3Sn, $^2J_{^1H-^{119}Sn} = 54.9$ Hz), 0.74 (s, 3 H, CH_3Sn, $^2J_{^1H-^{119}Sn} = 56.5$ Hz), 1.49 (s, 3 H, CH_3C), 1.62 (s, 3 H, CH_3C), 4.46 (m, 2 H, H–C(3a),C(4a), $^2J_{^1H-^{119}Sn} = 98.9$ Hz), 6.0–6.4 (overlapping br mult, 6 H, Cp); isomer **5b** δ −0.04 (s, 6 H, $(CH_3)_2Sn$, $^2J_{^1H^{111}Sn} = 56.5$ Hz), 1.46 (s, 6 H, $(CH_3)_2C$), 3.77 (m, 2 H, H–C(3a),C(4a), $^2J_{^1H-^{119}Sn} = 95.5$ Hz), 6.0–6.4 (overlapping br mult, 6 H, Cp). $^{13}C\{^1H\}$ NMR (THF-d_8, 26 °C) δ −8.96 (br), 30.95, 40.38, 127.26, 163.00. $^{13}C\{^1H\}$ NMR (THF-d_8, −90 °C), see Table I.

Acknowledgment. We are very grateful to the Varian Co. for long-term fruitful cooperation and for the opportunity to use the VXR-400 NMR spectrometer within the framework of an agreement on scientific–technical cooperation between Varian and Moscow State University.

Registry No. *cis*-3, 135734-11-1; *cis*-4, 135734-12-2; *trans*-4, 135734-14-4; *cis*-5, 134767-15-0; *trans*-5, 135734-15-5; 6, 135734-13-3; dicyclopentadienyldimethylmethane, 134459-15-7; cyclopentadiene, 542-92-7; dichlorodimethylsilane, 75-78-5; dimethyldichlorogermane, 1529-48-2; dimethyldichlorostannane, 753-73-1.

---

[14] Kronig, P.; Slongo, M.; Neuenschwander, M. *Makromol. Chem.* **1982**, *183*, 359.

Low Quantum Yields of Cr(CO)$_6$ Substitution in Fluorocarbon Solvent: Evidence That Metal–Fluorocarbon Interactions Are Very Weak

Suresh K. Nayak and Theodore J. Burkey*

Department of Chemistry, Memphis State University, Memphis, Tennessee 38152

Received June 6, 1990; Revised Manuscript Received April 19, 1991

The relative heats of CO photosubstitution on $Cr(CO)_6$ by cyclohexane, benzene, and 1,2-dichloroethane (as ligands) in perfluorocarbon solvents and in neat ligand have been determined by photoacoustic calorimetry. From these results and the quantum yield of CO substitution in neat ligand (0.67, 0.67, and 0.62, respectively), the quantum yield in perfluorodecalin was found to be 0.3. These results are confirmed by conventional actinometry. The low quantum yield in perfluorodecalin can be attributed to its weaker coordination of $Cr(CO)_5$. The quantum yield is independent of wavelength (254, 302, and 337 nm) in perfluorodecalin, indicating that the low quantum yield does not result from more efficient vibrational relaxation. The $Cr(CO)_5$ generated by photolysis of $Cr(CO)_6$ can recombine with photodissociated CO still in the solvent cage, and the relative strong coordination of cyclohexane, benzene, or 1,2-dichloroethane inhibits recombination of CO in the solvent cage, so that CO is forced to escape the cage. The results suggest a weak coordination of a fluorocarbon allows more cage CO to recombine, thus reducing the overall quantum yield of substitution. It is concluded that more efficient cage recombination of CO in a fluorocarbon solvent is primarily responsible for the lower quantum yield of substitution.

Introduction

There has been great interest in the interaction of $M(CO)_5$ (M = Cr, Mo, W) fragments with inert compounds. Early studies with matrix isolation techniques demonstrated that methane stereospecifically binds to $Cr(CO)_5$ at an octahedral site and that the Cr–methane interaction has the characteristics of a chemical bond.[1] This finding is supported by flash photolysis studies which demonstrate

---

[1] Perutz, R.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791.

0276-7333/91/2310-3745$02.50/0 © 1991 American Chemical Society

that $Cr(CO)_5$ coordinates other alkanes in room-temperature solutions.[2,3] Photoacoustic calorimetry (PAC) studies show that the $M(CO)_5$–alkane coordinate bond is surprisingly strong (ca. 10 kcal/mol),[4,5] and these results are in agreement with the $W(CO)_5$–alkane binding enthalpies recently determined from equilibrium studies of $W(CO)_5$ and alkanes in the gas phase.[6] These $M(CO)_5$–alkane complexes are examples of σ complexes, whose existence has only recently gained general acceptance. Since the metal–alkane coordinate bond is substantial and in some cases may be larger than 10 kcal/mol, these bonds may occur widely in intermediates of organometallic reactions and affect the course of those reactions. An important example is the σ complex that has been postulated to be an intermediate in the activation of alkane C–H bonds by the $(\eta^5\text{-}Me_5Cp)Rh(PMe_3)$ fragment.[7]

In contrast, available spectroscopic and kinetic evidence indicates that the interaction between $Cr(CO)_5$ and a perfluorocarbon is much weaker than that with alkanes, although the magnitude of the former interaction has not been determined.[1,2,8] Matrix isolation studies of $Cr(CO)_5$ show that the visible spectrum is very sensitive to the ionization potential of the matrix. A very weak interaction of $Cr(CO)_5$ with CF_4 is indicated by the spectrum of $Cr(CO)_5$ in CF_4, which is nearly the same as in Ne or in the gas phase.[1] At room temperature, $Cr(CO)_5$ reacts at a nearly diffusion-controlled rate with CO in perfluoromethylcyclohexane, a rate that is 10^3 faster than in cyclohexane.[2] A $Cr(CO)_5$–cyclohexane bond that is stronger than the $Cr(CO)_5$–perfluoromethylcyclohexane interaction would account for the slower reaction with CO in cyclohexane, since cyclohexane would be more difficult to displace. We have found that the quantum yield for photosubstitution of $Cr(CO)_6$ in a perfluorocarbon is significantly smaller than in a hydrocarbon, a result that can be attributed directly to the relatively weak interaction with the perfluorocarbon. Our initial measurements obtained by photoacoustic calorimetry were confirmed by conventional actinometry.

Experimental Section

Materials. All compounds were obtained from Aldrich unless otherwise noted. Chromium hexacarbonyl was sublimed under vacuum at least twice. Cyclohexane (CH) and heptane (HPLC or spectrophotometric grade) were distilled from sodium or potassium before use. Benzene (BZ) and 1,2-dichloroethane (DCE) were stirred overnight with phosphorus pentoxide and then distilled before use. Toluene was washed with sulfuric acid, followed by water, 5% NaOH, and then more water before distilling from P_4O_{10}. Piperidine (pip) was refluxed from KOH or sodium at least 3 h before distillation. Pyridine (py) was distilled from KOH immediately before use. $Cr(CO)_5(pip)$ was prepared as before.[9] Gases were zero grade (Air Products). Azobenzene was refluxed in ethanol for 5 h and then recrystallized. Dimethylanthracene was recrystallized from ethanol. Aberchrome (Aberchromics, Cardiff, U.K.) was used as received. Perfluoromethylcyclohexane (Lancaster), perfluorohexane (PFH), and 1,1,2-trichloro-1,2,2,-trifluoroethane (Freon 113) were used as received. Perfluorodecalin (PFD, 120 mL) was refluxed with a mixture of concentrated nitric (30 mL) and sulfuric acids (20 mL, Mallinckrodt) for 4 days, separated, extracted four times with 40-mL portions of water, vigorously stirred with 4 M NaOH (40 mL) for 4 days, separated from the aqueous phase, and then extracted four times with 40-mL portions of water. Finally, PFD was passed through 2 g of alumina in a funnel before distilling from calcium hydride. Heptane, CH, and PFD were refluxed overnight with respective drying agents before distillation.

PAC Sample Preparation. The preparation of chromium hexacarbonyl solutions and the operation of the photoacoustic calorimeter have been described previously.[4,9,10] All solutions containing chromium hexacarbonyl were prepared and used in the dark or with illumination by a Thomas safelight. The solutions were in foil-covered septum-sealed vessels, were purged with helium or argon, and were cannulated to avoid contamination by air. For PFD solutions, to aid dissolution, a thin film of a complex was deposited under vacuum in a round-bottom flask fitted with a Flikit stopcock. Under argon, a known volume of PFD was cannulated into the flask, and the resulting solution was then cannulated into a graduated reservoir for addition of ligand and more PFD. The graduated reservoir had a fritted bubbler which was used to pressurize and purge the reservoir with helium. The reservior was connected to a flow cuvette via a glass manifold with Teflon stopcocks.

PAC Measurements. Solutions in the flow cuvette were photolyzed with a pulsed nitrogen laser (337.1 nm, 20–30 mJ/pulse, 800 ps fwhi) at room temperature (23 ± 1 °C). The signal from a transducer clamped to the cuvette was obtained after each pulse and averaged on a digital oscilloscope. The flow of solution was increased until the transducer signal became independent of changes in the solution flow rate. The signal from the transducer was calibrated before and after each measuement of a metal carbonyl solution with use of a reference solution of ferrocene or *o*-hydroxybenzophenone, which deposits all the absorbed light energy as heat.[11] Absorbances of metal carbonyl solutions were typically between 0.08 and 0.11 for a 1-cm path length. The absorbance of a reference solution was adjusted to within 2% of that of a corresponding metal carbonyl solution. The measured heat, α, is expressed as a fraction of the photon energy absorbed and is determined from eq 1, where S_s and S_r

$$\alpha = (S_s/S_r)(P_r/P_s)(1 - T_r)/(1 - T_s) \qquad (1)$$

are the amplitudes of the transducer signal from the sample cell for a sample solution and a reference solution, respectively. The rest of eq 1 contains normalization factors for differences in the absorption of light by the sample and reference solutions $(1 - T)$ and for variation in laser power while signals from sample and reference solutions (P) are measured. As before, the transmission of a solution (T) was determined from PAC measurements, and the observed heats were corrected for differences in solution adsorptions and variations in laser pulse energies.[4,10]

Actinometry Sample Preparation. In a typical experiment 6 mg of $Cr(CO)_6$ was placed in an oven-dried septum-sealed volumetric flask filled with argon. The flask was evacuated three times to 50 μm of Hg and filled with argon. Freshly distilled DCE was cannulated into the flask, and 50 μL of freshly distilled pip was added with a Hamilton syringe. After dissolution of the $Cr(CO)_6$, DCE was cannulated to the mark. Argon was bubbled through the solution with the cannula to ensure mixing. The solution was then cannulated into a preweighed oven-dried septum-sealed cuvette (Wilmad #110CQ). Sample volumes were determined from the sample weights and the temperature of the samples in the thermostated cell holders. All actinometric samples were prepared to absorb all indicent light (>99.8%).

---

[2] Kelly, J. M.; Long, C.; Bonneau, R. *J. Phys. Chem.* **1983**, *87*, 3344.

[3] (a) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1989**, *93*, 291. (b) Wang, L.; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 8695. (c) Joly, A. G.; Nelson, K. A. *J. Phys. Chem.* **1989**, *93*, 2876. (d) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1987**, *91*, 5538. (e) Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* **1989**, *111*, 8963. (f) Yu, S.-C.; Xu, X.; Lingle, R., Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668. (g) Simon, J. D.; Xie, X. *J. Phys. Chem.* **1986**, *90*, 6751.

[4] Morse, J., Jr.; Parker, G.; Burkey, T. J. *Organometallics* **1989**, *8*, 2471.

[5] Yang, G. K.; Vaida, V.; Peters, K. S. *Polyhedron* **1988**, *7*, 1619.

[6] Brown, C. E.; Ishikawa, Y.-I.; Hackett, P. A.; Rayner, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 2530.

[7] (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (b) Weiller, B. H.; Wasserman, E. P.; Bergman, R. G.; Moore, C. B.; Pimental, G. C. *J. Am. Chem. Soc.* **1989**, *111*, 8288.

[8] Breckenridge, W. H.; Stewart, G. M. *J. Am. Chem. Soc.* **1986**, *108*, 364.

[9] Burkey, T. J. *Polyhedron* **1989**, *8*, 2681.

[10] Burkey, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8329.

[11] (a) Hou, S.-Y.; Hetherington, W. M., III; Korenowski, G. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *68*, 282. (b) Maciejewski, A.; Jaworska-Augustyniak, A.; Szeluga, Z.; Wojtczak, J.; Karolczak, J. *Chem. Phys. Lett.* **1988**, *153*, 227.

Actinometric Measurements. Samples were photolyzed with a 150-W high-pressure xenon lamp in an elliptical reflector housing by Photon Technologies International (Model A1010 with an LPS-220 power supply). The lamp output was passed through a 10-cm water filter and 337-nm interference filter (Oriel 52580). Alternatively the light was passed through the water filter, a Schott filter (UG5), a 6% neutral density filter, and a 337-nm filter (Corion P10F or P10R) before focusing the light through the sample. For 302 and 254 nm different interference filters were used (Corion G10F and G25F, respectively). Dimethylanthracene in Freon 113, diazobenzene in methanol, and Aberchrome in toluene were used as chemical actinometers to determine light intensity according to literature procedures.[12] The results were independent of the actinometer used. For comparison of quantum yields in PFD at different wavelengths ferrioxalate was used as an actinometer.[13] Light intensities were approximately 10^{-9} einstein s^{-1} over approximately a 0.5-cm^2 area. A sample cuvette for $Cr(CO)_6$ photolysis was calibrated by determining the absorbed light intensity in the sample cuvette and a reference cuvette with use of the same chemical actinometer solution. Light intensities were determined with the reference cuvette immediately before and after each $Cr(CO)_6$ sample was photolyzed. At least three samples of a stock $Cr(CO)_6$ solution were photolyzed and analyzed to make a determination.

Product formation was followed by visible (Gilford Response II spectrometer) or FTIR spectroscopy (Mattson Polaris NU 10000 FTIR instrument, 25 scans, 1-cm^{-1} resolution, 0.5 mm path length NaCl cell). The Mattson SQUANT programs were used to determine IR peak areas, from which product concentrations were directly obtained. During actinometric measurements, no more than 5% $Cr(CO)_6$ was photolyzed and corrections were made for inner-filter effects.[14]

The quantum yield of photosubstitution was determined from eqs 2 and 3, where Δ is the moles of product formed per second, I_0 the light intensity (einstein s^{-1}), A the change in absorbance of the actinometric solution after the photolysis for time t (s), Φ_{act} the quantum yield of the actinometer at the irradiating wavelength, ϵ_{act} the extinction coefficient of the actinometer at the observation wavelength, and l the cuvette path length. For dimethylanthracene, $\Phi_{act}\epsilon_{act}$ for 337-nm excitation was assumed to be the same as for 334 nm since $\Phi_{act}\epsilon_{act}$ varies only 3% from 334 to 395 nm.

$$\Phi_{sub} = \Delta / I_0 \tag{2}$$

$$I_0 = (A/t)/\Phi_{act}\epsilon_{act}l \tag{3}$$

Viscosity Measurements. The viscosities of PFD and perfluoromethylcyclohexane were determined with an Ostwald viscometer by use of eq 4, where t is the time it takes for the fluid to pass through the viscometer and ρ is the density of the fluid.

$$\eta / \eta_{std} = t\rho / t_{std}\rho_{std} \tag{4}$$

The standard solution was heptane (η_{std} = 0.409 cP, ρ_{std} = 0.6837 g/mL at 20 °C).[15] The times for PFD, perfluoromethylcyclohexane, and heptane were respectively 839, 219, and 159 s. The densities of PFD and perfluoromethylcyclohexane are 1.929 and 1.788 g/mL at 25 °C.[16] From these results we obtain viscosities of 6.02 and 1.47 cP, respectively, in good agreement with literature values.[16]

Results

Table I. Quantum Yields for Ligand Photosubstitution of $Cr(CO)_6$ at 337 nm

solvent	$[Cr(CO)_6]$, mM	n[a]	ligand (concn, mM)	ϵ, cm^{-1} M^{-1}	λ, nm	Φ
CH	10	2	pip (100)	3593	420	0.67 ± 0.01
CH	10	1	pyr (100)	5460[b]	394	0.65
BZ	2.6–2.8	3	pip (50)	3462	417	0.67 ± 0.02
DCE	2–3	3	pip (50)	3252	414	0.62 ± 0.05
PFD	1.9	3	pip (4.2)	2860	420	0.31 ± 0.01
PFD	1.9	1	pip (4.2)	2860	420	0.32[c]
PFD	2.5	3	pip (5.0)	2860	420	0.30 ± 0.01[d]
PFH	7.4	3	pip (0.05)	3300	420	0.48 ± 0.01

[a] Number of determinations. [b] Reference 14. [c] 302-nm filter, 10-nm bandwidth. [d] 254-nm filter, 10-nm bandwidth.

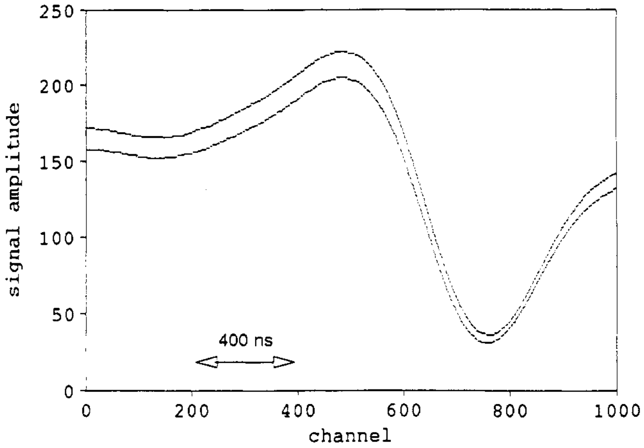


Figure 1. Photoacoustic signal for 337-nm photolysis. The upper plot is the reference signal for ferrocene in a DCE solution. The lower plot is the sample signal for $Cr(CO)_6$ (10^{-4} M) in DCE. Each plot is the average for ca. 70 laser shots.

Conventional actinometric techniques were used to determine the quantum yield for photosubstitution of $Cr(CO)_6$ with pip or py in CH, BZ, DCE, PFD, and PFH (eq 5, Table I). For the range of ligand and $Cr(CO)_6$ concentrations used in the current study, it has been shown that quantum yields for photosubstitution are independent of ligand concentration.[14,17] Extinction coefficients for the products had to be known accurately, since product yields were normally determined from electronic absorptions. As before, the extinction coefficients were found to be solvent dependent (Table I).[17] The quantum yields for 337-nm photolysis were 0.67 in CH and BZ and slightly lower in DCE. For CH the quantum yield was found to be unchanged when IR detection was used (1931.4 cm^{-1}, Φ = 0.66 ± 0.01 in CH with 10 mM $Cr(CO)_6$ and 0.1 M pip) and agrees with prevous studies.[14,17] The quantum yields were much lower in the fluorocarbons PFD and PFH (Table I). The value for perfluorohexane is in good agreement with the value of 0.47 reported recently.[17] Quantum yields obtained in PFD at 302 and 254 nm were the same as at 337 nm.

$$Cr(CO)_6 \xrightarrow{h\nu} Cr(CO)_5 + CO \xrightarrow{L} Cr(CO)_5L \tag{5}$$

$$L = \text{pip, py, CH, BZ, DCE}$$

Independent measurements of quantum yields were obtained by PAC. As discussed below, PAC provides quantum yields on a different time scale, providing further photochemical information. The thermochemistry of organometallic compounds has been studied previously with use of PAC,[4,5,9,10,18] and the technique has also been used to determine quantum yields.[19] Light from a pulsed laser

---

[12] (a) Adick, H.-J.; Schmidt, R.; Brauer, H.-D. *J. Photochem. Photobiol., A* **1988**, *45*, 89. (b) Gauglitz, G.; Hubig, S. *J. Photochem.* **1981**, *15*, 255. (c) Heller, H.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

[13] Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **1989**, *61*, 187.

[14] (a) Nasielski, J.; Colas, A. *Inorg. Chem.* **1978**, *17*, 237. (b) Nasielski, J.; Colas, A. *J. Organomet. Chem.* **1975**, *101*, 215.

[15] *Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C. Ed.; CRC: Boca Raton, FL, 1989; pp C295, F43.

[16] Maciejewski, A. *J. Photochem. Photobiol., A* **1990**, *51*, 87.

[17] Wieland, S.; van Eldik, R. *J. Phys. Chem.* **1990**, *94*, 5865.

[18] Klassen, J. K.; Yang, G. K. *Organometallics* **1990**, *9*, 874.

[19] (a) Bilmes, B. M.; Tocho, J. O.; Braslavsky, S. E. *Chem. Phys. Lett.* **1987**, *134*, 335. (b) Lynch, D.; Endicott, J. F. *Appl. Spectrosc.* **1989**, *43*, 826.

Table II. Observed Heats (α) and Quantum Yields at 337 nm for Photosubstitution of $Cr(CO)_6$ Determined by PAC

solvent	ligand[a]	n[b]	α	Φ	ΔH, kcal mol^{-1}
CH	CH	3	0.810 ± 0.006		24.2 ± 0.8
PFD	CH	3	0.919 ± 0.005	0.28 ± 0.02	
BZ	BZ	3	0.828 ± 0.003		21.8 ± 0.8
PFD	BZ	2	0.923 ± 0.003	0.30 ± 0.02	
DCE	DCE	2	0.845 ± 0.017		21.2 ± 2.9
PFD	DCE	2	0.933 ± 0.016	0.27 ± 0.08	

[a] Concentrations in PFD were 0.01–0.03 M. [b] Number of determinations.

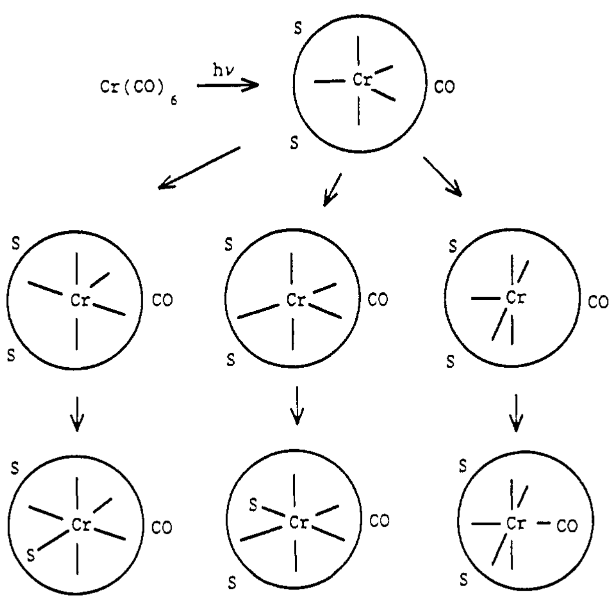
initiates chemical and physical processes that liberate heat, generating an acoustic wave that is detected with an ultrasonic pressure transducer (Figure 1). An important feature of the calorimeter is the time response of the transducer. It responds to heat liberated at rates faster or near its frequency response but not to heat liberated at rates much slower than its frequency responses. If the reactions occurring after the laser pulse are much faster or slower than the response of the transducer, then the amplitude of the transducer signal is proportional only to the heat released by the fast reactions.[20] The amplitude of the transducer signal is therefore a measure of the heat of the faster reactions. The heat observed after the laser pulse (αE_ν) is dependent on the energy of light absorbed (E_ν), the enthalpy of substitution (ΔH_5), and the quantum yield of substitution (Φ, eq 6). α, the observed heat ex-

$$\alpha E_\nu = E_\nu - \Phi \Delta H \qquad (6)$$

pressed as a fraction of the absorbed light energy, is equal to the ratio of the heat released by the sample solution to that of a reference solution that deposits all the light energy as heat (see the Experimental Section).

After photolysis of $Cr(CO)_6$, the $Cr(CO)_5$ fragment will first interact with a solvent molecule. For alkanes and more reactive solvents the half-life for the reaction of $Cr(CO)_5$ with solvent is less than 100 ps and is therefore going to be a cage reaction.[3] With reactive nonsolvent species kept at low concentrations, the solvent-coordinated $Cr(CO)_5$ will persist up to 1 ms in "reactive solvents" such as CH, BZ, and DCE, and the heat detected with a 1-MHz transducer will correspond to the enthalpy of reaction 5, where L is the solvent. ΔH_5 will be equal to the difference in the Cr–CO and Cr–L bonds and the difference in the solvation of reactants and products; however, previous studies show that the difference in solvation of organometallic reactants and products in hydrocarbon solvents is negligible.[21] For simplicity CH, BZ, and DCE will be referred to as ligands, since there is ample evidence that these compounds function as ligands. Aromatic compounds and halocarbons are known to be labile and stable ligands,[22] and the stereospecific metal–alkane bond observed for $Cr(CO)_5$–alkane complexes indicates the alkanes behave as ligands, albeit transient ones.

Scheme I



The heat released after photolysis of $Cr(CO)_6$ was determined in neat ligand (CH, BZ, and DCE) and 0.01–0.03 M ligand in PFD (Table II). For this range of ligand concentrations in PFD, with a 1-MHz transducer, the transducer signal amplitude did not change with ligand concentration. This indicates that the rate of reaction greatly exceeded the frequency response of the transducer. This is consistent with the expectation that the rate of reaction with ligand is near the diffusion-controlled rate in a fluorocarbon solvent[2] and indicates that all the heat of reaction 5 was being observed.[20] The signal amplitude did depend on which ligand was present. Flash photolysis studies show that $Cr(CO)_5$ reaction with alkyl halides and the rearrangement of $Cr(CO)_5$–RX to $Cr(CO)_5$–XR occurs in less that 1 ns.[23] Therefore, the heat observed in experiments with DCE will correspond to a Cr–Cl interaction.

It is clear that the heat observed for reaction in neat ligand is less than when the ligand is dispersed in PFD. Inspection of eq 6 indicates that the differences are likely to result from a change in Φ, since ΔH should not change. This allows the calculation of the quantum yield in PFD (Φ_{PFD}) from α and eq 7 (derived from eq 6) if the quantum

$$\Phi_{PFD}/\Phi_{REF} = (1 - \alpha_{PFD})/(1 - \alpha_{REF}) \qquad (7)$$

yield in a reference solvent (Φ_{REF}) is known. The reference solvent is dispersed in PFD as a ligand so that the same substitution reaction occurs in neat ligand and PFD and ΔH is unchanged. The quantum yields in PFD are summarized in Table II. The ΔH change with solvent (ligand) has also been reported in Table II. These ΔH values and those for other solvents are the subject of another study.[24]

Discussion

The results demonstrate that the quantum yield for photosubstitution of $Cr(CO)_6$ decreases upon going from organic to perfluorocarbon solvent. The quantum yields in PFD do not vary (within experimental error), even though the stability of the products and mode of bonding vary considerably. The PAC results further indicate that the product-determining step occurs on the order of 10 ns or less after photolysis, since all of the heat of reaction with

---

(20) (a) Rudzki, J.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849. (b) Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218. (c) Heihoff, K.; Braslavsky, S. E. *Chem. Phys. Lett.* **1986**, *131*, 183.

(21) (a) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444. (b) Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* **1983**, *105*, 6824. (c) Gonzales, A. A.; Zhang, K.; Nolan, S. P.; de la Vega, R. L.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

(22) See: (a) Zhang, S.; Dobson, G. R.; Zang, V.; Bajaj, H. C.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3477. (b) Zhang, S.; Zang, V.; Bajaj, H. C.; Dobson, G. R.; van Eldik, R. *J. Organomet. Chem.* **1990**, *397*, 279. (c) Zhang, S.; Dobson, G. R. *Polyhedron* **1990**, *20*, 2511 and references therein.

(23) (a) Xie, X.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 1130. (b) O'Driscoll, E.; Simon, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 6580.

(24) Burkey, T., unpublished results.

ligand was observed. It is interesting to note that determining quantum yields for L = CH, BZ, or DCE could only be determined with PAC since the products were not stable. The results are consistent with the quantum yields being determined by interactions between the solvent and the $Cr(CO)_5$ fragment. Most of the results can be explained by the current theory of the photochemistry of $Cr(CO)_6$.[25] It is postulated that photolysis of $Cr(CO)_6$ leads to ejection of CO and the formation of a trigonal-bipyramidal $Cr(CO)_5$ (Scheme I). The trigonal bipyramid relaxes by three pathways, each with equal probability, to a square-pyramidal geometry where two of the equatorial CO's open to nearly 180°. $Cr(CO)_5$ opens toward CO and promptly re-forms $Cr(CO)_6$ with a probability of one-third and toward a solvent cage molecule with a probability of two-thirds. This occurs before CO escapes from the solvent cage. If the solvent is an alkane or a more reactive solvent, the solvent coordination is strong enough to inhibit cage recombination with the remaining CO allowing the CO to diffuse away. The solvent-coordinated $Cr(CO)_5$ can then react with added ligand with an overall quantum yield of $^2/_3$. It is generally believed that the quantum yield is the same for all nonviscous solvents.[23a] We suggest that, in the case of perfluorocarbon solvents, the coordination is weak, and cage CO can more easily displace the fluorocarbon to recombine with $Cr(CO)_5$. This results in less $Cr(CO)_5$ available for reaction with dispersed ligand. The quantum yield in PFD suggests that half of the CO's that do not promptly recombine, recombine in the solvent cage with $Cr(CO)_5$, and the other half diffuse away. Hence, only one-third of the $Cr(CO)_5$ initially formed by photolysis is available for reaction with other ligands. This further indicates that the rate of cage escape is about the same as the rate of cage recombination. This model suggests a greater rate of CO recombination is responsible for the low quantum yield in PFD.

It might be expected that the greater viscosity of PFD relative to that of organic solvents is responsible for greater recombination with CO. In principle the increase in cage recombination can result from an increase in the rate of recombination, a decrease in the rate of cage escape, or both.[26] The known dependence of quantum yields on viscosity indicates that a reduced rate of CO cage escape is not primarily responsible for the decrease in Φ. The quantum yield for $Cr(CO)_6$ photosubstitution in Paraffin I is 0.51 (η = 140 cP).[14] Relative to the yield in cyclohexane (η = 0.97 cP[14]) the quantum yield decreases by only 0.16, and the viscosity increases by greater than 2 orders of magnitude. By comparison, the quantum yield in PFD decreases more than twice as much (0.37) yet the viscosity is only 6 times greater. If viscosity were the only factor responsible for differences in quantum yields, then in PFD the quantum yield ought to be greater than 0.51, not less.

Another possible cause of a decrease in the quantum yield would be more efficient relaxation of thermally excited $Cr(CO)_5$ and CO.[27] If excess thermal energy aids CO escape and PFD were to vibrationally couple with the fragments more efficiently than the other solvents, then PFD might relax the fragments more rapidly and the fragments would have less energy available to escape the solvent cage. Previous studies have shown that providing photolytic fragments with more thermal energy can increase the quantum yield.[28] As can be seen in Table II, the quantum yield in PFD at 254 nm is the same as at 337 nm, even though 28 kcal/mol more energy is initially available at 254 nm. Similar results have been obtained in cyclohexane.[14] It therefore appears that more efficient relaxation of the photolytic fragments by PFD is not responsible for the low quantum yield and excess energy is not needed for CO escape. This is consistent with recent picosecond flash photolysis studies.[3f,g] In particular it can be concluded that after photolysis the $Cr(CO)_5$ fragment binds cyclohexane before complete thermal relaxation. Simon and Xie have reported that $Cr(CO)_5$ is solvated in less than 1 ps, while the results of the Harris and Hopkins groups indicate that vibrational relaxation occurs on a much longer time scale.[3] In the Harris group, a 17-ps decay in the "tail" of the transients' visible absorption was attributed to vibrational relaxation. The authors suspect that the vibrational energy is dissipated via low-frequency modes and infer that the $Cr(CO)_5$ fragment binds cyclohexane within this time frame. Using Raman detection, the Hopkins group observed transient IR spectra which were assigned to the CO vibration of the $Cr(CO)_5$ fragment. The transient lifetime was on the order of 100 ps and was attributed to the vibrational relaxation of the $Cr(CO)_5$ fragment in agreement with the lifetime observed previously for the vibrational relaxation of $Cr(CO)_6$ in hexane (145 ps).[29] The authors concluded that the fragment is likely to be solvent-coordinated faster than relaxation of the CO vibration. The different vibrational relaxation lifetimes might be explained by poor coupling between the high-frequency CO and the low-frequency bond vibrations; the latter, of course, involve Cr–alkane bonds.[30] Thus, this interpretation indicates photolytically generated $Cr(CO)_5$ can bind a "reactive" solvent molecule before CO can diffuse out of the solvent cage, and the binding should be less efficient for a fluorocarbon solvent. Nevertheless, it should be pointed out that the above mechanism is not entirely consistent with the conclusions of recent kinetic IR studies.[3b,31]

Other data also suggest that cage recombination is enhanced in PFD. In perfluoromethylcyclohexane, $Cr(CO)_5$ reacts with dispersed CO at a nearly diffusion-controlled rate (3×10^9 M^{-1} s^{-1}),[2] and this rate can be taken as a lower limit for both CO diffusion in PFD and a cage reaction of $Cr(CO)_5$ with CO in PFD. The relative viscosities of PFD and perfluoromethylcyclohexane are 4:1; therefore, in PFD these values will be about 8×10^8 M^{-1} s^{-1}.[32] This value is much greater than the rate of reaction with dispersed CO in cyclohexane (4×10^6 M^{-1} s^{-1}),[33] which clearly indicates a slow rate of cage reaction of $Cr(CO)_5(CH)$ with CO since a diffusion-controlled reaction with CO (5×10^9 M^{-1} s^{-1})[32,34] greatly exceeds this value. Therefore, cage

---

(25) (a) Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147. (b) Turner, J. J.; Poliakoff, M. *ACS Symp. Ser.* **1983**, *No. 200*, 35.

(26) Lorand, J. *Prog. Inorg. Chem.* **1972**, *17*, 205.

(27) We thank Professor Poliakoff for suggesting this possibility.

(28) (a) Griller, D.; Clark, K. B. *Chem. Phys. Lett.* **1990**, *168*, 477. (b) Meadows, L. F.; Noyes, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 1872. Also see ref 26.

(29) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *Chem. Phys. Lett.* **1987**, *134*, 181.

(30) We thank Professor Harris for suggesting this interpretation of published work.

(31) (a) Spears, K. G.; Wang, L.; Zhu, X.; Arrivo, S. M. *Proc. SPIE-Int. Soc. Opt. Eng.* **1990**, *1209*, 32. (b) Wang, L.; Zhu, X.; Spears, K. G. *J. Phys. Chem.* **1989**, *93*, 2.

(32) Diffusion-limited rates are inversely proportional to viscosity and follow the form $k = a/\eta$, where a is a constant determined by temperature and the reacting species: Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; p 626.

(33) Church, S. P.; Grevels, F.-W.; Hermann, H.; Schaffner, K. *Inorg. Chem.* **1985**, *24*, 418.

(34) This value is calculated from the solvent viscosities of cyclohexane and perfluoromethylcyclohexane, the rate constant for the reaction of CO with $Cr(CO)_5$ in perfluoromethylcyclohexane, and the assumption that this reaction is diffusion-limited. This result is in good agreement with a literature value of 6.6×10^9 M^{-1} s^{-1} (see ref 32, p 627).

recombination in PFD is at least 200 times faster than in CH, while cage escape in PFD is only 6 times slower than in CH.[35] Another possible cause of lower quantum yields is the variation in the decay pathways of the excited state of $Cr(CO)_6$ with solvent changes.[36] While we cannot exclude this possibility, it seems unlikely to be a major contribution to quantum yield differences, since PFD and PFH would be expected to give the same quantum yields (Table I). We conclude that the low quantum yield in PFD can be attributed primarily to a faster rate of cage recombination.

Inspection of the quantum yields reported by Wieland and van Eldik and our yields for DCE reveals deviations from the "$^2/_3$ rule" for "reactive" solvents of low viscosity. Wieland and van Eldik pointed out that the deviations cannot be explained by variations in viscosity. The quantum yields are significantly larger for some solvents and smaller for others. The differences are likely due to differences in microscopic properties of the solvent and how they contribute to the interaction with $Cr(CO)_5$. As an example, we wish to speculate about one possible contribution to the differences in quantum yields. In terms of the Turner and Poliakoff model, yields higher than $^2/_3$ may indicate occasional solvent intervention when the $Cr(CO)_5$ reopens to face the CO, and the lower yields indicate the solvent cannot completely trap $Cr(CO)_5$ even when it opens toward the solvent. Therefore, it is not just a matter of whether $Cr(CO)_5$ faces CO or solvent; CO's ultimate escape is also determined by how efficiently a cage solvent molecule can collapse to trap $Cr(CO)_5$ (as in the case of PFD). Wieland and van Eldik obtained quantum yields in short-chain alkanes that were larger than that for CH. This might be attributed to the availability of methyl groups that are sterically less demanding and more mobile than a methylene. An analogous argument may explain the relative quantum yields in PFD and PFH. Further studies of aromatic and halogenated compounds are in progress.

Acknowledgment. The donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Memphis State Faculty Research Grant are acknowledged for partial support of this research.

---

(35) The rate constant for cage escape follows the form $k = a/\eta$, where a is a constant dependent on the size of the diffusing species.[14a]

(36) We thank a reviewer for this suggestion.

Platinum-Catalyzed Hydrosilylation of Alkynes

Larry N. Lewis,* Karen G. Sy, Garold L. Bryant, Jr., and Paul E. Donahue

GE Research and Development, Schenectady, New York 12301

Received April 26, 1991

The reaction of terminal alkynes with several SiH compounds was investigated. The alkynes included phenylacetylene and 1-pentyne. Silanes investigated were triphenylsilane, diphenylmethylsilane, phenyldimethylsilane, triethylsilane, and triethoxysilane. All the reactions were catalyzed by highly active platinum catalysts. Comparison of product yields to those of reactions with other platinum catalysts and with rhodium catalysts were made in a few cases. Comprehensive analysis of product distribution and structure was made by GC and ^1H and ^{13}C NMR spectroscopy (APT and HETCOR). Further structural confirmation was achieved with single-crystal X-ray structures for *trans*-$Ph_3SiCH{=}C(H)Ph$ (1-trans) and for $Ph_3Si(Ph)C{=}CH_2$ (1-α). Compound 1-trans, $C_{26}H_{22}Si$, was monoclinic, $P2_1$, with $a = 7.410$ (6) Å, $b = 11.349$ (8) Å, $c = 12.594$ (10) Å, $\beta = 99.43$ (6)°, and $Z = 2$. Compound 1-α, $C_{26}H_{22}Si$, was monoclinic, $P2_1/c$, with $a = 10.121$ (7) Å, $b = 10.225$ (6) Å, $c = 20.116$ (11) Å, $\beta = 93.03$ (5)°, and $Z = 4$.

Introduction

The hydrosilylation reaction (eq 1) is remarkable in its speed and selectivity. Typically, in the presence of parts

$$R_3SiH + H_2C{=}CHR' \xrightarrow{\text{catalyst}} R_3SiCH_2CH_2R' \quad (1)$$

per million of catalyst, SiH containing compounds add to terminal olefins at or slightly above room temperature in minutes or a few hours. In addition, hydrosilylation is a selective reaction, generally giving >98% "β addition" (as shown in eq 1).[1-7] The mechanism and nature of the catalytic species in this reaction have recently been investigated by these laboratories.[8-11]

As described by us[9] and others,[1,2,4,6] several metals catalyze the hydrosilylation reaction but rhodium and platinum are the most active. The type of platinum compound that would generate the highest activity is one in which reduction to or formation of a single Pt^0 atom and concomitant loss of ligands are facile.[8,11] The most active catalysts are therefore Pt^0L_x complexes where L is olefinic and least active catalysts are Pt^{II} or Pt^{IV} complexes with strongly binding ligands such as phosphines, amines, and sulfides.

As we[8,9] and others[2,4,6] have discussed, the rate and selectivity of hydrosilylation is adversely affected by certain

---

(1) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons, Ltd.: New York, 1989; p 1479.

(2) Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Vol. 2; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Vol. 2, p 117.

(3) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(4) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. In *Organometallic Chemistry Reviews, Journal of Organometallic Chemistry Library*; Seyferth, D., Davies, A. G., Fisher, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; Vol. 5.

(5) Harrod, J. F.; Chalk, A. J. In *Organic Synthesis Via Metal Carbonyls*; Wender, I., Pino, P.; Eds.; John Wiley: New York, 1977; p 673.

(6) Eaborn, C.; Bott, R. W. In *The Bond to Carbon*; MacDiarmid, A. G., Ed.; Marcel Dekker: New York, 1968; Vol. 1.

(7) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16.

(8) Lewis, L. N. *J. Am. Chem. Soc.* **1990**, *112*, 5998.

(9) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.

(10) Lewis, L. N.; Lewis, N. *Chem. Mater.* **1989**, *1*, 106.

(11) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228.

0276-7333/91/2310-3750$02.50/0 © 1991 American Chemical Society