tection of the gaseous monomer difficult. If one postulates the reaction

$$RuO_4(g) + RuO_2(g) \rightarrow 2RuO_3(g)$$

which is thermodynamically favored but, especially for $\lambda = 365$ nm, kinetically improbable, then somehow the RuO₃ produced must decompose to RuO₂(s) + $1/_2O_2(g)$ to match the observed final product, RuO₂. No evidence for RuO₃ is found in this region, however. We have observed that thermal decomposition of RuO₄(g) at room temperature appears to be catalyzed by deposited RuO₂(s) and, perhaps, in the far from equilibrium conditions during the irradiation, RuO₄(g) decomposition is rapidly catalyzed by the very small, developing RuO₂ clusters. For the continuous irradiation with $\lambda = 313$ nm, although slightly above the threshold shown in Figure 4 (318 nm), there is no evidence for the O atoms or RuO₃ production, as found for shorter wavelengths. This result is not inconsistent, especially bearing in mind the uncertainty in the estimated threshold.

Case III. For the flash photolysis radiation with $\lambda < \sim 300$ nm, 16–21 kJ/mol above the threshold for O atom production, one sees absorption by RuO molecules and Ru atoms. These two spectra always appeared together and with the same relative intensities, suggesting that these two species may be formed consecutively. For the continuous irradiation with $\lambda = 253.7$ nm the simultaneous formation of RuO₃ and RuO₂ suggests that both modes of primary decomposition occur. Similar behavior has been found for the photochemical decomposition of CCl₄ and other mixed halogen species.³⁷ Since both spectra (RuO and Ru) start to appear for the photolysis wavelength ≈ 300 nm and since one finds the more energetic thresholds shown in Figure 4 for photochemical dissociation of RuO₃ and RuO₂, the observed production of RuO and Ru must result from thermal reactions occurring subsequent to the primary photochemical production of RuO₂, RuO₃, O₂ molecules, and ground-state O atoms. The only

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reactions that appear energetically feasible and kinetically reasonable are

RuO₂(g) + O(g) → RuO(g) + O₂(g);
$$\Delta H^{\circ}_{298} = -13 \pm 8 - 12 \text{ kJ}$$

$$RuO(g) + O(g) \rightarrow Ru(g) + O_2(g); \Delta H^{\circ}_{298} =$$

+15 ± 8-12 kJ

 $2Ru(O)(g) \rightarrow Ru(g) + RuO_2(g) \text{ [less likely]; } \Delta H^\circ_{298} = +28 \pm 8-12 \text{ kJ}$

Of course, these flash photolysis reactions take place under extreme nonequilibrium conditions. All of these intermediate species should be produced with internal or translational kinetic energy in excess of the equilibrium values for 298 K, remembering that we have observed that the Ru(g) has an average of about 25 kJ/mol of electronic excitation energy (vide supra).

The unidentified continuous absorption seen between 270 and 240 nm could represent absorption by RuO_3 or RuO_2 ; if RuO_2 , it could well be a mixture of monomeric and small polymeric species.

Finally, it does not seem possible that the RuO and Ru spectra seen in flash heating of solid RuO_2 arise from vaporization of RuO_2 as molecules followed by photolysis of the gaseous RuO_2 . The radiation was filtered by the Pyrex liner; hence, the photon energy was insufficient to cause dissociation. More likely, the solid RuO_2 is thermally decomposed to the elements followed by vaporization of Ru and partial reaction with the gaseous O_2 produced.

To sum up, the primary photochemical processes for $\lambda < 370$ nm can be described simply in terms of two dissociation modes and thresholds, the complications being due to secondary thermal reactions.

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Excimer Laser Photolysis of Group 6 Metal Carbonyls in the Gas Phase¹

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The excimer laser photolysis of $M_0(CO)_6$ in the gas phase has been studied at 351, 308, 248, and 222 nm with laser-based, time-resolved infrared absorption spectroscopy. Results have also been obtained on the 308- and 222-nm photolysis of $Cr(CO)_6$ and on the 222-nm photolysis of $W(CO)_6$, complementing earlier studies and presenting a complete picture of group 6 metal carbonyl ultraviolet photodecomposition. Infrared spectra in the range $1700-2033 \text{ cm}^{-1}$ have been assigned for the coordinatively unsaturated species $M_0(CO)_5$, $M_0(CO)_4$, and $M_0(CO)_3$. As in the case of Cr and W, their gas-phase structures are the same as found in low-temperature matrices. Rates for the reaction of these species with CO and $M_0(CO)_6$ have been determined and are fast, within $\sim^1/_{10}$ th gas kinetic. Overall, the behavior of $M_0(CO)_6$ is similar to the other group 6 carbonyls. The photolysis wavelength dependence of the fragmentation patterns in the group 6 carbonyls shows no correlation with initially excited electronic excited states of $M(CO)_6$ but is consistent with a sequential dissociation proceeding entirely through ground electronic states of $M(CO)_x$ following rapid internal conversion of the initially populated state of $M(CO)_6$. The relative fragment yields support earlier indications that in $Cr(CO)_6$ the first M-CO bond dissociation energy, BDE6, is of the order of or smaller than the second (BDE5). The first case of buffer gas pressure dependence of the relative yields of $M(CO)_x$ and $M(CO)_{x-1}$ fragments has been observed for x = 5 following the 308-mm photolysis of $Cr(CO)_6$. The form of the dependence can be modeled by unimolecular reaction theory with BDE6 \simeq 37 kcal mol⁻¹.

Introduction

Recent studies of the UV photolysis of transition-metal carbonyls in the gas phase have revealed characteristics of their primary photodecomposition processes and a route to the study of the structure and reactivity of coordinatively unsaturated metal carbonyl species free from the disturbance of host matrix or solvent molecules.¹ Yardley et al. studied the KrF laser photolysis of

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Fe(CO)₅ in the gas phase using a chemical trapping technique.² The fragmentation patterns observed were explained by the sequential loss of carbon monoxide driven by a high degree of internal excitation resulting from the absorption of a UV photon.³ Using time-resolved infrared spectroscopy (TRIS), Seder et al. observed a strong dependence of the degree of fragmentation on the absorbed photon energy.⁴ Photofragmentation where only a single CO ligand is lost following single-photon absorption regardless of the excitation wavelength.⁵ This has been interpreted as due to the difference in collisional relaxation efficiency between the two phases.¹⁻³ Time-resolved absorption studies of the gas-phase photolysis of Cr(CO)₆,⁶⁻⁸ Co(CO)₃NO,⁹ Mn₂(CO)₁₀,¹⁰ V(CO)₆,¹¹ and W(CO)₆¹² have since shown this behavior to be characteristic of transition-metal carbonyls.

The strong photon energy dependence of the photofragmentation has provided the opportunity to produce one particular $M(CO)_x$ species by choice of an appropriate photolysis wavelength in order to study chemical interactions at specific unsaturated metal centers.¹³⁻¹⁵ Details of such interactions are useful in understanding the mechanisms of photocatalysis involving metal carbonyls¹⁶⁻¹⁸ and as models for heterogeneous catalysis at metal surfaces.¹⁹

In this paper, we report on the excimer laser photolysis of group 6 metal hexacarbonyls in the gas phase using TRIS. Our results focus on $Mo(CO)_6$, for which we have previously communicated assignments for the infrared spectra of $Mo(CO)_x$ (x = 5-3)²⁰ and also include some new results on $Cr(CO)_6$ and $W(CO)_6$. Together with existing work, a comprehensive picture of the photochemistry of group 6 metal carbonyls emerges. This is discussed in terms of group properties. The work is a background for studies of the reactivity of coordinatively unsaturated molybdenum carbonyl species. While this paper was in preparation, a TRIS study of the photolysis of $Mo(CO)_6$ at fluoride excimer wavelengths has been published.²¹ We find essentially the same results for XeF

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Figure 1. Time-resolved IR difference absorption spectra following the 351-nm photolysis of $Mo(CO)_6$ (24 mTorr) in Ar buffer gas (total pressure 6 Torr). The XeF fluence was 3.5 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 1- μ s intervals in the range 1.0-5.0 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.



Figure 2. Time-resolved IR difference absorption spectra following the 308-nm photolysis of $Mo(CO)_6$ (17 mTorr) in Ar buffer gas (total pressure 10 Torr). The XeCl fluence was 3 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 2- μ s intervals in the range 1.0-9.0 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.



Figure 3. Time-resolved IR difference absorption spectra following the 248-nm photolysis of $Mo(CO)_6$ (12 mTorr) in Ar buffer gas (total pressure 4 Torr). The KrF fluence was 3 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 2- μ s intervals in the range 2-10 μ s. An up arrow indicates ΔOD increasing with time and a down arrow shows it decreasing.

laser photolysis in terms of the infrared assignments and reactivity for $Mo(CO)_5$, but significant differences emerge in the case of KrF laser photolysis regarding the relative yields of fragments and the reactivity of $Mo(CO)_4$. Results obtained at the inter-



Figure 4. Time-resolved IR difference absorption spectra following the 222-nm photolysis of Mo(CO)₆ (8 mTorr) in Ar buffer gas (total pressure 4 Torr). The KrCl fluence was 0.5 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 2- μ s intervals in the range 2–10 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.

mediate chloride excimer wavelengths are important to understanding the 248-nm case.

Experimental Section

The experimental apparatus employed in this study is similar in concept to others described in recent literature.^{1,9,12,22,23} Gas mixtures consisting of the metal hexacarbonyl, CO where required, and Ar buffer gas were flowed slowly through the brass reaction cell, which had an effective path length of 12 cm for UV photolysis light and 24 cm for IR monitoring light. The flowing sample was irradiated with an excimer laser (Lumonics Model 860-1 for XeF and KrF; Model 861-4 for XeCl and KrCl). The laser pulse width was ~ 20 ns and a fluence of a few mJ cm⁻² was typically employed. A line tunable, liquid nitrogen cooled, CW CO laser was used to detect transient intermediates in IR absorption by means of a MCT detector/fast preamplifier combination (rise time ~ 300 ns). The preamplifier signal was fed to a Tektronix differential amplifier and a Biomation Model 8100 transient digitizer and the average of 100 traces stored in a computer (DEC LSI 11/23). Time-resolved difference IR absorption spectra were reconstructed by the computer from transient absorption signals for each CO laser line.

 $Mo(CO)_6$, $Cr(CO)_6$, and $W(CO)_6$ were purchased from Alfa Products. They were degassed by several freeze-thaw cycles with dry ice/methanol and were used without further purification. Argon was obtained from Air Products (research grade, >99.995%) purity) and CO from Linde (CP grade, >99.995% purity).

Results

1. Excimer Laser Photolysis of Mo(CO)₆. 1.1. Photon Energy Dependence of Fragmentation of $Mo(CO)_6$. Figures 1-4 show time-resolved infrared difference absorption spectra in the wavenumber region 1850-2033 cm⁻¹ observed when $Mo(CO)_6$ in ${\sim}5$ Torr of Ar buffer gas was photolyzed at different excimer wavelengths. In the case of XeF laser and XeCl laser photolysis, the spectra are complicated somewhat by the secondary reaction of coordinatively unsaturated primary fragments, $Mo(CO)_x$ (x \leq 5), with Mo(CO)₆ because of the high concentration of Mo- $(CO)_6$ that was required as to get sufficient decomposition as Mo(CO)₆ has small absorption coefficients at the longer wavelengths.

Figure 1 shows time-resolved infrared difference absorption spectra obtained after XeF photolysis of Mo(CO)₆ under 4.3 Torr of total pressure with Ar buffer gas. The primary processes are

almost completed within 1 μ s (Figure 1a). Our spectrum at 800 ns is essentially the same as the single spectrum reported by Ganske and Rosenfeld (GR).²¹ The Δ OD decrease at 2003 cm⁻¹ corresponds to the photodecomposition of the parent molecule, $Mo(CO)_{6}^{24}$ and the ΔOD increase at around 1910, 1940, 1970 and 1985 cm⁻¹ corresponds to the photoproduction of primary fragments. Both the blue-shifting and the sharpening of these peaks, associated with collisional relaxation of the nascent internal energy of the fragments,¹ can be seen at early times, especially in the peaks at 1940 and 1985 cm⁻¹. From the kinetic behavior of these four bands with CO, vide infra, and comparisons with the spectra of $M(CO)_6$ species in low-temperature matrices²⁵ and the spectra of $Cr(CO)_x^7$ and $W(CO)_x^{12}$ in the gas phase, the bands at around 1940 and 1985 cm⁻¹ are assigned respectively as the lower A_1 and E modes of C_{4v} Mo(CO)₅ and bands at around 1910, 1940 and 1970 are assigned to the B_2 , A_1 , and B_1 modes of C_{2v} $Mo(CO)_4$. At later times (Figure 1b), the bands assigned to $Mo(CO)_4$ decrease accompanied by the growth of new bands at around 1990 and 2015 cm⁻¹. As these changes accompany the secondary decrease of $Mo(CO)_6$, this secondary product is assigned to $Mo_2(CO)_{10}$ produced in the reaction

$$Mo(CO)_4 + Mo(CO)_6 \rightarrow Mo_2(CO)_{10}$$
(1)

This secondary reaction will be seen more clearly in the XeCl photolysis where $Mo(CO)_4$ is the main photofragment. Although the rate constant for this reaction cannot be determined exactly in our experiment due to the uncertainty of the $Mo(CO)_6$ concentration, it is estimated to be of the order of 2×10^7 Torr⁻¹ s⁻¹. The same value is reported by GR. The similar secondary reaction involving Mo(CO)₅ was not obvious. However, this does not exclude the possibility of the formation of $Mo_2(CO)_{11}$ because spectral overlap could mask the reaction

$$Mo(CO)_5 + Mo(CO)_6 \rightarrow Mo_2(CO)_{11}$$
 (2)

Figure 2 shows time-resolved infrared difference absorption spectra after XeCl photolysis of Mo(CO)₆ at 4.1 Torr of total pressure with Ar buffer gas. At early times, three absorption bands grow at around 1911, 1946, and 1972 cm⁻¹ together with depression of the parent band at 2003 cm⁻¹ (Figure 2a). These three bands, which are significantly clearer at this photolysis wavelength, are assigned to the B_2 , A_1 , and B_1 modes of $Mo(CO)_4$ consistent with the XeF photolysis results. The possibility that the major contribution to the small band at around 1946 cm⁻¹ is due to $Mo(CO)_5$ is excluded by the absence of the stronger E mode band of Mo(CO)₅ expected at ~1985 cm^{-1.27} Mo(CO)₅ is a very minor product at this photolysis wavelength, if formed at all. At later times (Figure 2b), the bands at 1911 and 1972 cm⁻¹ decrease while new absorptions grow in at around 1940, 1990, and 2011 cm⁻¹. On the same time scale, further decomposition of the parent occurs. This transient behavior is consistently interpreted as a secondary reaction of $Mo(CO)_4$ with $Mo(CO)_6$ (reaction 1).

At early times after KrF photolysis (Figure 3), five absorption bands grow in at around 1890, 1910, 1940, 1970, and >2033 cm⁻¹ together with depression of the parent band at 2003 cm⁻¹. While a slight blue shift can be noticed in the three bands assigned to $Mo(CO)_4$, the new absorption band centered at around 1890 cm⁻¹ does not exhibit the characteristic behavior of internally excited species. This suggests that the fragment with the 1890-cm⁻¹ band is produced through higher fragmentation than $Mo(CO)_4$. The absorptions at 1990 and >2033 cm⁻¹, which appear to be due to one broad absorption straddling the parent transmission band, are attributed to vibrationally excited CO (v = 2 or 3).¹² GR have proposed that this absorption and the absorption at $\sim 1944 \text{ cm}^{-1}$ is due to $Mo(CO)_5$. However, the absorption at 1990 cm⁻¹ is peaked too far to the blue for this. Also, as $Mo(CO)_5$ is hardly, if at all, formed with 308-nm photolysis, vide supra, it is not

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expected as a stable product at this higher photolysis energy. Vibrationally excited CO is detected with exaggerated sensitivity by CO laser absorption and is expected to lead to just such an apparent broad absorption as is seen here. Recently, time-resolved diode laser studies have confirmed excited CO as the cause of similar absorptions observed in the ArF laser photolysis of Fe- $(CO)_5$.²⁶ The band at 1944 cm⁻¹ is due to the A₁ mode of Mo- $(CO)_4$ as discussed above. In contrast to GR, we conclude that Mo(CO)₅ is not a significant product of KrF photolysis. At later times (Figure 3b), secondary reactions are observed. The Mo- $(CO)_4$ bands at 1910, 1944, and 1970 decrease while new absorptions grow at 1940, 1990, and 2011 cm⁻¹.

On the same time scale, further decomposition of the parent occurs. This kinetic behavior is consistent with reaction 2. The band at 1890 cm⁻¹, which is assigned to the E mode of $C_{4\nu}$ Mo-(CO)₃, also disappears. This is assumed to be due to reaction of Mo(CO)₃ with parent molecules to form a binuclear complex as in reaction 3, although no absorptions due to Mo₂(CO)₉ are

$$Mo(CO)_3 + Mo(CO)_6 \rightarrow Mo_2(CO)_9$$
 (3)

identified in our spectra. $Mo(CO)_3$ is also expected to show a weaker A_1 band at ~1990 cm⁻¹. Broad absorptions are observed in this region, but overlap with absorptions by "hot" CO, Mo-(CO)₄, and binuclear species prevent us from identifying this band. The rate constant for the loss of $Mo(CO)_3$ is estimated to be of the order of the collision frequency (~2 × 10⁷ Torr⁻¹ s⁻¹).

After KrCl laser photolysis (Figure 4), the ΔOD increase at around 1890 cm⁻¹ synchronous with the photodecomposition of $Mo(CO)_6$ is the main feature of the early spectra. The spectra also show weak absorptions at \sim 1990 and >2033 cm⁻¹, presumably due to hot CO, and broad weak absorptions in the range 1900–1975 cm⁻¹, attributable to $Mo(CO)_4$. As the photon energy of the KrCl laser is higher than that of the KrF laser by 14 kcal mol^{-1} , relatively more $Mo(CO)_3$ is expected and the $Mo(CO)_4$ produced by KrCl laser photolysis can be expected to be significantly internally excited compared to Mo(CO)₄ produced by KrF laser photolysis. This explains the initially broad Mo(CO)₄ bands and their subsequent blue-shifting and sharpening seen in Figure 4a. The $Mo(CO)_3$ band at 1891 cm⁻¹ does not show this behavior. From this apparent lack of significant internal excitation, we conclude that $Mo(CO)_3$ is the smallest fragment in KrCl photolysis. A combination of reactions 2 and 3 then explains the secondary transient behavior seen at later times (Figure 4b).

The effect of excimer laser fluence was studied for XeCl and KrF laser photolyses. The observed time-resolved spectra were scaled linearly with fluence in each case over the ranges studied (XeCl, 3-8 mJ cm⁻²; KrF, 1-3 mJ cm⁻²), demonstrating the absence of a fluence dependence in relative $Mo(CO)_x$ yields. These observations are consistent with the linear fluence dependencies of fragment yields reported in the excimer laser photolysis of $Cr(CO)_6^6$ and $W(CO)_6^{12}$ and also found for $Cr(CO)_6$ in this work, vide infra. Together these results are consistent with a single-photon mechanism for the excimer laser photolysis of group 6 carbonyls with secondary photolysis of fragments playing an unimportant role in determining product distributions at moderate fluences.

1.2. Excimer Laser Photolysis of $Mo(CO)_6$ in the Presence of CO. The kinetics of the reactions of $Mo(CO)_x$ (x = 3-5) with added CO confirm the above infrared assignments. Consecutive CO addition reactions were found to proceed to form $Mo(CO)_6$ as follows:

$$Mo(CO)_3 + CO + M \rightarrow Mo(CO)_4^{\dagger} + M$$
 (4a)

$$Mo(CO)_4^{\dagger} + M \rightarrow Mo(CO)_4 + M$$
 (4b)

$$Mo(CO)_4 + CO + M \rightarrow Mo(CO)_5^{\dagger} + M$$
 (5a)

$$Mo(CO)_5^{\dagger} + M \rightarrow Mo(CO)_5 + M$$
 (5b)

$$Mo(CO)_5 + CO + M \rightarrow Mo(CO)_6^{\dagger} + M$$
 (6a)

$$Mo(CO)_6^{\dagger} + M \rightarrow Mo(CO)_6 + M$$
 (6b)

where $Mo(CO)_x^{\dagger}$ indicates hot $Mo(CO)_x$. The role of the hot product in the recombination of CO with unsaturated metal



Figure 5. Time-resolved IR difference absorption spectra following the 351-nm photolysis of $Mo(CO)_6$ (6 mTorr) in the presence of CO (2 Torr) in Ar buffer gas (total pressure 4.6 Torr). The XeF fluence was 6.3 mJ cm⁻². Early spectra (a) are shown at 0.1- μ s intervals in the range 0.1-0.5 μ s. Intermediate spectra (b) are shown at 0.1- μ s intervals in the range 0.6-1.0 μ s. Later spectra (c) are shown at 0.5- μ s intervals in the range 1.0-3.0 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.



Figure 6. Time-resolved IR difference absorption spectra following the 308-nm photolysis of $Mo(CO)_6$ (10 mTorr) in the presence of CO (0.4 Torr) in Ar buffer gas (total pressure 10 Torr). The XeCl fluence was 3.2 mJ cm⁻². Early spectra (a) are shown at 0.1- μ s intervals in the range 0.1-0.5 μ s. Intermediate spectra (b) are shown at 0.3- μ s intervals in the range 0.8-2.0 μ s. Later spectra (c) are shown at 1- μ s intervals in the range 2-6 μ s. An up arrow indicates Δ OD increasing with time and a down shows arrow it decreasing.

carbonyls has been detailed in the case of $W(CO)_5^{28}$ where we showed that the collision complex can be stabilized with respect to spontaneous redissociation at internal product energies higher than the dissociation limit. This behavior is expected to be ubiquitous. The above mechanism is, of course, a simplification. Figures 5–8 show typical time-resolved infrared difference absorption spectra obtained when Mo(CO)₆ was photolyzed in the presence of CO and Ar buffer gas.

Following XeF laser photolysis in the presence of 2 Torr of CO (Figure 5), the primary absorptions are due to $Mo(CO)_5$ produced through direct photofragmentation and the recombination of

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Figure 7. Time-resolved IR difference absorption spectra following the 248-nm photolysis of $Mo(CO)_6$ (12 mTorr) in the presence of CO (0.3 Torr) in Ar buffer gas (total pressure 4.2 Torr). The KrF fluence was 3.5 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Intermediate spectra (b) are shown at 0.4- μ s intervals in the range 1.2-2.8 μ s. Later spectra (c) are shown at 2- μ s intervals in the range 3-11 μ s. An up arrow indicates Δ OD indicates with time and a down arrow shows it decreasing.



Figure 8. Time-resolved IR difference absorption spectra following the 222-nm photolysis of $Mo(CO)_6$ (4 mTorr) in the presence of CO (0.5 Torr) in Ar buffer gas (total pressure 4.2 Torr). The KrCl fluence was 0.6 mJ cm⁻². Early spectra (a) are shown at 0.1- μ s intervals in the range 0.1-0.5 μ s. Intermediate spectra (b) are shown at 0.4- μ s intervals in the range 0.7-2.3 μ s. Later spectra (c) are shown at 1- μ s intervals in the range 3-7 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.

 $Mo(CO)_4$ with CO, which is rapid at this pressure of CO. In the middle time region (Figure 5b), the $Mo(CO)_5$ bands gradually disappear and a new band at ~1995 cm⁻¹, overlapping the parent band on its red side, appears. Subsequently, this band itself disappears, and parent absorption is recovered. This behavior was first observed in the recombination of $W(CO)_5$ with CO and proved, through a study of buffer gas pressure effects, to be due to the role of internally excited $W(CO)_6$ as an intermediate.²⁸ By analogy, the intermediate absorption in this case is assigned to $Mo(CO)_6^{\dagger}$ formed in reaction 6a and decaying by relaxation through collisions with Ar buffer gas, reaction 6b. In general, we expect to observe intermediate absorption due to $M(CO)_x^{\dagger}$ when collisional relaxation is the rate-determining step; i.e., the recombination reaction occurs faster than the relaxation. This



Figure 9. CO pressure dependence of the pseudo-first-order decay rates (k_d') of Mo(CO)₃ (O), produced in the KrF laser photolysis of Mo(CO)₆ (14 mTorr, 3 mJ cm⁻²), and of Mo(CO)₄ (\square), produced in the XeCl laser photolysis of Mo(CO)₆ (18 mTorr, 4.5 mJ cm⁻²), in the presence of CO and Ar buffer gas (total pressure 10 Torr, open symbols, and 40 Torr, filled symbols). Mo(CO)₃ was monitored at 1885 cm⁻¹ and Mo(CO)₄ at 1969 cm⁻¹.

is controlled by the make up and pressure of the gas mix (CO/Ar).

Following XeCl photolysis in the presence of 0.4 Torr of CO (Figure 6), Mo(CO)₄, with bands at 1911, 1946, and 1972 cm⁻¹, is the main primary product as in the absence of CO. In the time range of Figure 6b, these absorption bands disappear while two bands, corresponding to the absorption bands of Mo(CO)₅, grow in at 1942 and 1990 cm⁻¹. This behavior is explained by formation of Mo(CO)₅ through reaction 5. The Δ OD change at 1940 cm⁻¹ is slight because of overlap between the A₁ bands of Mo(CO)₄ and Mo(CO)₅. Finally (Figure 6c), the transient evolution shows recovery of Mo(CO)₆ through reaction 6. As the CO pressure was low compared to Ar buffer gas, absorptions due to Mo(CO)_x[†] species are not observed in these spectra.

Following KrF photolysis in the presence of 0.3 Torr of CO, the primary processes (Figure 7a) follow those observed in the absence of CO (Figure 3a). Bands due to Mo(CO)₄, at 1911, 1946, and 1972 cm⁻¹; Mo(CO)₃, at 1891 cm⁻¹; and hot CO, at 1990 and >2033 cm⁻¹ are observed. Before nascent $Mo(CO)_4$ is even completely relaxed, recombination reactions 4 and 5 are observed to take place. The $Mo(CO)_3$ band at 1981 cm⁻¹ starts to decrease at about 0.8 μ s while the Mo(CO)₄ bands continue to grow. In the middle time region (Figure 7b), the $Mo(CO)_3$ band and the Mo(CO)₄ bands at 1911 and 1990 cm⁻¹ decrease, the $Mo(CO)_4$ band at 1946 cm⁻¹ changes slightly, and a new band grows at 1990 cm⁻¹. The new band and the changed band now at ~1940 cm⁻¹ are attributed to Mo(CO)₅. At later times (Figure 7c), these Mo(CO)₅ bands decrease while the parent band at 2003 cm⁻¹ finally recovers. Again, conditions did not favor the observation of Mo(CO),

KrCl photolysis in the presence of 0.5 Torr of CO gives essentially the same result as KrF photolysis except that the initial yield of $Mo(CO)_3$ is substantially higher than that of $Mo(CO)_4$. Figure 4a shows the initial appearance of $Mo(CO)_3$, hot $Mo(CO)_4$, and hot CO. The transient changes observed in Figure 8b,c are again interpreted as following the consecutive scheme of reactions 4, 5, and 6.

The consistent interpretation of these CO addition experiments forms strong support for the $Mo(CO)_x C-O$ stretching frequency assignments.

1.3. Reaction Rates of $Mo(CO)_x$ (x = 3-5) with CO. It has been reported that coordinatively unsaturated metal carbonyls, except for Fe(CO)₄, react with CO at near gas kinetic rates.^{1,11,12} The TRIS reported in section 1.2 already show that $Mo(CO)_x$ species react with CO at high rates. Bimolecular rate constants for the reaction of $Mo(CO)_x$ were obtained from the CO pressure dependence of the pseudo-first-order decay rates of $Mo(CO)_x$ and the recovery rates of $Mo(CO)_{x+1}$.

Figure 9 shows the CO pressure dependence of the pseudofirst-order decay rates of $Mo(CO)_3$, monitored at 1885 cm⁻¹ following KrF laser photolysis, and $Mo(CO)_4$, monitored at 1969 cm⁻¹ following XeCl photolysis. In both these systems, the re-



Figure 10. CO pressure dependence of the pseudo-first-order decay rate (k_d') of Mo(CO)₅ species and the reproduction rate (k_p') of Mo(CO)₆ observed in the XeF, XeCl, and KrF laser photolyses of mixtures of Mo(CO)₆, CO, and Ar. Conditions were as follows: XeF, 20 mTorr of Mo(CO)₆, 4.1-Torr total pressure, 7 mJ cm⁻² fluence, Mo(CO)₅ monitored at 1980 cm⁻¹ (O), Mo(CO)₆ monitored at 2003 cm⁻¹ (\bullet); XeCl, 18 mTorr of Mo(CO)₅ nonitored at 1985 cm⁻¹ (\Box), Mo(CO)₆ monitored at 2003 cm⁻¹ (\bullet); XeCl, 10, KrF, 14 mTorr of Mo(CO)₆, 10-Torr total pressure, 3 mJ cm⁻² fluence, Mo(CO)₅ monitored at 1985 cm⁻¹ (Δ), Mo(CO)₆ monitored at 2003 cm⁻¹ (Δ).

ported fragment is the smallest produced and their kinetic behavior is not complicated by concurrent formation in recombination reactions. The linear dependence of these rates on CO pressure gives rate constants of $(1.4 \pm 0.4) \times 10^6$ Torr⁻¹ s⁻¹ for reaction 4 and $(2.2 \pm 0.4) \times 10^6$ Torr¹⁻ s⁻¹ for reaction 5 under conditions where the recombination is the rate-determining step. For reaction 4, our results at total pressures of 10 and 40 Torr are superimposable, indicating that this value is the high-pressure-limited rate constant. In contrast, GR reported a pressure dependence in the rate of reaction 4 with a high-pressure limit ~10 times greater than our observed rate measured at 40 Torr of Ar. Reasons for the disagreement are unclear but may be found in the relatively high Mo(CO)₆ pressures employed by GR, leading to interference by binuclear species.

Results for reaction 6 are shown in Figure 10. Total pressures were kept constant at ~ 4 Torr in the XeF laser photolysis and at 10 Torr in the XeCl and KrF laser photolysis with Ar buffer gas. $Mo(CO)_5$ decay rates were measured at 1980 cm⁻¹, and $Mo(CO)_6$ recovery rates were measured at 2003 cm⁻¹. In each excimer laser experiment, these decay and reproduction rates were found to depend linearly on the CO pressure. The transient behavior supports the simple consecutive recombination mechanism of reactions 4-6. The coincidence of the three sets of experimental results, including results at 4 and 10 Torr, indicates that under these conditions the reactions are at or near their high-pressure limits and that the recombination is the rate-determining step. The slope of $(1.4 \pm 0.3) \times 10^6$ Torr⁻¹ s⁻¹ can be attributed to the bimolecular rate constant for reaction 6 as follows. In a consecutive mechanism, the product rate of the final product, in this case $Mo(CO)_6$, and the decay rate of its intermediate precursor, in this case $Mo(CO)_5$, are determined by the rate of the slowest step. In the XeF laser photolysis, the mechanism consists of reactions 5 and 6 only. The rate constant of reaction 5 is already determined, by a separate experiment, to be $(2.2 \pm 0.4) \times 10^{6}$ Torr⁻¹ s⁻¹, which is larger than the slope in Figure 10, sufficient for the rate-determining step to be associated with reaction 6 as the only alternative. The kinetic data obtained for the reactions of Mo(CO), species with CO are summarized in Table I together with literature values for $Cr(CO)_x$ and $W(CO)_x$.

2. Excimer Laser Photolysis of $W(CO)_6$. It has been reported that $W(CO)_5$ is the only primary product in the XeF and XeCl laser photolysis of $W(CO)_6$ whereas $W(CO)_4$ is the main product in the KrF photolysis.¹² Figure 11 shows the transient infrared absorption spectra obtained following KrCl laser photolysis of $W(CO)_6$ under 4.2 Torr of Ar buffer gas. This shorter wavelength

TABLE I: Bimolecular Rate Constants $(10^6 \text{ Torr}^{-1} \text{ s}^{-1})$ for M(CO)_x + CO Reactions at Room Temperature in the Gas Phase



Figure 11. Time-resolved IR difference absorption spectra following the 222-nm photolysis of W(CO)₆ (6 mTorr) in Ar buffer gas (total pressure 4.2 Torr). The KrCl fluence was 0.7 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 3- μ s intervals in the range 2-14 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.

photolysis gave results very similar to KrF laser photolysis. In the early time region (Figure 11a), two absorption bands of W(CO)₄ at 1909 and 1957 cm⁻¹ and one broad band of hot CO at >2033 cm⁻¹ grow in together with the transmission at 1999 cm⁻¹ due to parent depletion. The two absorption bands of W(CO)₄ are slightly broader than those observed in the KrF photolysis (Figure 3 in ref 12). This is expected from the higher energy (148 cf. 115 kcal mol⁻¹) deposited by a 222-nm photon. Importantly, the additional energy is insufficient to produce W(CO)₃, which, by analogy with Cr(CO)₃⁷ and Mo(CO)₃, we would expect to observe if formed. The spectral evolution observed in the later time range is the result of binuclear complex formation through the reaction of W(CO)₄ with W(CO)₆.¹²

3. Excimer Laser Photolysis of $Cr(CO)_6$. 3.1. Photon Energy Dependence of Fragmentation of $Cr(CO)_6$. UV photolysis studies of $Cr(CO)_6$ in the gas phase have revealed details of its initial photodecomposition processes and of the structure and reactivity of coordinatively unsaturated chromium carbonyls.^{6-8,16} The studies of Seder et al. indicate that the extent of fragmentation depends strongly on the photon energy: mainly $Cr(CO)_5$ and a small amount of $Cr(CO)_4$ with XeF laser photolysis, mainly $Cr(CO)_4$ and a small amount of $Cr(CO)_2$ with KrF laser photolysis.⁷ In this study, XeCl and KCl laser photolyses of $Cr(CO)_6$ in the gas phase have been carried out to obtain additional data on the photon energy dependence of fragmentation at intermediate wavelengths.

Figure 12 shows the time-resolved infrared difference absorption spectra obtained when $Cr(CO)_6$ (~20 mTorr in 4.1 Torr of Ar buffer gas) was photolyzed with the XeCl laser. The primary processes (Figure 12a) show a ΔOD decrease at 1999 cm⁻¹, corresponding to $Cr(CO)_6$ depletion, and increases at 1916, 1954, and 1977 cm⁻¹, corresponding to primary products. The expected relaxation of internally excited fragments is observed. The relaxed peaks, observed at ~1 μ s at 1916 and 1954 cm⁻¹ can be assigned to $Cr(CO)_4$ and those at 1950 and 1976 cm⁻¹ to $Cr(CO)_5$ by comparison with Seder et al.'s results using XeF and KrF laser photolyses. $Cr(CO)_4$ is the major product at this wavelength. The



Figure 12. Time-resolved IR difference absorption spectra following the 308-nm photolysis of $Cr(CO)_6$ (20 mTorr) in Ar buffer gas (total pressure 4.1 Torr). The XeCl fluence was 3 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2-1.0 μ s. Later spectra (b) are shown at 3- μ s intervals in the range 1-13 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.

later appearance of peaks at 1920, 1977, and 2007 at the expense of the Cr(CO)₄ peaks at 1916 and 1954 cm⁻¹ (Figure 12b) implies that Cr₂(CO)₁₀ formed by reaction of Cr(CO)₄ with Cr(CO)₆ is largely responsible for the spectrum at late times. A similar spectrum is observed following the reaction of W(CO)₄ with W(CO)₆. There may be a small contribution from Cr₂(CO)₁₁ that has previously been assigned to absorptions at 1991 and 1999 cm⁻¹. The Cr(CO)₆ pressure dependence of the decay rates monitored at 1954 cm⁻¹ and of the secondary decomposition rates at 1999 cm⁻¹ gives a rate constant of $(1.7 \pm 0.3) \times 10^7$ Torr⁻¹ s⁻¹ for this reaction. The value agrees well with that reported by Fletcher and Rosenfeld.⁶

Time-resolved infrared absorption spectra taken following the XeCl laser photolysis of $Cr(CO)_6$ in the presence of CO support a consecutive CO addition mechanism equivalent to reactions 5 and 6. The participation of the internally excited species $Cr(CO)_{5}^{\dagger}$ and $Cr(CO)_6^{\dagger}$ is indicated by bands observed on the red side of the corresponding relaxed species, $Cr(CO)_5$ and $Cr(CO)_6$. Especially the production of $Cr(CO)_6^{\dagger}$ resulted in distortion of the T_{1u} band of $Cr(CO)_6$ in a similar manner to that observed for $W(CO)_6^{\dagger, 28}$ We therefore find the observation of hot recombination products to be general for the group 6 carbonyls, including Cr. In their reported work on $Cr(CO)_{6}$,⁷ Seder et al. did not report such findings; however, their CO pressure was relatively low (0.3-0.5 Torr in \sim 5 Torr of Ar), suggesting that, under these conditions, recombination rather than relaxation is the rate-determining step. We found the same for $Mo(CO)_6$ in similar gas mixtures, see text above.

A rate constant of $(1.3 \pm 0.4) \times 10^6 \text{ Torr}^{-1} \text{ s}^{-1}$ was found for the recombination reaction of $Cr(CO)_5$ with CO from the CO pressure dependence of $Cr(CO)_5$ decay and $Cr(CO)_6$ recovery following XeF photolysis. A rate constant of $(1.2 \pm 0.2) \times 10^6$ Torr⁻¹ s⁻¹ was found for the reaction of $Cr(CO)_4$ with CO from the CO pressure dependence of the $Cr(CO)_4$ decay following XeCl photolysis. These kinetic results are summarized and compared with reported values in Table I. The photoproduction yield of $Cr(CO)_4$ and the photodecomposition yield of $Cr(CO)_6$ estimated by TRIS were found to depend linearly on XeCl laser fluence up to at least 8 mJ cm⁻².

Figure 13 shows time-resolved infrared difference absorption spectra observed following KrCl photolysis of $Cr(CO)_6$ in Ar buffer gas. Correlation of these spectra with those Seder et al. found using KrF and ArF laser photolysis leads to the assignment of the primary transient peaks to $Cr(CO)_3$ (1887 cm⁻¹), $Cr(CO)_4$ (1916 and 1954 cm⁻¹), and hot CO (~1980 and >2033 cm⁻¹). Binucleation reactions account for the behavior at later times. In contrast to the ArF laser photolysis, no evidence could be found for the production of $Cr(CO)_2$.

3.2. Ar Buffer Gas Pressure Effect on XeCl Laser Photolysis of $Cr(CO)_6$. Both TRIS and chemical trapping studies demon-



Figure 13. Time-resolved IR difference absorption spectra following the 222-nm photolysis of $Cr(CO)_6$ (13 mTorr) in Ar buffer gas (total pressure 4.1 Torr). The KrCl fluence was 0.7 mJ cm⁻². Early spectra (a) are shown at 0.2- μ s intervals in the range 0.2–1.0 μ s. Later spectra (b) are shown at 2- μ s intervals in the range 2–10 μ s. An up arrow indicates Δ OD increasing with time and a down arrow shows it decreasing.



Figure 14. Ar pressure effect on the product distribution in the XeCl laser photolysis of $Cr(CO)_6$. The XeCl fluence was kept constant at 3 mJ cm⁻². Time-resolved IR difference absorption spectra were taken (a) at 2.8 Torr of Ar (shown at 0.4- μ s intervals in the range 0.4-2.0 μ s); (b) at 9.8 Torr of Ar (shown at 0.2- μ s intervals in the range 0.2-1.0 μ s); (c) at 40 Torr of Ar (shown at 0.2- μ s intervals in the range 0.2-1.0 μ s).

strate that the degree of fragmentation in the gas phase increases with photon energy in contrast to the condensed photolysis that results in the cleavage of a single metal–CO bond.^{1,5,25,29} The interpretation is that sequential loss of CO proceeds until insufficient energy is retained in $M(CO)_x$ for further fragmentation to take place. The initial energy deposited and competition between relaxation and dissociation determines the fragmentation pattern. This suggests that the buffer gas pressure should effect the extent of fragmentation in certain cases. However, such an effect, which would be strong support for the sequential mechanism, has not been reported to date. This is probably because the excimer laser wavelengths and carbonyl systems studied happened not to produce $M(CO)_x$ species of the required energy content for relaxation and reaction to compete at Ar pressures in the range 2–50 Torr.

Such a pressure effect is observed in the XeCl laser photolysis of Cr(CO)₆. The primary photofragments at ~5 Torr of Ar are Cr(CO)₄ and Cr(CO)₅ (Figure 12). Cr(CO)₄ ($C_{2\nu}$ symmetry) has absorption bands at 1916 (A₁ and B₂ modes) and 1954 cm⁻¹ (B₁ mode) with an absorption intensity ratio of 1 to 2. Cr(CO)₅ ($C_{4\nu}$ symmetry) has bands at 1948 (A₁ mode) and 1980 cm⁻¹ (E

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Figure 15. Ar pressure effect on the ratio of $Cr(CO)_4$ to $Cr(CO)_5$ produced in the XeCl laser photolysis of $Cr(CO)_6$ (10 mTorr, 3 mJ cm⁻²). [$Cr(CO)_5$]/[$Cr(CO)_4$] was calculated as (Δ OD at 1954 cm⁻¹)/(Δ OD at 1976 cm⁻¹) – 0.25, see text.

mode) with a ratio of 1 to $4.^7$ Figure 14 shows the effect of Ar buffer gas pressure on the primary fragmentation. It can be seen that the relative yield of $Cr(CO)_5$ to $Cr(CO)_4$ increases with increasing Ar pressure. These results suggest a sequential CO elimination mechanism of the form

$$\operatorname{Cr}(\operatorname{CO})_6 + h\nu \to \operatorname{Cr}(\operatorname{CO})_5^* + \operatorname{CO}$$
 (7)

$$Cr(CO)_5^* + M \rightarrow Cr(CO)_5 + M$$
 (8)

$$Cr(CO)_5^* \rightarrow Cr(CO)_4^\dagger + CO$$
 (9)

$$Cr(CO)_4^{\dagger} + M \rightarrow Cr(CO)_4 + M$$
 (10)

where $Cr(CO)_x^*$ indicates $Cr(CO)_x$ internally excited above its dissociation limit. The relative yield of $Cr(CO)_4$ to $Cr(CO)_5$ is governed by competition between reactions 8 and 9. The ratio of final yields $[Cr(CO)_4]/[Cr(CO)_5]$ is related to the ratio, *R*, of ΔOD at 1954–1976 cm⁻¹ by

$$\frac{[Cr(CO)_4]}{[Cr(CO)_5]} = \frac{(R - \beta/\alpha)}{\gamma/\alpha}$$

where γ/α and β/α are ratios of the absorption coefficients of $Cr(CO)_4$ and $Cr(CO)_5$ at 1954 cm⁻¹, respectively, to that of $Cr(CO)_5$ at 1976 cm⁻¹. Comparison of spectra observed following XeF laser photolysis (main product $Cr(CO)_5$) and XeCl laser photolysis at low pressure (main product $Cr(CO)_4$), normalized to the same parent depletion, leads to $\gamma/\alpha \simeq 1$ and $\beta/\alpha = 0.25$.

Figure 15 shows $[Cr(CO)_4]/[Cr(CO)_5]$ as a function of inverse Ar pressure. Were reactions 7-10 a strict description of the system, a straight line dependence would be expected. However, $Cr(CO)_5$ * represents an ensemble of highly excited molecules with a distribution of internal energies, F(E), determined by the dynamics of the photodissociation of $Cr(CO)_6$ and having an energy dependent rate constant for unimolecular dissociation, k(E). The system is analogous to a chemical activation reaction³⁰ and can be modeled in a similar manner. To this end, F(E) was estimated from a starting room-temperature thermal distribution in Cr(CO)₆ and a distribution for energy release in reaction 7 based on recent observations of the energy partitioning to CO in $M(CO)_6$ photodissociation.^{31,32} The energy dependence of k(E) for Cr(CO)₅ dissociation was calculated using RRKM theory. The result of such a model is sensitive to a number of variables, including the bond dissociation energies (BDEs) for Cr(CO)₆ and Cr(CO)₅, log A for reaction 9 and the model used to describe collisional energy transfer in the stabilization channel. With the BDE for $Cr(CO)_6$ taken as 36.8 kcal mol⁻¹, as estimated by infrared-laser-sensitized pyrolysis,³³ log A = 15.8, by comparison with known values for M-CO and other diatomic releasing dissociation reactions, and with use of a step-ladder model for collisional deactivation with $\Delta E = 0.5$ kcal mol⁻¹, the fit in Figure 15 is obtained numerically by adjusting the BDE for Cr(CO)₅ to 36.5 kcal mol⁻¹. A more detailed description of the model including a sensitivity analysis and an assessment of the value of such experiments for obtaining BDEs for the dissociation of reactive species is under preparation for future publication. Here, we show that a "chemical activation" model can successfully and plausibly describe branching ratios in the photodissociation of metal carbonyls.

Discussion

It is generally accepted that the photofragmentation of transition-metal carbonyls, $M(CO)_n$, in the gas phase involves sequential CO loss through unimolecular decomposition of M(CO)_x* $(x \leq n)$ to an extent determined largely by the photon energy and the M-CO bond strength.¹ Our results on the Ar pressure dependence of fragmentation patterns in the XeCl laser photolysis of $Cr(CO)_6$ support this picture. Less is known about the photophysical processes involved in the initial step, which eventually produces ground-state $M(CO)_{n-1}^*$. Most results to date are consistent with rapid internal conversion taking place following absorption of an ultraviolet photon to produce highly excited ground-state $M(CO)_n^*$. Our model, which successfully describes the pressure dependence of the $[Cr(CO)_4]/[Cr(CO)_5]$ branching ratio in the XeCl photolysis of $Cr(CO)_6$, is based on this or an equivalent mechanism. Another possibility is that dissociation follows an excited-state pathway in the first step. Measurements on energy disposal in the CO fragments formed following 351-nm photolysis of $W(CO)_6^{31}$ and 193-nm photolysis of $Fe(CO)_5^{32}$ argue against this possibility. The similar electronic structure of the group 6 carbonyls together with the increase in M-CO bond dissociation energy found going down the group form a framework to test this further. Apart from the XeF laser, the individual excimer lasers access the same excited states in all three carbonyls.⁵ Exciner lasers access the same excited states in all three carbonyls.³ The common absorption bands at 308, 248, and 222 nm are assigned as the ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g} (t_{2g}^{6} \rightarrow t_{2g}^{5}e_{g}^{1}) LF$ transition, the ${}^{1}A_{1g}$ $\rightarrow {}^{1}T_{2g} (t_{2g}^{6} \rightarrow t_{2g}^{5}e_{g}^{1}) LF$ transition, and the ${}^{1}A_{1g} \rightarrow d{}^{1}T_{1u}$ (M $\rightarrow \pi^{*}CO) CT$ transition, respectively. At 351 nm, the absorption is attributed to the ${}^{1}A_{1g} \rightarrow {}^{3}T_{1g} (t_{2g}^{6} \rightarrow t_{2g}^{5}e_{g}^{1}) LF$ transition in the case of Mo(CO)₆ and W(CO)₆ but to the tail of the ${}^{1}A_{1g} \rightarrow$ ${}^{1}T_{1g} (t_{2g}^{6} \rightarrow t_{2g}^{5}e_{g}^{1}) LF$ transition in the case of Cr(CO)₆.⁵ The fragmentation patterns revealed in Table II show no correlation fragmentation patterns revealed in Table II show no correlation with the initial excited state and appear to depend only on the photon energy and the M-CO bond dissociation energy, again supporting the ground-state pathway for $M(CO)_6$ photodissociation in the gas phase.

The wavelength dependence of the product fragment distributions are broadly in line with what is known of the BDEs for CO loss from $M(CO)_x$ species. Reported values are, for Cr, Mo, and W, respectively, 36.8, 40.5, and 46.0 kcal mol⁻¹ for the first bond dissociation, BDE6 (M(CO)₆ \rightarrow M(CO)₅ + CO),³³ and 25.8, 36.3 and 42.5 kcal mol⁻¹ for the average bond dissociation energy.³⁴ Recognizing that energy is lost through collisional relaxation as well as chemical reaction, we find that the product distributions given in Table II are individually consistent with these values and the relevant photon energy. There is, however, an apparent inconsistency when we compare the Cr and Mo results. If we assume that the ratio of peak infrared absorption coefficients between the $M(CO)_x$ species is the same for Cr and Mo, then our results suggest that the ratio of $Mo(CO)_4$ to $Mo(CO)_5$ in the 351- and 308-nm photolysis cases and the ratio of $Mo(CO)_3$ to $Mo(CO)_4$ in the 248- and 222-nm photolysis cases are larger than the corresponding ratios observed in the case of $Cr(CO)_6$. This suggests that the BDEs averaged over the first three CO ligands are in the order $Mo(CO)_6 < Cr(CO)_6 < W(CO)_6$, against the trends in the reported values for the first and average BDEs. The first BDEs come from kinetic measurements of the energy of activation for metal carbonyl thermal dissociation measured with an infrared-laser-sensitized pyrolysis technique by Lewis et al.³³

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TABLE II: Photon Energy Dependence of Fragment Distributions in the Photolysis of Mononuclear Transition-Metal Carbonyls in the Gas Phase^a

		excimer laser							
	XeF (351; 81)	XeCl (308; 93)	KrF (248; 115)	KrCl (222; 129)	ArF (193; 149)	ref			
Fe(CO) ₅	Fe(CO) ₄	$Fe(CO)_{4}^{b}$				1-4	-		
	$Fe(CO)_3$	$Fe(CO)_3^b$	$Fe(CO)_3$	$Fe(CO)_{3}^{b}$					
			$Fe(CO)_2$	$Fe(CO)_2^b$	$Fe(CO)_2$ ¹ $Fe(CO)_3^c$				
V(CO) ₆	V(CO) ₄	V(CO) ₄	V(CO) ₄ V(CO) ₃			11			
$Cr(CO)_{6}$	Cr(CO) ₅	Cr(CO)	$Cr(CO)_5$			6-8 and this work			
	$Cr(CO)_{4}$	$Cr(CO)_4$	Cr(CO) ₄	$Cr(CO)_4$	$Cr(CO)_4$				
			$Cr(CO)_3$	$Cr(CO)_3$	$Cr(CO)_3$				
					$Cr(CO)_{2}$				
Mo(CO) ₆	Mo(CO)	$Mo(CO)_{5}$				this work			
	Mo(CO) ₄	Mo(CO)₄	Mo(CO) ₄	$Mo(CO)_4$					
			Mo(CO) ₃	Mo(CO) ₃					
W(CO) ₆	W(CO) ₅	W(CO) ₅	W(CO) ₅ W(CO) ₄	$W(CO)_5$ $W(CO)_4$		12 and this work			
	Fe(CO)5 V(CO)6 Cr(CO)6 Mo(CO)6 W(CO)6	XeF (351; 81) $Fe(CO)_5$ $Fe(CO)_4$ $Fe(CO)_5$ $V(CO)_4$ $V(CO)_6$ $V(CO)_4$ $Cr(CO)_6$ $Cr(CO)_5$ $Cr(CO)_6$ $Mo(CO)_5$ $Mo(CO)_6$ $Mo(CO)_5$ $Mo(CO)_6$ $W(CO)_5$	XeF (351; 81) XeCl (308; 93) Fe(CO) ₅ Fe(CO) ₄ $Fe(CO)_4^b$ Fe(CO) ₅ V(CO) ₄ V(CO) ₄ V(CO) ₆ V(CO) ₄ V(CO) ₄ Cr(CO) ₆ Cr(CO) ₅ Cr(CO) ₅ Mo(CO) ₆ Mo(CO) ₅ $Mo(CO)_5$ W(CO) ₆ W(CO) ₅ W(CO) ₅ W(CO) ₆ W(CO) ₅ W(CO) ₅	$ \frac{excimer laser}{XeF (351; 81)} \frac{xeCl (308; 93)}{XeCl (308; 93)} \frac{KrF (248; 115)}{KrF (248; 115)} $ $ \frac{Fe(CO)_5}{Fe(CO)_3} \frac{Fe(CO)_4}{Fe(CO)_3} \frac{Fe(CO)_4}{Fe(CO)_2} \frac{Fe(CO)_2}{V(CO)_5} \frac{V(CO)_4}{Cr(CO)_5} \frac{V(CO)_4}{Cr(CO)_5} \frac{Cr(CO)_5}{Cr(CO)_4} \frac{Cr(CO)_5}{Cr(CO)_4} \frac{Cr(CO)_4}{Cr(CO)_4} \frac{Cr(CO)_4}{Cr(CO)_4} \frac{Mo(CO)_4}{Mo(CO)_4} \frac{Mo(CO)_4}{Mo(CO)_4} \frac{Mo(CO)_4}{Mo(CO)_5} \frac{Mo(CO)_5}{W(CO)_5} \frac{W(CO)_5}{W(CO)_5} \frac{W(CO)_5}{W(CO$	$ \frac{excimer laser}{XeF (351; 81)} \frac{XeCl (308; 93)}{XeCl (308; 93)} \frac{KrF (248; 115)}{KrCl (222; 129)} \frac{KrCl (222; 129)}{KrCl (222; 129)} $ $ Fe(CO)_{5} \frac{Fe(CO)_{4}}{Fe(CO)_{3}} \frac{Fe(CO)_{4}^{b}}{Fe(CO)_{3}} \frac{Fe(CO)_{3}^{b}}{Fe(CO)_{2}} \frac{Fe(CO)_{2}^{b}}{Fe(CO)_{2}^{b}} $ $ V(CO)_{6} \frac{V(CO)_{4}}{Cr(CO)_{5}} \frac{Cr(CO)_{5}}{Cr(CO)_{4}} \frac{Cr(CO)_{4}}{Cr(CO)_{4}} \frac{Cr(CO)_{4}}{Cr(CO)_{3}} \frac{Cr(CO)_{4}}{Cr(CO)_{3}} \frac{Cr(CO)_{4}}{Cr(CO)_{3}} \frac{Cr(CO)_{4}}{Cr(CO)_{3}} \frac{Cr(CO)_{4}}{Cr(CO)_{3}} \frac{Mo(CO)_{4}}{Mo(CO)_{4}} \frac{Mo(CO)_{4}}{Mo(CO)_{4}} \frac{Mo(CO)_{4}}{Mo(CO)_{3}} \frac{Mo(CO)_{4}}{Mo(CO)_{3}} \frac{Mo(CO)_{5}}{W(CO)_{5}} \frac{W(CO)_{5}}{W(CO)_{5}} \frac{W(CO)_{5}}{W(CO)_{4}} \frac{W(CO)_{5}}{W(CO)_{4}} \frac{W(CO)_{5}}{W(CO)_{4}} \frac{W(CO)_{5}}{W(CO)_{4}} \frac{W(CO)_{5}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{4}}{W(CO)_{4}} \frac{W(CO)_{5}}{W(CO)_{5}} W(C$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $		

^a $M(CO)_x$ is a major fragment. $M(CO)_x$ is a minor fragment. Species in standard type are present in approximately equal amounts. ^bUnpublished data. ^cThere is an indication that excited singlet state Fe(CO)₃ may be a product in the ArF laser photolysis of Fe(CO)₅.⁴ ^d Values in parentheses are λ (nm) and $h\nu$ (kcal mol⁻¹), respectively.

TABLE III: Gas-Phase M(CO)_x C-O Stretching Frequencies (cm⁻¹)

			Cr		Мо		W	
	assignmt		this work	lit.	this work	lit.	this work	lit.
M(CO) ₆	O _h	T_{1u}	1999	2000ª	2003	2003ª		1999 ^b 1998 ^a
M(CO) ₅	C_{4v}	\mathbf{A}_1						
		E	1976	1980°	1990	1983ª		1980°
		A_1	1950	1 94 8°	1942	1940 ^d		1942 ⁶
$M(CO)_4$	C_{2r}	A_1						
x 7 4	20	\mathbf{B}_{1}	1954	1957°	1972	1970 ^d		1957°
		$\dot{A_1}$			1946		(1942)	
		B ₂	1916	1920 ^c	1911	1914 ^d	()	1909
M(CO) ₃	C_{3n}	\mathbf{A}_{1}^{2}				1990 ^{d,e}		
	50	E	1887	1880°	1891	1888 ^d		
$M(CO)_{2}$			1914°					

^aReference 24. ^bReference 12. ^cReference 7. ^dReference 21. ^eNot confirmed in this work.

In the same study, they argue that in the case of Mo and W BDE6 is the largest by at least 4 kcal mol⁻¹ but that for Cr the highest BDE is associated with the loss of a subsequent CO ligand, probably the second. Their conclusions are based on their ability to trap intermediate unsaturated fragments with added CO or PF₃ only in the case of Cr. Our implication that the average of the first three M-CO BDEs has the order Mo < Cr < W qualitatively supports these findings in that if the first BDEs are correct (Cr < Mo < W), we require the second and/or third BDEs to be larger in the case of Cr than in the case of Mo. It is not unusual to find Mo out of step with the other group 6 metals. The relative ease of formation of Mo(CO)₄ and Mo(CO)₃ by photolysis of $Mo(CO)_6$ in low-temperature matrices compared with Cr and W²⁵ may be linked to low values for BDE5 and BDE4 in Mo. Also, the CO stretching frequencies in $Mo(CO)_5$ and $Mo(CO)_4$ are shifted relative to the corresponding Cr and W complexes both in the gas phase (Table III) and in low-temperature matrices.²⁵ Whereas for $M(CO)_6$, the CO stretching frequency is ~2000 cm⁻¹ for all three metals. These shifts may reflect a lower intrinsic M-C bond strength in Mo(CO)₅ and Mo(CO)₄ but could also be due to differences in the degree of interaction between the CO ligands. A detailed analysis is not possible due to limited available data.

In our modeling to fit the pressure dependence of observed branching ratios for unimolecular dissociation and stabilization of $Cr(CO)_5^*$, we found an admittedly not unique fit to our data for BDE6 \simeq BDE5 \simeq 37 kcal mol⁻¹. This is consistent with the trapping experiments. From energy of activation estimates, made on the assumption that loss of the second CO is the rate-determining step, Lewis et al. estimated BDE5 \simeq 40 kcal mol⁻¹ for Cr. Both sets of results require that BDE6 and BDE5 are significantly larger than the average thermal Cr–CO BDE, 26 kcal mol⁻¹. In addition, the fragment distributions at 248 and 222 nm suggest that BDE4 is also large, of the order of 35 kcal mol⁻¹. The implication is that the CO binding in the lower fragments must be relatively weak. Atomic Cr has a ⁷S ($3d^54s^1$) ground state. A promotional energy to an atomic or hybrid configuration more suitable for CO coordination counters the intrinsic bond strength contribution to the thermochemical BDEs. This may well be more significant at a low level of coordination. Note that $Cr(CO)_x$ (x = 3-6) species have singlet ground states and geometric shapes that can all be rationalized on the basis of a d⁶ metal center^{1,35} and cannot correlate to ground-state Cr. Major changes in the atomic configuration of Cr must take place through x = 0-3.

Table III summarizes the C–O stretching frequencies for $M(CO)_x$ observed to date in the gas phase. The structural assignments, C_{4v} for $M(CO)_5$, C_{2v} for $M(CO)_4$, and C_{3v} for $M(CO)_3$ made in condensed phases are also consistent with the infrared absorption spectra all the $M(CO)_x$ species observed in the gas phase without exception. The A_1 mode of C_{2v} $M(CO)_4$, seen at 1946 cm⁻¹ for $Mo(CO)_4$, is only observed as a shoulder at 1942 cm⁻¹ on the red edge of the B_1 band of $W(CO)_4$ and is presumed to be obscured by the B_1 band in the case of $Cr(CO)_4$. Differences between the frequencies reported here and those reported by Weitz et al.⁷ and Ganske and Rosenfeld²¹ are within the limits of this type of experiment, which result from the spectral resolution (~4 cm⁻¹) and from the broadness of the absorption bands.

Conclusions

The ultraviolet laser photolysis of group 6 transition-metal carbonyls at moderate fluences show trends in photofragmentation patterns that depend on the group properties of bond dissociation energies and initial electronic states in a manner that forms added

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support for a photodecomposition mechanism involving sequential CO elimination from $M(CO)_x$ in its electronic ground state. Qualitative estimates of the nascent internal energy content of the product fragments $M(CO)_x$ and CO are also consistent with this mechanism. In addition, we have observed, for the first time, the expected buffer gas pressure effects on the relative yields of $Cr(CO)_5$ and $Cr(CO)_4$ in the case of 308-nm photolysis. Our relative fragment yields between Cr and Mo support previous indications that in Cr(CO)₆ the first M-CO BDE is not the largest whereas it is in the cases of Mo and W.

Unlike $W(CO)_6$, presumably as a consequence of the lower CO binding energy, there are no excimer laser wavelengths that exclusively produce a single $Mo(CO)_6$ species. $Mo(CO)_4$ is the major product at 308 nm and may be tractable for reactive studies; however, at 351 nm there is also a significant amount of $Mo(CO)_{4}$ produced that may thwart attempts to study $Mo(CO)_5$.

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Registry No. Mo(CO)₆, 13939-06-5; Cr(CO)₆, 13007-92-6; W(CO)₆, 14040-11-0; Cr(CO)₅, 26319-33-5; Cr(CO)₄, 56110-59-9; Mo(CO)₄, 44780-98-5; Mo(CO)₃, 55979-29-8; Mo(CO)₅, 32312-17-7; CO, 630-08-0.

Kinetics and Products of the Reactions of NO_3 with Monoalkenes, Dialkenes, and Monoterpenes

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Rate constants for the reactions of NO₃ with a number of aliphatic mono- and dialkenes and monoterpenes have been determined in a 420 1 reaction chamber at 1-bar total pressure of synthetic air by 298 K with a relative kinetic method. The products of these reactions have been investigated also at 1-bar total pressure of synthetic air with in situ FT-IR spectrometry and gas chromatography. In all cases, the initial formation of thermally unstable nitrooxy-peroxynitrate-type compounds containing the difunctional group $-CH(OONO_2)-CH(ONO_2)$ has been observed. The experimental results are consistent with a mechanism involving the formation of nitrooxy-alkoxy radicals, -CH(O)-CH(ONO₂)-, via the self-reaction of the nitrooxy-peroxy radicals. The further reactions of the nitrooxy-alkoxy radicals then determine the final products. The main reaction pathways are (i) reaction with O₂ to form nitrooxy-aldehydes or -ketones and HO₂ and (ii) thermal decomposition forming aldehydes/ketones and NO₂. The mechanisms leading to the final products are discussed, and their possible relevance for the chemistry in the troposphere is considered.

Introduction

A large number of hydrocarbons is known to be emitted to the atmosphere from natural sources.¹ The most important biogenic hydrocarbons released from various types of plants and trees are isoprene and monoterpenes.²⁻⁵ Their emission source strengths on a global scale are much larger than those of anthropogenic non-methane hydrocarbons. They represent a significant source of reactive organic compounds to the atmosphere whose role in the chemistry of tropospheric oxidant formation is not well understood. At present, attention is being focused on the degradation processes of these natural hydrocarbons and in particular on those processes leading to the formation of oxidants that might develope phytotoxic properties within forest areas.

Isoprene and the monterpenes are known to react rapidly with O_3^6 and OH radicals.⁷ Recently, it has been shown that NO_3 also reacts rapidly with these compounds.8-12 These fast reactions taken in conjunction with the atmospheric concentrations of NO₃, which have been observed in the nighttime troposphere as high as 350 pptv, $^{13\text{--}15}$ have led to the suggestion that reaction with NO_3 may dominate the nighttime chemistry of volatile biogenic organic compounds. Product studies have so far only been reported in the literature for the reactions of NO_3 with propene,¹⁶⁻²⁰ a series of sulfur compounds,²¹ formaldehyde,²² acetaldehyde,²³ and tetramethylethylene.24

The aim of the present study was to investigate the mechanisms and products of the reactions of NO₃ with atmospherically important alkenyl hydrocarbons. Many of the expected products such as peroxynitrates, nitrates, and organic acids are potential phytotoxicants; a detailed knowledge of their mechanisms of formation and product yields will allow a better evaluation of their possible impact on forest ecosystems.

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