Mechanisms of Metal Atom Formation in the Multiphoton Dissociation of Organometallic Molecules

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I. Introduction

Research on the photochemistry of gas-phase molecules has been underway for several decades now, with most of the studies performed thus far concentrating on small organic and inorganic molecules. Surprisingly, metal complexes and organometallics were largely ignored until relatively recently. Indeed, one of the first definitive investigations of the single-photon chemistry of gas-phase organometallics was published by Yardley and co-workers in 1980.[1,2]

Yardley's experiments are important because they reveal a basic difference between the photochemical behavior of organometallics and small organic or inorganic molecules. In the photodissociation of organic or inorganic species, only one bond is usually broken because the energy required to break the weakest bond is not a great deal less than that supplied by a single UV photon.[1,2] In contrast, Yardley and co-workers showed in experiments on $Fe(CO)_5$ that several metal-carbonyl bonds can be broken upon absorption of one UV photon. This result was not anticipated, but it is fairly easy to understand in retrospect why such multiple fragmentation processes occur. The energy of one UV photon is 2–3 times greater than the energy required to break the first metal–carbonyl bond in $Fe(CO)_5$. A very large fraction of the excitation energy is therefore carried away by the primary photoproducts, $Fe(CO)_4$ and CO. Although much of this energy is lost to product translational degrees of freedom, as well as to rovibrational excitation of the CO product,[3] $Fe(CO)_4$ retains more than enough energy to dissociate further.[4] Dissociation continues until there is no longer sufficient energy left to break the next bond. Later experiments by several groups have shown that analogous multiple fragmentation processes are quite typical in metal carbonyls and metal alkyls.[5,6] In condensed-phase photodissociation experiments, however, multiple fragmentation is not normally observed,[7] since the primary metal-containing photoproduct gives up its excess internal energy to the surrounding medium before it dissociates.

At approximately the same time as the Yardley work, investigations of the laser-induced multiphoton dissociation (MPD) of organometallics were initiated. Zare and co-workers showed that by focusing the output of an excimer laser into a cell containing gaseous $Fe(CO)_5$, or other organometallics, emission from electronically excited metal atoms could be readily observed.[8] A large fraction of the metal atoms was produced in very highly excited states. Clearly, the intense output of the focused excimer laser is able to drive a multiphoton process that not only cleaves all the metal–ligand bonds, but also pushes the bare metal atom to very high levels of excitation. An intense laser source is not needed, however, to form metal atoms via MPD of metal carbonyls, as Callear and Oldman's flashlamp experiments had shown years earlier.[9] While the Zare and the Callear and Oldman work did not specifically address the number of photons absorbed in the metal-atom formation process, we know from Yardley's work that one UV photon can break several metal–ligand bonds. Perhaps only two or three UV photons can completely dissociate a metal complex to produce a bare metal atom. Our work has shown that this is indeed the case.[10-13] Additional studies by several research groups have shown that metal atoms can also be formed by laser-induced MPD of organometallics at near-UV or even visible wavelengths.[14]

Also in the early 1980s, it was discovered that laser photodissociation of organometallics could be used to deposit metallic, semiconductor, and dielectric films for applications in microelectronics. For example, it was shown that metallic circuit lines could be deposited with high spatial resolution onto an integrated circuit by focusing the output of a CW UV laser onto the silicon substrate in the presence of an organometallic vapor and translating the substrate underneath the laser beam.[15,16] In addition, it was shown that blanket films of various materials could be deposited at relatively cool temperatures from organometallic vapor sources aided by photodissociation with a UV lamp or laser.

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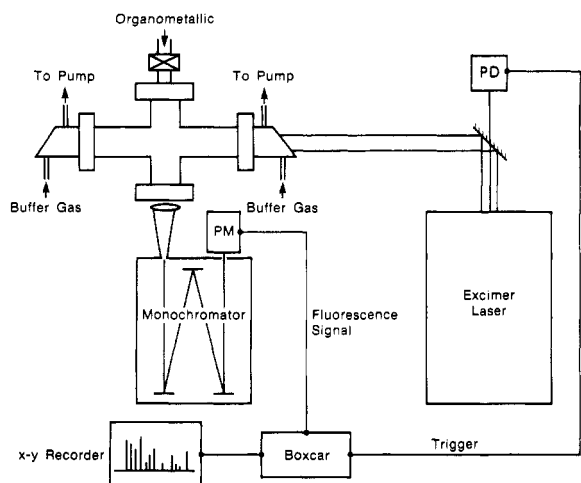(12) Tyndall, G. W.; Larson, C. E.; Jackson, R. L. J. Phys. Chem. 1989, 93, 5508.
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Figure 1. Experimental apparatus. (Reprinted with permission from ref 11. Copyright 1988 American Institute of Physics.)

The promise held by these applications, plus the discoveries made in the fundamental arena, sparked tremendous interest in gas-phase organometallic photochemistry that continues today.

Initially, we were interested in the MPD of organometallics because of possible applications in microelectronics, but we became intrigued by the MPD process itself, since the mechanisms were not well-understood. Mechanistic proposals to explain the formation of metal atoms via MPD of organometallics invoked a sequental process, where the products formed upon absorption on the first photon repeat the one-photon absorption/fragmentation sequence until all metal–ligand bonds are broken.[8,14] This proposal is a reasonable extension of the mechanism discovered in Yardley's one-photon experiments. Still, it was unclear to us that a sequential mechanism of this kind could account for the formation of highly excited metal atoms, since in cases where relatively few photons are absorbed, the excitation energy would have to be very efficiently channeled into bond-breaking and Cr electronic excitation. This runs counter to observations that product translation as well as rovibrational excitation of the CO products take away substantial amounts of energy in metal carbonyl photodissociation processes.[3,5]

In this account, we will address the mechanisms operating in the MPD of organometallics, drawing from MPD experiments performed on several organochromium compounds in our laboratory.[10–12] The results of this work show that the sequential mechanism is *not* the primary pathway for the formation of high-energy excited states of Cr atoms upon MPD of $Cr(CO)_6$ and related arene chromium tricarbonyls. Instead, it appears that highly excited Cr atoms are formed by a "direct" process, where the parent complex absorbs several photons prior to fragmentation, and then rapidly dissociates to produce a broad, statistical distribution of Cr atom excited states.

II. Experimental

We used a very simple experimental setup to detect excited products formed in the photodissociation of $Cr(CO)_6$[10,11] and a series of arenechromium carbonyls.[12] In the experimental apparatus shown in Figure 1, the organometallic flows through a stainless steel cell and the beam from an unfocused excimer laser passes down
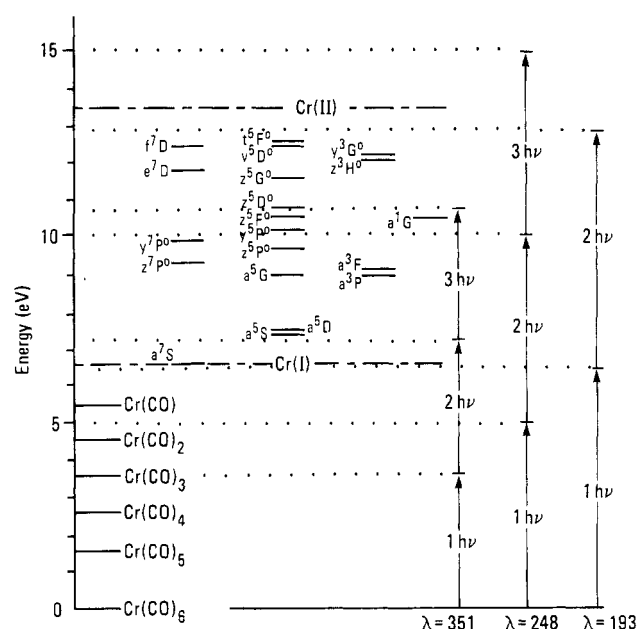
Figure 2. Energy diagram for the MPD of $Cr(CO)_6$ at 193, 248, and 351 nm. (Reprinted with permission from ref 11. Copyright 1988 American Institute of Physics.)

the length of the cell to induce dissociation. The excimer laser was operated at 193 nm (ArF), 248 nm (KrF), or 351 nm (XeF) at fluences of 3–30 mJ/cm^2. Emission from electronically excited photoproducts was detected at 90° relative to the excimer laser beam by a simple fluorescence spectrometer, consisting of a 1-m monochromator and a photomultiplier tube. The fluorescence signal was averaged over several excimer laser pulses using a boxcar integrator; the integrator gate was set at the peak of the fluorescence decay curve for the Cr states of interest. Note that it is not necessary to focus the excimer laser to observe Cr atom emission in these experiments. In fact, Cr emission is detectable at excimer-laser fluences as low as 3 mJ/cm^2.

The experiments described in this paper are simple, but they show distinctly which Cr electronic states are formed. Also, because the experiments are performed in a flow cell, the effects of pressure on the yield of the various Cr states may be specifically examined. No information on ground-state products is available, however, and since metal carbonyls generally do not fluoresce, information on molecular species is also lost.

III. Results of MPD Experiments on $Cr(CO)_6$

First, we will examine the MPD of $Cr(CO)_6$ at 248 nm. Figure 2 shows the Cr states that might be observable and the energy required to form them from the ground state of $Cr(CO)_6$. As the diagram shows, at least two photons are required to produce ground-state Cr atoms from $Cr(CO)_6$ at 248 nm. Higher energy Cr states require at least three photons. The Cr states that will be most easily observable in our experiments are the higher energy states of odd parity (denoted by a superscript o), since these states emit a photon in the visible or near-UV, radiating to the even-parity ground state (a^7S) and the two lowest-energy excited states (a^5D and a^5S).

On the basis of the suggestions of previous MPD studies of metal carbonyls, we began our work under the assumption that Cr was produced via a series of single-photon absorption/dissociation steps, where the

products of one step absorb a photon and then dissociate to form the products of the next step. We have a good picture of the first two steps of this process from prior work. Research groups headed by Weitz[5] and Rosenfeld[17] have shown that the dominant photoproduct formed upon single-photon dissociation of $Cr(CO)_6$ at 248 nm is $Cr(CO)_4$. In accord with the mechanism first discussed by Yardley, the actual primary photoproduct is $Cr(CO)_5$, but this species is formed sufficiently hot that it undergoes spontaneous secondary dissociation with nearly 100% probability. Consequently, little $Cr(CO)_5$ remains as a final product.[5,13,17] A small percentage of the $Cr(CO)_4$ actually dissociates further to yield $Cr(CO)_3$.[5,13]

We extended these one-photon studies to include the next step, i.e. photodissociation of the single-photon products.[13] Using a mass spectrometer to detect $Cr(CO)_x$ photoproducts formed in a molecular beam, we found that the predominant single-photon product, $Cr(CO)_4$, undergoes photodissociation with a large cross section at 248 nm, yielding primarily $Cr(CO)_2$. $Cr(CO)$ and Cr are also minor products. Vibrationally hot $Cr(CO)_3$ is presumably the photo-intermediate that ultimately yields all of these products by a Yardley-type mechanism.

Note that one 248-nm photon provides 115 kcal/mol, which is enough to break five of the Cr–CO bonds in $Cr(CO)_6$, while two photons provide 230 kcal/mol, which is enough to break all six Cr–CO bonds *and* to drive Cr to fairly high levels of electronic excitation. Nevertheless, only two CO ligands are lost on average in the one-photon dissociation process, while only a total of four or five ligands are lost on average in the two-photon sequential dissociation process. Dissociation does not proceed further because much of the excitation energy is lost to product translation and to rovibrational excitation of the CO products. We can thus expect the following outcome from the sequential 248-nm MPD of $Cr(CO)_6$. A two-photon sequential process will produce a very low yield of Cr atoms in the lowest-lying states. A three-photon process should produce a larger yield of Cr atoms, but given the energy losses that mount with each dissociation step, even a three-photon process is unlikely to yield very high-energy states of Cr. Four photons or more should be required to form high-energy states. Measurements of the number of photons required to form the higher energy Cr electronic states can thus provide valuable mechanistic information.

Examination of the Cr state distribution formed in MPD experiments conducted at high total pressures can provide even more valuable mechanistic information. As shown by Yardley initially, the key to the multiple-fragmentation processes observed upon photodissociation of metal carbonyls is that the primary $M(CO)_x$ photoproduct is formed sufficiently hot that it will dissociate spontaneously. Under high-pressure conditions, however, the degree of spontaneous dissociation will be reduced as collisional energy transfer relaxes the hot $M(CO)_x$ photoproduct population. Indeed, this phenomenon has been observed by Rayner and co-workers for single-photon dissociation of $Cr(CO)_6$ in the presence of a buffer gas.[18] We thus expect

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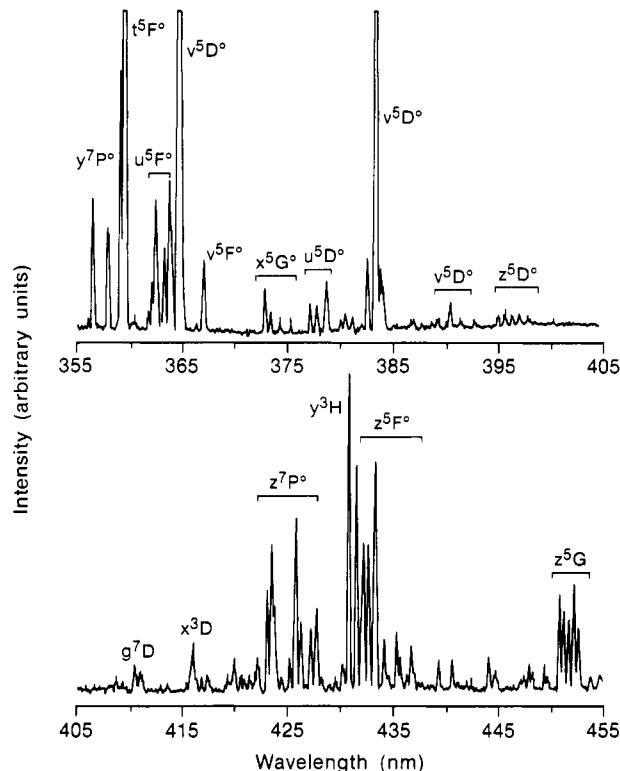(18) Rayner, D. M.; Ishikawa, I.; Brown, C. E.; Hackett, P. A. *J. Chem. Phys.* **1991**, *94*, 5471.

Figure 3. Cr atom emission spectrum obtained upon 248-nm MPD of $Cr(CO)_6$.

the final Cr state distribution resulting from a sequential MPD process to favor lower energy states as the pressure increases.

Now that our expectations for the sequential 248-nm MPD of $Cr(CO)_6$ are established, we examine our experimental results to see if they match these expectations. As shown in Figure 3, we observed a congested Cr emission spectrum upon 248-nm MPD of $Cr(CO)_6$—over 200 Cr emission lines were assigned, some involving very high-energy states. We found that each state is formed via absorption of the *minimum* number of photons (two or three) required energetically.[11] The number of photons absorbed was determined by measuring the fluorescence intensity for a given state of Cr vs the intensity of the excimer laser. In the absence of saturation, the fluorescence intensity scales as I^n, where I is the intensity of the excimer laser and n is the number of photons absorbed.[11] The yield of Cr atom states was also *unaffected* by the addition of He, Ar, or CO up to the highest pressures examined ($\sim$100 Torr). These observations clearly do not match our expectations for a sequential MPD process.

To make sure that the results of our 248-nm MPD experiments are not simply an anomaly, we performed identical experiments at 351 and 193 nm.[11] Analogous results were obtained. Fewer Cr emission lines were observed in the 351-nm and 193-nm experiments than in the 248-nm experiments, but we found that each state was formed by the minimum number of photons required energetically. The final Cr state distribution is also independent of buffer-gas pressure. We must conclude that none of our results matches those expected for a sequential MPD process.

Of course, two questions immediately arise from the results we have discussed thus far: (1) what *is* the mechanism, and (2) is the sequential mechanism
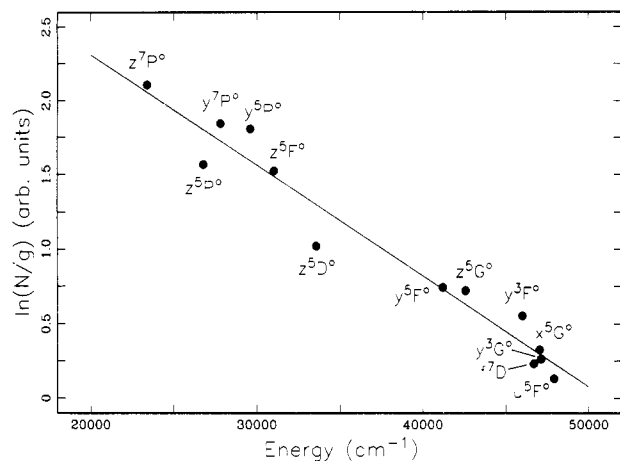
Figure 4. Population plot of the natural log of the population (N) divided by the degeneracy (g) vs energy for the Cr atom states observed in the 248-nm MPD of $Cr(CO)_6$. The populations were determined from emission intensities, as described in ref 11. The populations of the $z^7P°$, $z^5P°$, and $y^7P°$ states are corrected for the effects of radiation trapping, as described in ref 11. The line represents a least-squares fit to a Boltzmann distribution, giving a temperature of 9400 K.

important in the formation of *any* Cr state? We will consider each of these questions in turn.

If MPD does not occur as a sequence of one-photon absorption/fragmentations steps, only one possibility remains: at least two photons must be absorbed by $Cr(CO)_6$ prior to any fragmentation. Beyond that conclusion, however, our experiments do not firmly establish the mechanism of the MPD process. We therefore propose the following picture to account for our results. $Cr(CO)_6$ absorbs two, three, or four photons (depending on wavelength and laser fluence), probably in a coherent manner, preparing a very highly excited electronic state of the intact complex. This state is metastable with respect to loss of all CO ligands and dissociates explosively, probably losing all ligands simultaneously. Such a "direct" dissociation process would occur quickly, probably on the time scale of a single vibration, so it would not be possible to alter the product distribution via collisions. In addition, one could expect to produce at least some fraction of the highest energy Cr states allowed by energy conservation. This is because dissociation occurs in a more or less concerted fashion, rather than stepwise, where energy lost to product translation and CO rovibrational excitation mounts with each step.

Additional experimental observations help to clarify the nature of this direct MPD process. As shown in Figure 4, the populations of the various Cr states produced via MPD at 248 nm are very well defined by a simple Boltzmann distribution. Analogous results were obtained in the 351-nm and 193-nm MPD experiments.[11] There is no preference for states of a particular spin multiplicity or for states of a specific orbital angular momentum. Instead, the population of a given state is determined solely by its energy and degeneracy. The electronic "temperature" of this distribution does not depend on laser fluence, but it does depend on the energy supplied in excess of that required to break all six CO ligands (see Table I). On the basis of these observations, we view the dissociation process in terms of a half-collision, where the highly excited state of $Cr(CO)_6$ prepared by multiphoton

Table I. Electronic Temperature of the Cr Electronic State Distribution vs the Quantity of Energy Supplied via the MPD Process in Excess of That Required To Remove All CO Ligands from $Cr(CO)_6$

excitation wavelength (nm)	excess energy (kcal/mol)	Cr state distribution temp (K)
193	147[a]	8700
248	95[b]	4200
351	196[b]	9400

[a] Two photons absorbed. [b] Three photons absorbed.

absorption can cross onto one of a multitude of potential surfaces, each representing a specific state of Cr within a field of six unbound CO ligands. The probability of accessing a particular potential surface is determined by statistics, within the constraints of energy and angular momentum conservation, resulting in a Boltzmann distribution of Cr states. Obviously, this picture is a simplification of an enormously complicated process, but it is interesting that the final outcome of this process is remarkably simple.

Before proceeding with additional discussion of the direct mechanism, we would like to address our second question, i.e. whether the sequential mechanism is important at all in the formation of Cr. Our fluorescence data indicate that it is not important in the formation of higher energy Cr states, but what about the lowest energy excited states and the ground state? Our earlier molecular beam experiments suggest that at least a small yield of Cr is formed via a two-photon sequential process at 248 nm.[13] We cannot observe low-energy Cr states directly in the fluorescence experiments, but in the 248-nm MPD experiments, we can observe the two lowest-lying excited states of Cr—the a^5D and a^5S states (see Figure 2)—by making use of absorption lines of these states that lie near 248 nm. Fortuitously, the $v^5D_3°\leftarrow a^5S_2$ transition (248.55 nm) and the $t^5F_2°\leftarrow a^5D_2$ transition (248.12 nm) lie within the relatively broad output of the KrF laser, centered at 248.3 nm; the $v^5D_3°$ and $t^5F_2°$ states fluoresce strongly in the near-UV. The a^5S and a^5D states are thus observable in our 248-nm MPD experiments via laser-induced fluorescence (LIF), rather than by spontaneous emission as in the other experiments described thus far. Indeed, the LIF process gives rise to the two most intense emission lines observed in the overall Cr emission spectrum (see Figure 3). The intensity of the LIF lines scales as I^3, indicating that two photons are involved in the formation of the a^5D and a^5S states (the third photon drives the LIF process). Two photons are the minimum required to form each state from $Cr(CO)_6$.

We found that the LIF line intensities are tremendously sensitive to added buffer gas, as shown in Figure 5. For reasons discussed in detail elsewhere,[10,11] we know that quenching is not due simply to collisional electronic deactivation of the a^5D and a^5S states, or of the $t^5F_2°$ and $v^5D_3°$ states formed in the LIF process. Quenching occurs because the yield of the a^5S and a^5D states is reduced as the pressure increases. Looking back at the expectations spelled out earlier for the sequential mechanism, we see that the pressure-dependent behavior of the a^5S and a^5D states is exactly what we expected from the sequential mechanism. The yield of the a^5D and a^5S states is reduced because vibrational energy is removed from the $Cr(CO)_x$ inter-
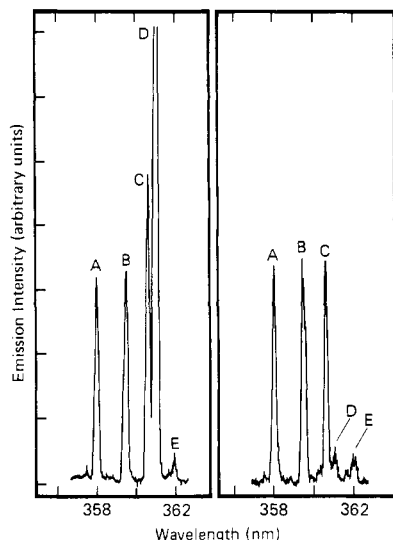
Figure 5. Portion of the Cr atom emission spectrum showing quenching of the LIF line involving the a^5D state, peak D. Right: CO pressure = 1 Torr. Left: CO pressure = 5 Torr. The remaining peaks are spontaneous emission lines that are not quenched, involving the y^7P^o state (peaks A, B, and C) and the x^5H^o state (peak E). (Reprinted with permission from ref 10. Copyright 1987 American Chemical Society.)

mediates via collisions with buffer gas along the sequence of steps that yield these states. Energy removed via collisions only serves to heat the buffer gas and cannot contribute to the bond-breaking and Cr atom excitation processes, thus favoring lower energy products.

Unfortunately, we cannot quantitatively compare the yield of Cr produced via the direct and sequential mechanisms in the 248-nm MPD of $Cr(CO)_6$, since each process is observed by a different experimental method (LIF vs spontaneous emission). We can make the following qualitative observations about the relative importance of each process, however. On the basis of the results of our spontaneous emission experiments, we have already concluded that the sequential mechanism is not important in the formation of higher energy states of Cr. Given that the a^5S and a^5D LIF lines can be completely quenched by added buffer gas, however, it appears that the sequential mechanism is the *predominant* pathway for the formation of these lower energy states. We thus conclude that the energy of the excited state is critical in determining the extent to which the sequential and direct mechanisms operate. The sequential mechanism strongly favors the formation of lower energy states, while the direct mechanism strongly favors the formation of higher energy states.

IV. Results of MPD Experiments on Arene Chromium Tricarbonyls

To gauge the applicability of the conclusions reached in the MPD experiments on $Cr(CO)_6$ to other organochromium compounds, we performed similar experiments on a series of arene chromium tricarbonyls,[12] which we will denote as $(Ar)Cr(CO)_3$. Here, (Ar) represents an η^6-benzene or an η^6-alkylbenzene ligand. In the experiments described below, we looked at 248-nm excimer laser MPD of four $(Ar)Cr(CO)_3$ complexes,

where (Ar) = benzene, toluene, n-propylbenzene and *tert*-butylbenzene.[19]

The only significant difference among the four (Ar)-$Cr(CO)_3$ complexes is the size of the alkyl substituent on the arene ligand. The size of this substituent has virtually no effect on the overall dissociation energy of the complex, which is ~120 kcal/mol. Thus the number of photons required to form Cr, as well as the energy available for electronic excitation of Cr via the MPD process, will be identical for each complex. The size of the alkyl substituent profoundly affects the vibrational state density of the arene ligand, however. The effect of this state density on the sequential and direct MPD mechanisms will differ in a major way.

In the sequential mechanism, each step along the path from the parent complex to the metal atom involves a separate one-photon absorption–fragmentation process. Within each step, some fraction of the photon energy is partitioned to the product degrees of freedom. From earlier work on the single-photon dissociation of metal carbonyls,[17,20–22] we know that vibrational excitation of the departing ligands occurs to a significant degree. In the cases reported in the literature thus far,[3,20–22] it appears that the excitation energy is distributed more or less statistically among the various product degrees of freedom during the dissociation process. The fraction of the excitation energy carried away by the arene ligand will thus be directly proportional to its vibrational state density, so less energy will be available for electronic excitation of the Cr atom as the size of the arene ligand increases. Hence, the final Cr state distribution should favor lower energy states as the size of the arene ligand increases, if Cr is formed by the sequential mechanism.

Very different behavior is expected for the direct mechanism. We have proposed that in the direct process, dissociation occurs on the time scale of a vibrational period from a very highly excited state of the parent complex. For a fast dissociation process of this kind, there is insufficient time for energy to be partitioned with any degree of efficiency among all the product vibrational degrees of freedom. The size of the ligand should thus play little role in determining the final Cr state distribution resulting from the MPD process. The direct mechanism should yield a Boltzmann distribution of excited states, as we observed for $Cr(CO)_6$, with the electronic temperature varying little with the size of the arene ligand.

The Cr fluorescence spectrum observed upon MPD of the four $(Ar)Cr(CO)_3$ species is consistent with our expectations for the direct mechanism. As shown in Figure 6, we obtained a Boltzmann distribution of the higher energy Cr excited states. The electronic temperature was identical, within experimental error, for all four compounds. Clearly, the arene ligand acts only as a spectator in the dissociation process, much as we expect from our description of the direct mechanism. Note that energy partitioning in the direct mechanism is statistical with respect to the electronic states of

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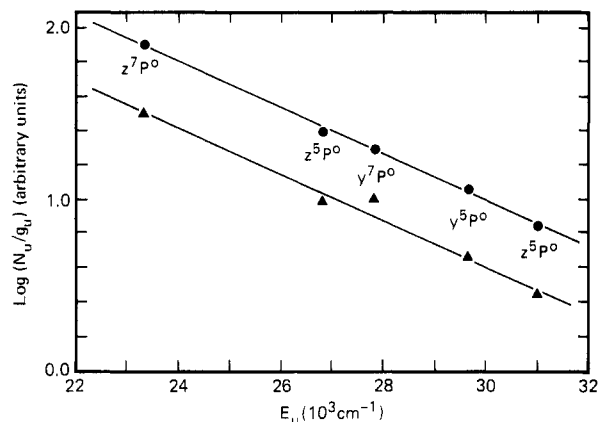
Figure 6. Population plot, as in Figure 4, showing the distribution of Cr excited states observed in the 248-nm MPD of (Ar)Cr-(CO)$_3$: (●) Ar = benzene, (▲) = *tert*-butylbenzene. The lines represent a least-squares fit to a Boltzmann distribution, giving a temperature of 8500 K. (Reprinted with permission from ref 12. Copyright 1989 American Chemical Society.)

Table II. Comparison of the LIF Line Intensity Observed for the a^{5}D State to the Spontaneous Fluorescence Line Intensity Observed for the y^{7}P° State upon 248-nm MPD of (Ar)Cr(CO)$_3$ Compounds

(Ar)Cr(CO)$_3$ compound	a^{5}D LIF vs y^{7}P° spont emission int (arb units)
Ar = benzene	1.00
Ar = toluene	0.62
Ar = *n*-propylbenzene	0.37
Ar = *tert*-butylbenzene	0.28

Cr—due to the efficient electronic curve-crossing process we discussed earlier—but energy partitioning is highly *nonstatistical* with respect to the vibrational modes of the departing ligands.

The results for the lower energy a^{5}D and a^{5}S states—which we observed by LIF as in the Cr(CO)$_6$ experiments—are quite different. We see a distinct effect of the size of the arene ligand on the population of the a^{5}D and a^{5}S states. This effect is quantified by measuring the intensity of the LIF lines relative to the intensity of the spontaneous fluorescence emitted by one of the higher energy states (y^{7}P°). These relative intensity values—which are given in Table II—are directly proportional to the relative yield of the a^{5}D

(23) For related work on the MPD of organoiron complexes, see: (a) BelBruno, J. J.; Kobsa, P. H.; Carl, R. T.; Hughes, R. P. *J. Phys. Chem.* 1987, *91*, 6168. (b) Nagano, Y.; Achiba, Y.; Kimura, K. *J. Phys. Chem.* 1986, *90*, 1288.

and a^{5}S states, since we have already seen that the relative yield of the higher energy states is unaffected by the size of the arene ligand. The yield of the a^{5}D and a^{5}S states drops significantly as the size of the arene ligand increases. This is exactly the result we expected for the sequential mechanism. As the arene ligand increases in size, it carries away more of the excitation energy, leaving less energy available for Cr atom excitation.

To summarize, the results we obtained from the MPD experiments on the arene chromium carbonyls very nicely parallel the results obtained for Cr(CO)$_6$. The higher energy states are formed by the direct mechanism, while the lower energy states are formed by the sequential mechanism. More work remains, but these two mechanisms appear to be general for all of the organochromium compounds we have examined thus far.[10,11]

V. Conclusion

Our fluorescence experiments show that the mechanism for the formation of metal atoms upon MPD or organometallic compounds may not be as simple as earlier proposals suggested. Our data lead us to conclude that the sequential mechanism—where the pathway from parent compound to metal atom proceeds as a series of discrete one-photon absorption/fragmentation steps—is not involved in forming the highly excited states that dominate the intense Cr atom emission spectrum observed upon MPD of Cr(CO)$_6$ and (Ar)Cr(CO)$_3$ complexes. Instead, the highly excited Cr states appear to be formed by a direct process, where the parent compound absorbs two or more photons before fragmenting, and then dissociates extremely rapidly to produce a broad Boltzmann distribution of Cr states. The sequential mechanism does indeed appear to be the primary pathway, however, for the formation of lower energy excited states and possibly also the ground state of Cr.[19] As more data become available from MPD experiments on organometallic compounds, it will be interesting to see if the sequential and direct mechanisms for the formation of metal atoms turn out to be important for the organometallics of other metals.[23]