in a variety of systems. Related reactions are the coupling of carbyne ligands with carbonyl ligands[14] as well as the coupling of two carbonyl ligands[15a] and of two isocyanide ligands.[15b]

Acknowledgment. This work was supported by the National Science Foundation (CHE-8411023).

---

(14) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem.* **1976**, *88*, 649-650; *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632-633.

(15) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311-313. (b) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617-618.

UV Multiple-Photon Dissociation of $Cr(CO)_6$ to Cr* and CO: Evidence for Direct and Sequential Dissociation Processes

George W. Tyndall and Robert L. Jackson*

IBM Almaden Research Center
San Jose, California 95120

Received July 14, 1986

Gas-phase photodissociation of metal carbonyls to metal atoms and CO is well-known.[1-8] Multiphoton ionization experiments have shown that dissociation of the carbonyls to ground- and excited-state metal atoms is unexpectedly efficient relative to competing ionization processes.[9-13] Because the mechanisms behind metal atom formation are not entirely clear, we have investigated the KrF* laser (248 nm) multiple-photon dissociation of $Cr(CO)_6$ to Cr* and CO in the gas phase. We present evidence that Cr* is formed by two processes: (1) a direct process, where $Cr(CO)_6$ is excited into a dissociative continuum, and (2) a sequential process, where a $Cr(CO)_4$ intermediate photoproduct absorbs an additional photon to produce Cr*.

We monitored formation of Cr* by detecting the emission obtained upon unfocused KrF* laser irradiation of ~20 mtorr of $Cr(CO)_6$ contained in a flow cell. Laser fluences ranged from 3 to 40 mJ cm^{-2}. Emission normal to the laser beam was dispersed by a monochromator (resolution 0.5-2 Å) and detected by a photomultiplier tube in conjunction with a boxcar integrator. Standard lamps were used to calibrate the optical system.

KrF* laser photodissociation of $Cr(CO)_6$ produces a rich Cr emission spectrum. Emission from more than 40 states was detected.[14] The relative populations[15] of the Cr* states follow a statistical distribution.[8] Emission is not quenched by CO, Ar, and He at pressures from 1 to 10 torr (except for two states, see below). The laser-fluence-dependence of the emission intensity indicates that production of Cr* occurs via both two-photon and three-photon processes. All states of Cr* for which ΔE_{298} of formation[16] from $Cr(CO)_6$ is less than the energy of two photons (115 kcal/mol each) are indeed formed by a two-photon process, whereas all other states are formed by a three-photon process.

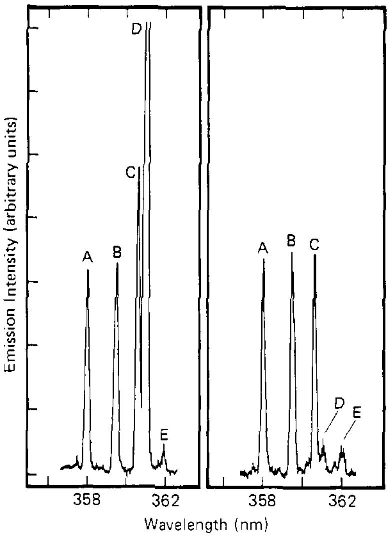


Figure 1. Cr emission spectrum at 2-Å resolution, showing quenching of Cr($t^5F^o_{1,2}$) emission (peak D) by CO. At left, p_{CO} = 1 torr; at right, p_{CO} = 5 torr. Peak assignments are as follows, with the upper state energy vs. the a^7S_3 ground state noted in parentheses: (A) $y^7P^o_4 \rightarrow a^7S_3$ (27 935 cm^{-1}); (B) $y^7P^o_3 \rightarrow a^7S_3$ (27 820 cm^{-1}); (C) $y^7P^o_2 \rightarrow a^7S_3$ (27 729 cm^{-1}); (D) $t^5F^o_{1,2} \rightarrow a^5G_{2,3}$ (0.56-Å spacing not resolved) (48 210 and 48 218 cm^{-1}); (E) $x^5H^o_7 \rightarrow a^5G_6$ (48 140 cm^{-1}).

One-photon KrF* laser photodissociation of $Cr(CO)_6$ gives predominantly,[18,19] or exclusively,[20] vibrationally hot $Cr(CO)_4$, suggesting that Cr* may be formed in our experiments by reactions 1 and 2. If Cr* formation proceeds by this pathway, however,

$$Cr(CO)_6 + 1h\nu \rightarrow Cr(CO)_4{}^{\dagger} + 2CO \qquad (1)$$

$$Cr(CO)_4{}^{\dagger} + 1(2)h\nu \xrightarrow{k_2} Cr^* + 4CO \qquad (2)$$

quenching of Cr* emission by added CO might be expected to occur by competition of reaction 3 with reaction 2. Only five

$$Cr(CO)_4{}^{\dagger} + CO \xrightarrow{k_3} Cr(CO)_5 \qquad (3)$$

of the Cr* states we detected are thermodynamically accessible from $Cr(CO)_5$ with the observed fluence dependence;[21] thus, quenching of Cr* emission should be readily apparent if $k_3[CO] \gtrsim k_2$.[23] These rates should in fact be comparable: at a CO pressure of 10 torr,[24] $k_3[CO] \approx 5\text{-}7 \times 10^7$ s^{-1}, k_2 is not known, but we estimate[25] that $k_2 \approx 5 \times 10^7$ s^{-1} at a typical laser fluence of 20 mJ cm^{-2}. The lack of quenching thus indicates that for-

---

(1) Callear, A. B. *Proc. R. Soc. London, A* **1961**, *265*, 71.

(2) Callear, A. B. *Proc. R. Soc. London, A* **1961**, *265*, 88.

(3) Callear, A. B.; Oldman, R. J. *Nature (London)* **1966**, *210*, 730.

(4) Callear, A. B.; Oldman, R. J. *Trans. Faraday Soc.* **1967**, *63*, 2888.

(5) Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33.

(6) Hellner, L.; Masanet, J.; Vermeil, C. *Nouv. J. Chem.* **1979**, *3*, 721.

(7) Krasinski, J.; Bauer, S. H.; Kompa, K. L. *Opt. Commun.* **1980**, *35*, 363.

(8) Gerrity, D. P.; Rothberg, L. J.; Vaida, V. *J. Phys. Chem.* **1983**, *87*, 2222.

(9) Duncan, M. A.; Dietz, T. G.; Smalley, R. E. *Chem. Phys.* **1979**, *44*, 415.

(10) Gerrity, D. P.; Rothberg, L. J.; Vaida, V. *Chem. Phys. Lett.* **1980**, *74*, 1.

(11) Engelking, P. E. *Chem. Phys. Lett.* **1980**, *74*, 207.

(12) Fisanick, G. J.; Gedanken, A.; Eichelberger, T. S., IV; Kuebler, N. A.; Robin, M. B. *J. Chem. Phys.* **1981**, *75*, 5215.

(13) Whetten, R. L.; Fu, K.-J.; Grant, E. R. *J. Chem. Phys.* **1983**, *79*, 4899.

(14) Based upon assignments of: Kiess, C. C. *J. Res. Natl. Bur. Stand.* **1953**, *51*, 247.

(15) Populations calculated from the data of: Sugar, J.; Corliss, C. *J. Chem. Phys. Ref. Data* **1977**, *6*, 317.

(16) Calculated from Cr state energies[14] and the $Cr(CO)_6$ dissociation energy (ΔE°_{298} = 150 ± 0.6 kcal/mol[17]).

(17) Pichler, G.; Ware, M. J.; Pittam, D. A. *J. Less-Common Met.* **1975**, *42*, 223.

(18) Seder, T. A.; Church, S. P.; Weitz, E. *J. Am. Chem. Soc.* **1986**, *108*, 4721.

(19) Tumas, W.; Gitlin, B.; Rosan, A. M.; Yardley, J. T. *J. Am. Chem. Soc.* **1982**, *104*, 55.

(20) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1985**, *107*, 2203.

(21) See ref 16. $Cr(CO)_5$-CO bond energy = 37 kcal/mol.[22]

(22) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

(23) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978; pp 246-248.

(24) Fletcher, T. R.; Rosenfeld, R. N. *J. Am. Chem. Soc.* **1986**, *108*, 1686.

(25) Estimated from $k = \sigma F \tau^{-1} \phi$, where σ is the absorption cross section of $Cr(CO)_4$ at 248 nm, F is the photon flux, τ is the laser pulse length, and ϕ is the quantum yield. At 20 mJ cm^{-2} and τ = 25 ns as measured, assuming that $\phi = 1$ and that $\sigma = \sigma_{Cr(CO)_6}$ at 248 nm (5.3×10^{-17} cm^2), $k = 5 \times 10^7$ s^{-1}.

0002-7863/87/1509-0582$01.50/0

mation of the vast majority of Cr* states we observed does not proceed by this sequential mechanism, or indeed by *any* sequential mechanism involving an intermediate that reacts efficiently with CO.

We are not certain of the process by which Cr* is formed, but one pathway that readily accounts for the lack of CO quenching involves multiple-photon excitation of $Cr(CO)_6$ into a dissociative continuum, forming Cr* and CO directly. This pathway was proposed in a study of vacuum UV dissociation of $Fe(CO)_5$, in which CW argon and krypton resonance lamp irradiation was found to form Fe* in a one-photon process that clearly does not proceed via a sequential mechanism.[6] If the repulsive surfaces corresponding to each of the Cr* states are strongly intermixed, the branching ratios into the various Cr states could be expected to follow a statistical distribution,[26] as observed. Experiments are in progress to establish the mechanism more conclusively.

While most of the Cr states we detected are higher energy states, we were able to detect two lower lying Cr states indirectly. Formation of the emissive $t^5F^\circ_{1,2}$ and $v^5D^\circ_3$ states proceeds via 248-nm excitation of the low-lying a^5S_2 and a^5D_2 states,[27] from which emission was not observed. The laser-fluence dependence of the emission intensity indicates that the a^5S and a^5D states are formed in a two-photon process, as expected. The emission is exceptionally intense at low pressure, indicating that the a^5S and a^5D states are formed in very high yield relative to other Cr states. Most importantly, $Cr(t^5F^\circ_{1,2})$ and $Cr(v^5D^\circ_3)$ emission is completely quenched at ~5 torr of CO, Ar, and He (Figure 1). This indicates that quenching occurs within a few collisions, since only about 2–5 collisions occur at 5 torr during our data collection cycle (≤40 ns).

We can rule out quenching via collisional relaxation of the emitting Cr* states or of the a^5S and a^5D states, since collisional relaxation of electronically excited atoms by CO, Ar, and He occurs at a rate several orders of magnitude below the hard-sphere collision rate.[8,28,29] Quenching must therefore occur by inhibition of $Cr(a^5S)$ and $Cr(a^5D)$ formation. This strongly suggests that $Cr(a^5S)$ and $Cr(a^5D)$ are produced via reactions 1 and 2, with CO quenching occurring via reaction 3. The rate of reaction 3 is 0.1–0.5 times the hard-sphere collision rate, depending on CO pressure over the range 1–10 torr,[24] consistent with our observation that quenching requires only a few collisions. Reactions analogous to (3) do not occur with Ar and He,[24] but quenching by Ar and He, and in part by CO, can occur by collisional cooling of vibrationally hot $Cr(CO)_4$. ΔE_{298} for formation of $Cr(a^5S_2)$ and $Cr(a^5D_2)$ from $Cr(CO)_4$ is ~110 kcal/mol.[31] Thus, if only a small fraction of the 115 kcal/mol excitation energy in reaction 2 is partitioned into the CO products, $Cr(a^5S)$ and $Cr(a^5D)$ will not be accessible from thermalized $Cr(CO)_4$ by a one-photon process.

In conclusion, we have observed two pathways for KrF* laser multiple-photon dissociation of $Cr(CO)_6$ to Cr*. Higher energy Cr* states are apparently produced by a nonsequential process, involving direct excitation of $Cr(CO)_6$ into a dissociative continuum. Two lower energy Cr* states were found to be formed by a sequential mechanism, via a $Cr(CO)_4$ intermediate.

Acknowledgment is made to Dr. E. E. Marinero for the use of equipment, Dr. P. B. Comita for helpful discussions, and Prof. R. N. Rosenfeld for providing data on $DH^\circ[Cr(CO)_4–CO]$ prior to publication.

---

[26] See the theoretical discussion by: Ohmichi, N.; Silberstein, J.; Levine, R. D. *Chem. Phys. Lett.* **1981**, *84*, 228.

[27] The a^5S_2 and a^5D_2 states lie 7593 and 7927 cm^{-1}, respectively, above the a^7S_3 ground state.

[28] Cundall, R. B. In *Transfer and Storage of Energy by Molecules. Electronic Energy*; Burnett, G. M.; North, A. M., Eds.; Wiley-Interscience: London, 1968; Vol. I, pp 1–63.

[29] Convincing evidence against quenching via Cr* collisional relaxation is obtained from identical experiments on $C_6H_6Cr(CO)_3$, where quenching of $Cr(t^5F_{1,2})$ and $Cr(v^5D_3)$ is *not* observed.[30]

[30] Tyndall, G. W.; Jackson, R. L., unpublished results.

[31] See ref 16 and 21. $Cr(CO)_4$–CO bond energy = 24 ± 6 kcal/mol.[32]

[32] Flectcher, T. R.; Rosenfeld, R. N., unpublished results.

External and Internal Heavy-Atom Effects on the Rate of Spin-Forbidden Proton Tunneling in the Triplet Ground State Biradical, 1,3-Perinaphthadiyl

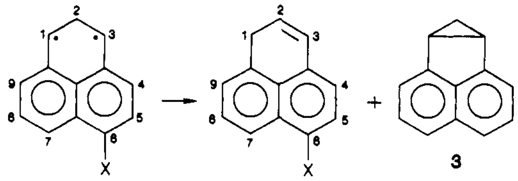
Jeffrey J. Fisher and Josef Michl*[1]

Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received October 10, 1986

We wish to report that below ~100 K the rearrangement[2] of the 1,3-perinaphthadiyl biradical (**1**) by 2,1-hydrogen shift to yield phenalene (**2**) proceeds at a temperature-independent rate, which we attribute to quantum mechanical tunneling from the triplet ground state[3,4] of **1** to the singlet ground state of **2**. Support for the spin-forbidden nature of the rate-determining tunneling step was obtained from external and internal heavy-atom effects on the observed first-order rate constant.

Since **1** is readily accessible by UV irradiation of the cyclopropane **3** in rigid matrices, has been well characterized by several spectroscopic techniques,[2-5] is already known[2] to undergo a thermally activated 2,1-hydrogen shift to **2** at 119–133 K (1-pentanol glass, $E_a = 4.5 \pm 0.6$ kcal/mol, $A = 10^{4.5\pm1}$ s^{-1}), and belongs to the class of 1,3-biradicals whose properties and reactivity are of considerable current interest,[6] we have investigated the kinetics of the dark decay of **1** in solid polyethylene at 10–160 K. Depending on temperature and isotopic substitution,[4] the products are **2** and/or **3**. The observed rate of formation of **3** does not obey simple first-order kinetics and can be understood in terms of site effects.[7] On the other hand, the formation of **2**, which involves a much smaller geometrical change, follows the first-order law accurately over at least three half-lives and presently we consider only conditions under which **2** is the sole product.



3

1, X = H
6-Br-**1**, X = Br

2, X = H
6-Br-**2**, X = Br

The Arrhenius plot for the reaction **1** → **2** (Figure 1) consists of a short linear segment above ~120 K ($E_a = 5.3 \pm 1.0$ kcal/mol, $A = 10^{5.1\pm1.0}$ s^{-1}) and a temperature-independent segment below ~100 K ($E_a = 0.0 \pm 0.1$ kcal/mol, $A = k = 10^{-6.1\pm0.5}$ s^{-1}). This suggests that tunneling from the ground triplet state of **1** into the ground singlet state of **2** dominates the reaction rate in the low-temperature limit. Indeed, at these temperatures the rate constant for the rearrangement of **1**-*2,2-d₂* is $k = 10^{-9.2\pm0.5}$ s^{-1}, a deuterium kinetic isotope effect of 1300.

Direct evidence for the spin-forbidden nature of the rate-determining step was obtained by varying the atomic number of the surrounding solid solvent atoms (Table I).[8] To our knowledge,

---

[1] New address: Department of Chemistry, University of Texas at Austin, Austin, TX 78712-1167.

[2] Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629.

[3] Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

[4] Fisher, J. J.; Penn, J. H.; Döhnert, D.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 1715.

[5] Cofino, W. P.; van Dam, S. M.; Kamminga, D. A.; Hoornweg, G. Ph.; Gooijer, C.; MacLean, C.; Velthorst, N. H. *Spectrochim. Acta, Part A* **1984**, *40A*, 219.

[6] Buchwalter, S.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. Dowd, P.; Chow, M. *J. Am. Chem. Soc.* **1977**, *99*, 6483. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Lazzara, M. G.; Harrison, J. J.; Rule, M.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 2233. Jain, R.; Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7294. Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774. Mizuno, K.; Ichinose, N.; Otsuji, Y.; Caldwell, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 5797. Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 299. Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 2788.

[7] Fisher, J. J.; Penn, J. H.; Döhnert, D.; Michl, J., unpublished results.

0002-7863/87/1509-0583$01.50/0