Pulsed Laser Photolysis of Chromium Hexacarbonyl in the Gas Phase

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Abstract: Transient absorption spectra observed after pulsed laser photolysis of $Cr(CO)_6$ in the gas phase are assigned to $Cr(CO)_5$ and $Cr(CO)_5{\cdot}Q$ complexes (with Q = $Cr(CO)_6$, N_2, NH_3, methanol, acetone, ethylene, and silane) and an unknown product formed by the reaction of two $Cr(CO)_5$ molecules. A simple kinetic model is proposed, and calculations are performed to show that the model is consistent with the observed data.

Pulsed laser photolysis of chromium hexacarbonyl in the gas phase provides a convenient method of generating coordinatively unsaturated metal carbonyl fragments. Depending upon the photolysis conditions, one or more CO ligands can be removed to produce everything from chromium pentacarbonyl ($Cr(CO)_5$) to Cr atoms.[1–6] Of particular interest to us are the kinetics and reactivity of $Cr(CO)_5$. Previous matrix,[7] solution,[8–10] and gas-phase[1] photolysis work has shown that $Cr(CO)_5$ can form complexes, $Cr(CO)_5{\cdot}Q$, with a variety of chemically rather "inert" ligands. In addition, the UV–vis absorption spectrum of the complex $Cr(CO)_5{\cdot}Q$ depends quite sensitively upon the ligand Q. For example, in rare-gas matrices, the lowest frequency visible absorption band of $Cr(CO)_5Ne$ has an absorption maxima at 620 nm, while the corresponding band in $Cr(CO)_5Ar$ absorbs at 520 nm.[7] In the work described in this paper, $Cr(CO)_5$ has been generated by gas-phase laser photolysis of $Cr(CO)_6$, and the subsequent visible transient absorption spectra have been measured. We have been able to observe directly the transient visible absorption spectrum of "naked" $Cr(CO)_5$ and monitor its subsequent reactions with itself and various ligands.

Experimental Section

$Cr(CO)_6$ is photolyzed at 355 nm with a frequency-tripled Nd:YAG laser (Molectron MY-32). At this wavelength, the laser delivers up to 40 mJ of energy in a 12-ns pulse. The measured shot-to-shot variation in output energy is about 10%. Quartz optics and a beam splitter were used to reflect the laser light into a 20-cm sample cell with a beam diameter of 6 mm. The initial percent decomposition of $Cr(CO)_6$ (to $Cr(CO)_5$ + CO) after a laser shot was typically about 2% but was estimated to vary from 0.5 to 8% depending on laser power and $Cr(CO)_6$ pressure. For pulse energies of greater than 12 mJ, some net decomposition of $Cr(CO)_6$ was observed after 50 or more laser shots. At lower energies, no net decomposition was apparent. The spectra presented here were collected with pulse energies of 8 mJ or less and were taken with fewer than 30 laser shots per sample. The pressure of $Cr(CO)_6$ within the heated cell was maintained between 2 and 22 torr (the ambient vapor pressures at 45 and 80 °C, respectively).

The laser light and light from a 2500-W continuum Xe arc lamp were aligned coaxially through the sample cell. Light from the arc lamp was passed through a water filter and a 400-nm cutoff filter prior to entering the sample cell. In addition, the arc lamp was shuttered so that its light was passed through the sample cell for only 110 ms per laser shot. A monochromator (Jarrell Ash 82-000) was used to disperse the white light with slit widths giving a resolution of 2 nm. Two cutoff filters ($\lambda \geq 380$ nm) were placed in front of the entrance slit of the monochromator to block the laser light. The dispersed light was detected by a photomultiplier tube (Hamamatsu R928) wired to withstand (and operate linearly during) the 100-ms burst of high intensity light.[11] The transient absorption time profile was measured by either a transient digitizer (Biomation 8100) or a storage oscilliscope (Tektronix 7834). The length of the excitation pulse and the light intensity of the arc lamp limited the time resolution to about 20 ns. The absorption spectra of transient intermediates were obtained by determining for various monochromator wavelength settings the optical density at a given time delay after the laser pulse.

The $Cr(CO)_6$ used in these experiments was purchased from Strem Chemicals with a stated purity of ≥98%. Prior to use it was vacuum-sublimed and stored under vacuum in a blackened bulb. All other chemicals used were similarly purified by passing gases through cryogenic traps and subjecting liquids to several freeze–thaw cycles.

Results

When $Cr(CO)_6$ was photolyzed alone or in the presence of up to 400 torr of He buffer gas, three distinct transient absorptions were observed (see Figure 1) with absorption maxima at 620, 500, and 410 nm. The 620-nm transient has a system-limited rise time of 20 ns or less. It decays rapidly to a small positive asymptote at a rate comparable to the appearance of the 500-nm and 410-nm transients. The maximum absorbance at 620 nm increased linearly with laser pulse energy. The decay rate of the 620-nm transient (~100–500 ns) was increased by increasing the vapor pressure of $Cr(CO)_6$ or by adding large amounts of He buffer gas. The 500-nm transient had a rise time identical with the decay time of the 620-nm transient. It then decayed in a nonexponential fashion with a lifetime of about 100 μs. Addition of excess CO changed the decay to an exponential decay and accelerated its rate (see Figure 2).

The 410-nm transient has roughly the same rise time as the 500-nm transient. Over the millisecond or so that we can observe the transient intermediates before they diffuse out of the path of the arc lamp, it does not decay appreciably. In fact, in some samples with very low background pressures of $Cr(CO)_6$, it continues to slowly increase in intensity after its fast initial rise. Addition of excess CO did not increase the rate of decay of this transient species. The intensities of the transients at 410 and 500 nm also exhibit different characteristics with respect to laser pulse energy. As the laser pulse energy is varied from 4 to 28 mJ per pulse, the intensity of the 500-nm transient increases less than linearly. Over the same range of excitation pulse energies, the intensity of the 410-nm transient increases more than linearly.

The spectra obtained with the buffer gases argon, methane, and propane did not differ from the transient absorption spectra obtained with helium as a buffer gas. However, addition of N_2, NH_3, methanol, acetone, ethylene, or silane produced quite different transient absorption spectra (Figures 3–8). In each case, the 620-, 500-, and 410-nm transients were entirely absent, and in their place, a single new feature appeared. With the exception of the transient obtained in the presence of silane, these new transient

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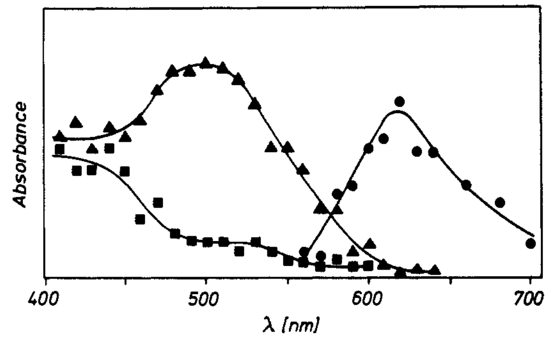

Figure 1. Transient absorption spectra following photolysis of $Cr(CO)_6$ at 355 nm. Conditions: temperature, 58 °C; laser energy, 8 mJ/pulse; $Cr(CO)_6$ pressure, 5 torr; no added buffer gas. (●) time delay of 20 ns; (▲) time delay of 1 μs; (■) time delay of 200 μs.

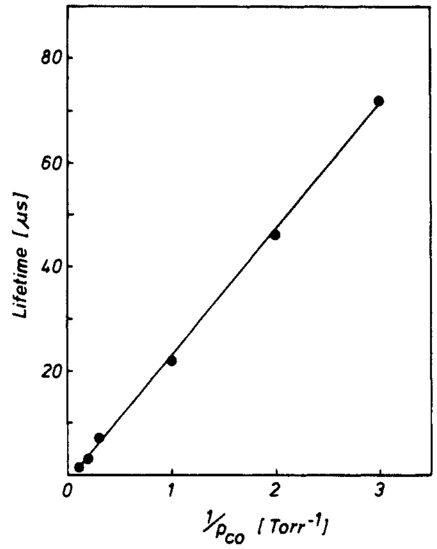

Figure 2. Lifetime of absorption transient at 500 nm vs. inverse CO pressure at 53 °C (no added buffer gas); $Cr(CO)_6$ pressure, 4 torr.

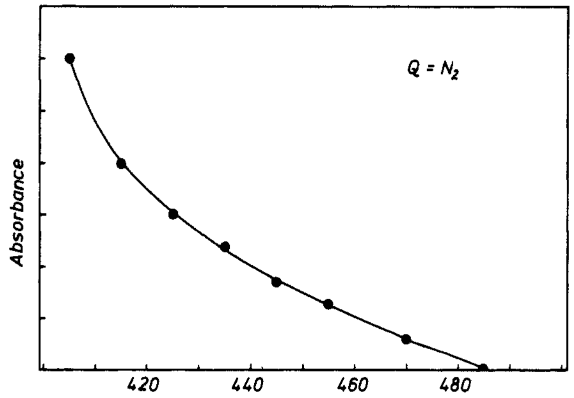

Figure 3. Transient absorption spectrum following photolysis of 6 torr of $Cr(CO)_6$ and 115 torr of N_2 at 60 °C; laser power, 6 mJ/pulse; time delay, 1 μs.

features did not decay noticeably on a millisecond time scale.

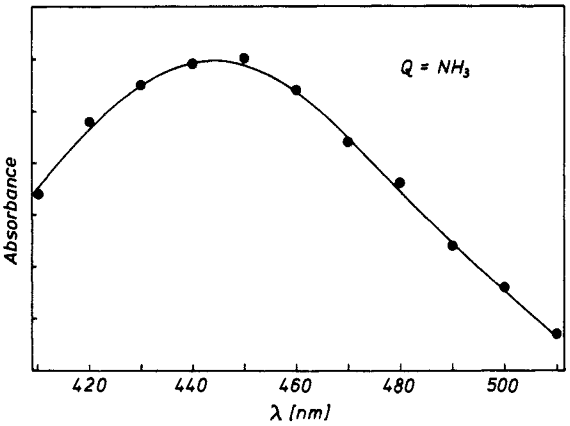

Figure 4. Transient absorption spectrum following photolysis of 7 torr of $Cr(CO)_6$ and 105 torr of NH_3 at 64 °C; laser power, 8 mJ/pulse; time delay, 1 μs.

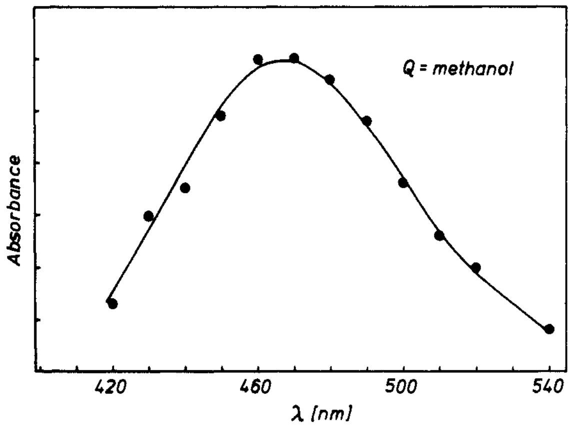

Figure 5. Transient absorption spectrum following photolysis of 2 torr of $Cr(CO)_6$ and 200 torr of methanol at 45 °C; laser power, 8 mJ/pulse; time delay, 1 μs.

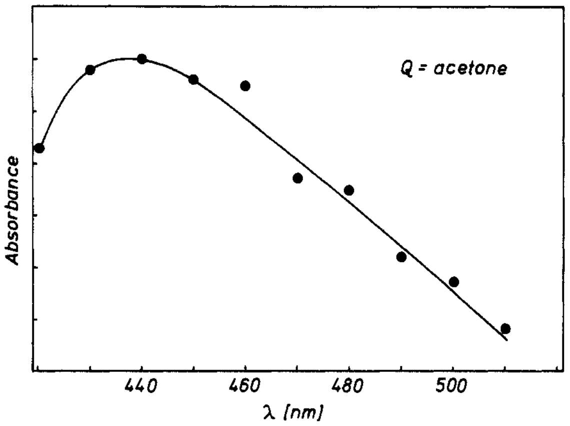

Figure 6. Transient absorption spectrum following photolysis of 2 torr of $Cr(CO)_6$ and 120 torr of acetone at 45 °C; laser power, 8 mJ/pulse time delay, 1 μs.

Discussion

Under our experimental conditions, we believe that the primary photolysis product is $Cr(CO)_5$ formed by single-photon excitation. Two photons of 355-nm radiation have more energy (160 kcal/mol) than is required to remove all six CO ligands from $Cr(CO)_6$ (156 kcal/mol). The lack of decomposition observed under our experimental conditions and the linear rise in the magnitude of the 620-nm transient with increasing laser power indicate that multiphoton events are at best a very minor channel under our conditions. Since 37 kcal/mol is required to remove one CO ligand and 77 kcal/mol to remove two CO ligands from $Cr(CO)_6$[12,13] there is sufficient energy in the 355-nm excitation pulse (80 kcal/mol) to remove two CO ligands with one photon. However, RRKM calculations performed assuming that the decomposition takes place on the ground-state surface and that the first CO ligand ejected carries off a negligible amount of energy indicate that ejection of the second CO would still be extremely slow (~100 μs). We do not expect, therefore, to be able to

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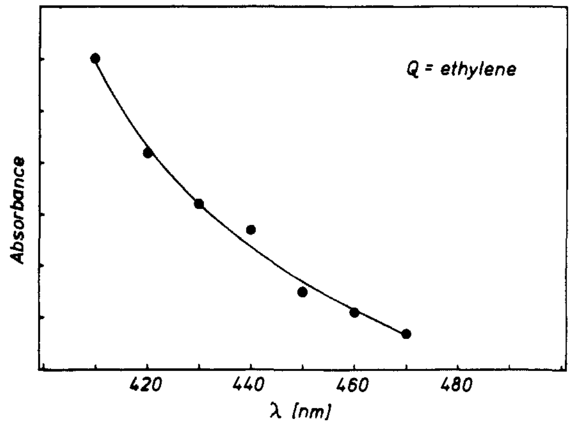

Figure 7. Transient absorption spectrum following photolysis of 2 torr of $Cr(CO)_6$ and 100 torr of ethylene at 45 °C; laser power, 8 mJ/pulse; time delay, 1 μs.

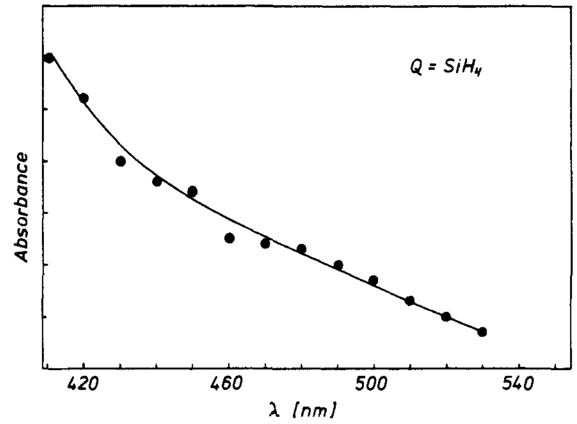

Figure 8. Transient absorption spectrum following photolysis of 2 torr of $Cr(CO)_6$ and 100 torr of SiH_4 at 45 °C; laser power, 8 mJ/pulse; time delay, 1 μs.

produce meaningful amounts of $Cr(CO)_4$ with single-photon excitation.

Assuming that the sole primary product is $Cr(CO)_5$, we are able to rationalize our data by proposing that $Cr(CO)_5$ is capable of undergoing two reactions. One is a reaction with a ligand Q to form $Cr(CO)_5Q$ (where Q is $Cr(CO)_6$, ethylene, N_2, NH_3, methanol, acetone, or silane) and the other is a reaction with itself to form a product of unknown stoichiometry and structure, possibly $Cr_2(CO)_{10}$ or $Cr_2(CO)_9$.

Under these assumptions, we can make the following spectral assignments. The 620-nm transient in Figure 1 is the initial photoproduct, $Cr(CO)_5$. This assignment is supported by the fast rise time (≤ 20 ns) at 620 nm and the subsequent fast decay, consistent with the reactivity expected for a 16-electron species. The location of the visible absorption maxima also agrees well with the spectra of "nearly free" $Cr(CO)_5$ obtained in liquid fluorinated hydrocarbons[8] and a Ne matrix.[7]

The transient shown at 500 nm in Figure 1 we assign to the species $Cr(CO)_5$–$(CO)Cr(CO)_5$. The rise time of the 500-nm transient increases linearly with increasing $Cr(CO)_6$ pressure and also increases somewhat with He pressure. The latter pressure dependence we attribute to the requirement that the primary photoproduct $Cr(CO)_5$ lose some of its excess energy from photolysis (up to 43 kcal/mol) before it can bind to the $Cr(CO)_6$ in what must be a relatively weak interaction. The location of the absorption maxima also agrees well with the known absorption maxima of 490 nm for $Cr_2(CO)_{11}$ observed in solution work.[8] Similarly we assign the spectra in Figures 3–8 to the species $Cr(CO)_5$·Q, formed by reaction of $Cr(CO)_5$ with excess Q, where Q is, respectively, the ligands N_2, NH_3, methanol, acetone, ethylene, or silane.

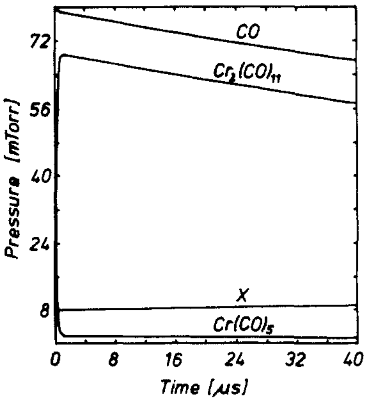

Figure 9. Results of model kinetics calculations (see text). Initial concentrations of CO and $Cr(CO)_5$, 0.08 torr; initial concentration of $Cr(CO)_6$, 4 torr.

Finally, we must assign the transient at 410 nm. Its rise time indicates that it is formed by the subsequent reaction of a primary photoproduct. Also, it is clear that its formation competes with the formation of $Cr_2(CO)_{11}$. Its supralinear dependence on the laser energy (initial concentration of primary photoproduct) is also consistent with its formation from two $Cr(CO)_5$ molecules reacting with each other. The exact identity of this complex is unknown. Two possible candidates are a $Cr_2(CO)_{10}$ complex and a $Cr_2(CO)_9$ molecule. The latter, presumably similar in structure to the known stable species bis(η^6-aryl)tricarbonyldichromium,[14] a molecule containing a Cr–Cr triple bond and three bridging CO's, is perhaps a more reasonable structure chemically. Efforts to isolate the product responsible for the 410-nm transient after the laser photolysis experiments were unsuccessful.

In conclusion, we propose the following general mechanism to explain our results for photolysis of pure $Cr(CO)_6$:

$$Cr(CO)_6 + h\nu \rightarrow Cr(CO)_5 + CO$$

$$Cr(CO)_5 + Cr(CO)_6 \underset{k_{1-}}{\overset{k_{1+}}{\rightleftharpoons}} Cr(CO)_5{\cdot}Cr(CO)_6 \qquad (1)$$

$$2Cr(CO)_5 \underset{k_{2-}}{\overset{k_{2+}}{\rightleftharpoons}} X \qquad (2)$$

$$Cr(CO)_5 + CO \xrightarrow{k_3} Cr(CO)_6 \qquad (3)$$

$$Cr(CO)_5{\cdot}Cr(CO)_6 + CO \xrightarrow{k_4} 2Cr(CO)_6 \qquad (4)$$

where X is an unknown reactant product absorbing at 410 nm. The value of k_3 has been measured independently by two research groups[4,5] and has been found to be about 1.0 μs^{-1} $torr^{-1}$. From our measurements of the rise times of the 500-nm and 410-nm transients, we can estimate the values of k_{1+} and k_{2+} to be about 1.3 and 15 μs^{-1} $torr^{-1}$, respectively. Also the absence of any decay of the 410-nm transient on an observable time scale means that k_{2-} must be taken to be very small: $k_{2-} < .001$ μs^{-1}.

In order to test our model, we have performed model calculations by integrating the resulting differential equations using the LSODE program package. A sample result is shown in Figure 9. In addition to the rate constants that are either known or measured, we obtained the best results by choosing $k_{1-} = 0.50$ μs^{-1} and $k_4 = 0.38$ μs^{-1} $torr^{-1}$. The model calculations reproduce several of the phenomena we observe:

(1) $Cr(CO)_5$ decays quickly to a positive asymptope and thereafter remains at a relatively constant concentration, maintained by its equilibrium with $Cr_2(CO)_{11}$.

(2) Product X, the result of two $Cr(CO)_5$ species reacting with each other, has a fast initial rise time. At low overall background pressure of $Cr(CO)_6$, it continues to increase in concentration at a much slower rate.

(3) The model predicts that for pure $Cr(CO)_6$, the decay of $Cr_2(CO)_{11}$ will be pseudo-second-order (and thus nonexponential)

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because the concentrations of $Cr_2(CO)_{11}$ and CO in reaction 4 are very similar (see Figure 9). In the presence of excess CO, the decay of $Cr_2(CO)_{11}$ becomes exponential with a pseudo-first-order rate constant directly proportional to the CO pressure, as observed experimentally (see Figure 2).

(4) The qualitative dependence of the 410-nm transient intensity on laser intensity (greater than linear) is reproduced because of the increasing rate of reaction 2, producing X, vs. reaction 1. Similarly, the less than linear increase in the maximum intensity of the 520-nm transient is also predicted by the model since reaction 2 siphons off more and more of the $Cr_2(CO)_{11}$ precursor in reaction 1 as the laser intensity, and thus $[Cr(CO)_5]_{initial}$, increases.

One possible alternative for our proposed reaction scheme would be to assume that both $Cr(CO)_4$ and $Cr(CO)_5$ are produced by photolysis at 355 nm. Rosenfeld and co-workers have shown that $Cr(CO)_4$ (generated by photolysis of $Cr(CO)_6$ at 248 nm) reacts rapidly with $Cr(CO)_6$ to form a product they formulate as $Cr_2(CO)_{10}$.[4] Like our unknown product X, their complex decays very slowly ($k \leq 0.001\ \mu s^{-1}$) even in the presence of excess CO. However, Weitz and co-workers using the same detection scheme but photolyzing at 351 nm instead of 248 nm obtained no evidence for the formation of *large* amounts of $Cr(CO)_4$;[5] a very weak IR absorption was tentatively assigned to $Cr(CO)_4$, but since the signal-to-noise ratio for this absorption was quite low, even the assignment is somewhat questionable. From matrix-isolation studies, $Cr(CO)_4$ is thought to have an absorption maxima near 400 nm.[15] If we were producing substantial amounts of $Cr(CO)_4$, we would expect to see a detector-limited rise time of an absorption transient near 400 nm. However, the rise time of the 410-nm transient we do observe is slower (100–500 ns) than the 20-ns resolution limit of our apparatus. Also, in trapping experiments with ligands that form more or less permanent compounds with $Cr(CO)_5$, we see evidence for the formation of only one product (Figures 3–8), not two as might be expected if large amounts of $Cr(CO)_4$ were being formed.

We now discuss briefly the absorption spectra shown in Figures 3–8, which have been assigned as $Cr(CO)_5{\cdot}Q$ complexes formed by reaction of $Cr(CO)_5$ with excess Q. The longest-wavelength absorptions of the $Cr(CO)_5$–L complexes of the type studied here are through to be ligand-field transitions with a great deal of metal d-orbital character in both ground and excited states.[16-18] The wavelength of the transition is usually determined by the energy difference between the highest filled orbitals of e symmetry (d_{xy}, d_{yz} π-bonding character) and the lowest unfilled orbital of a_1 symmetry (d_{z^2} σ^*-antibonding character). These energies, in turn, are dependent on the π-acceptor and σ-donor character, respectively, of ligand L as compared to CO. Weak σ donors with little π-acceptoring capacity will thus have absorptions at the longest wavelengths.

The spectrum of gaseous $Cr(CO)_5N_2$, Figure 3, appears to have an absorption maximum at $\lambda \leq 400$ nm, consistent with spectra of this relatively stable species reported in liquid fluorocarbons[8] and in solid neon[16] ($\lambda_{max} \approx 370$ nm). The spectra assigned to gaseous $Cr(CO)_5NH_3$, Figure 4, ($\lambda_{max} = 445$ nm) are also similar to the spectrum reported for this known, stable complex in cyclohexane solution ($\lambda_{max} = 434$ nm).[7] It is interesting to note that this $Cr(CO)_5NH_3$ absorption shifts substantially to the blue with solvents other than cyclohexane,[7] so that the gas-phase spectrum reported here is a useful "base line" in that it is the spectrum of a completely solvent-free complex. It was also observed after several laser shots under conditions similar to those of Figure 4 that needlelike yellow crystals begin to form on the walls of the gas cell, presumably the yellow crystalline compound[20] $Cr(CO)_5NH_3$.

The spectra assigned by us to $Cr(CO)_5{\cdot}MeOH$ and $Cr(CO)_5{\cdot}$acetone are almost identical with the spectra of long-lived species observed[21] in studies of flash photolysis of $Cr(CO)_6$ in CO-saturated cyclohexane solutions with excess MeOH and acetone ($\lambda_{max} = 460$ and 438 nm, respectively). These intermediates were postulated to be $Cr(CO)_5L$ complexes, with L = MeOH or acetone, on the basis of kinetic data.[21]

The species $Cr(CO)_5$–ethylene has apparently never been prepared, but calculations by Hoffmann and co-workers[18] indicate that the complex should exist; other complexes of ethylene with d^6 metal centers have been reported.[18] Similarly, $Cr(CO)_5{\cdot}SiH_4$ has not been reported in the literature; in this case, there is the possibility that the species observed is actually $HCr(CO)_4SiH_3$, formed by displacement of a CO from $Cr(CO)_5$, with the H–SiH_3 species occupying two coordination sites.

In summary, we have observed the formation of uncomplexed $Cr(CO)_5$ in the gas-phase laser photolysis of $Cr(CO)_6$ at 355 nm. We have confirmed that the position of the lowest-energy absorption maximum of naked $Cr(CO)_5$ is 620 nm, a value previously inferred from flash photolysis experiments in fluorinated hydrocarbons[8] and rare-gas matrices.[7] We have been able to rationalize our data with a simple kinetic model which involves the reaction of $Cr(CO)_5$ with itself or with various added ligands. Spectra of gaseous $Cr(CO_5{\cdot}Q$ complexes, formed by reaction of $Cr(CO)_5$ with various ligands Q present in large excess, have also been reported.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. One of us (W.H.B.) thanks J. Turner and M. Poliakoff for helpful and stimulating conversations.

Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5$, 26319-33-5; N_2, 7727-37-9; NH_3, 7664-41-7; MeOH, 67-56-1; $Cr(CO)_5N_2$, 34416-63-2; $Cr(CO)_5NH_3$, 15228-27-0; $Cr(CO)_5{\cdot}MeOH$, 99643-20-6; $Cr(CO)_5{\cdot}$acetone, 83510-94-5; $Cr(CO)_5$–ethylene, 71407-77-7; $HCr(CO)_4SiH_3$, 99643-21-7; acetone, 67-64-1; ethylene, 74-85-1; silane, 7803-62-5.

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