Sonoluminescence from Metal Carbonyls

Kenneth S. Suslick,* Edward B. Flint, Mark W. Grinstaff, and Kathleen A. Kemper

School of Chemical Sciences, University of Illinois at Urbana-Champaign, 505 S. Mathews Avenue, Urbana, Illinois 61801

Received: February 9, 1993

Spectrally resolved sonoluminescence is observed from the ultrasonic irradiation of organometallic compounds in silicone oil solutions. Specifically, ultrasonic irradiation of solutions of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ produces atomic line emission from metal atom excited states. The intensity of this sonoluminescence is the highest yet observed. Sonoluminescence arises from acoustic cavitation (the formation, growth, and implosive collapse of bubbles), which produces localized hot spots with extreme temperatures and pressures and very short lifetimes. The mechanism proposed for this observed sonoluminescence invokes the extreme temperatures created during acoustic cavitation to strip carbon monoxide from the metal complexes and to thermally populate electronic excited states of the metal atoms.

Sonoluminescence, the light emitted during ultrasonic irradiation of liquids, was first observed for water[1] in 1934 and for organic liquids[2] in 1937. The sonoluminescence of aqueous solutions has been well explored since that time.[3] It is only recently, however, that the first spectrally resolved sonoluminescence spectra from nonaqueous liquids were reported.[4–6] We now describe the first observed sonoluminescence from the ultrasonic irradiation of organometallic compounds. Specifically, ultrasonic irradiation of $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in silicone oil produces atomic line emission from excited-state Fe, Cr, Mo, and W atoms, respectively.

The sonochemical reactions associated with the ultrasonic irradiation of metal carbonyl solutions are quite diverse. Cluster formation,[7] ligand substitution,[7–9] alkene isomerization,[7] and amorphous metal powder formation reactions[10] all have been observed, and the parameters which control these reactions have been well established. The mechanism responsible for these observed reactions is acoustic cavitation: the formation, growth, and implosive collapse of bubbles in liquids.[11,12] Acoustic cavitation concentrates the low density energy associated with sound waves into a form which can drive chemical reactions. The temperature reached during acoustic cavitation has been experimentally determined by chemical rate thermometry to be 5200 ± 650 K, at 20 kHz under Ar with a solvent vapor pressure of 5 Torr.[8] Flint and Suslick have recently also determined the emission temperature of excited-state C_2 to be 5075 ± 156 K during cavitation of silicone oil.[6]

As shown in Figures 1 and 2, the atomic emission lines[13] for chromium, iron, molybdenum, and tungsten are seen during ultrasonic irradiation[14] of $Cr(CO)_6$, $Fe(CO)_5$, $Mo(CO)_6$, and $W(CO)_6$, respectively. Atomic emission lines have also been reported from metal carbonyls with other high-energy excitation methods such as laser irradiation,[15] argon plasmas,[16] graphite furnaces,[17] flames,[18] and shock waves.[19] In Figure 1, low-resolution sonoluminescence spectra of the visible region are shown for $Cr(CO)_6$ and $Fe(CO)_5$. For comparison, the metal atomic emission spectra from hollow cathode lamps are also shown in the higher-resolution spectra of Figure 2. The individual atomic emission lines are resolved for Cr at 425.4 nm ($4p^1z^7P_4^0 \rightarrow 4s^1a^7S_3$), 427.5 nm ($4p^1z^7P_3^0 \rightarrow 4s^1a^7S_3$), and 429.0 nm ($4p^1z^7P_2^0 \rightarrow 4s^1a^7S_3$); for Fe at 372.0 nm ($3d^64s^14p^1z^5F_5^0 \rightarrow 3d^6$-$4s^2a^5D_4$), 373.5 nm ($3d^74p^1y^5F_5^0 \rightarrow 3d^74s^1a^5F_5$), 373.7 nm ($3d^64s^14p^1z^5F_4^0 \rightarrow 3d^64s^2a^5D_3$), 375.0 nm ($3d^74p^1y^5F_4^0 \rightarrow 3d^7$-$4s^1a^5F_4$), 375.8 nm ($3d^74p^1y^5F_3^0 \rightarrow 3d^74s^1a^5F_3$), 382.0 nm ($3d^74p^1y^5D_5^0 \rightarrow 3d^74s^1a^5F_5$), and 386.0 nm ($3d^64s^14p^1z^5D_4^0 \rightarrow 3d^64s^2a^5D_4$); for Mo at 379.8 nm ($4d^55p^1z^7P_4^0 \rightarrow 4d^55s^1a^7S_3$),
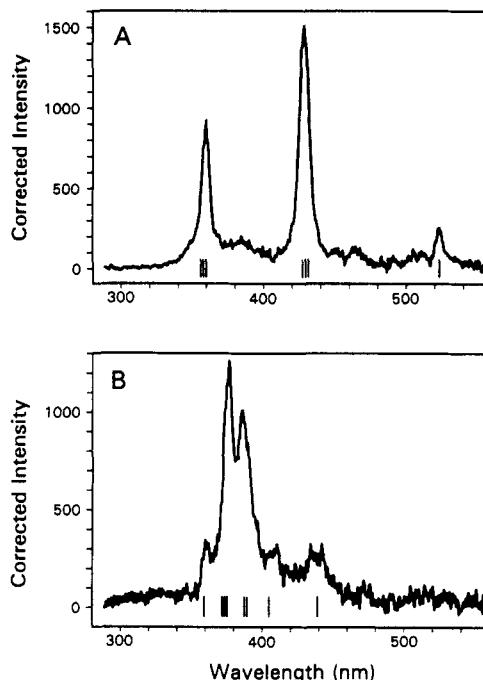
Figure 1. Low-resolution sonoluminescence spectrum from the ultrasonic irradiation of metal carbonyls. (A) 0.01 M $Cr(CO)_6$ in dodecane at a cell temperature of 16 °C. (B) 0.01 M $Fe(CO)_5$ in dodecane at a cell temperature of 5 °C. Vertical lines mark the known positions of the most intense atomic emission lines of chromium and iron. The spectrograph resolution was 2 nm. Spectra have been corrected for self-absorption from the metal carbonyls and for background sonoluminescence from the dodecane solvent.

386.4 nm ($4d^55p^1z^7P_3^0 \rightarrow 4d^55s^1a^7S_3$), and 390.3 nm ($4d^55p^1z^7P_2^0 \rightarrow 4d^55s^1a^7S_3$); and for W at 400.9 nm ($5d^56p^1z^7P_4^0 \rightarrow 5d^56s^1a^7S_3$), 407.4 nm ($5d^56p^1z^7P_3^0 \rightarrow 5d^5$-$6s^1a^7S_3$), and 429.5 nm ($5d^56p^1z^7P_2^0 \rightarrow 5d^56s^1a^7S_3$).

The high temperatures created during cavitation thermally populate the excited states of the metal atoms. These excited-state metal atoms are probably formed in a two-step process: an initial ligand dissociation (eq 1) followed by thermal excitation to the excited state (eq 2) through collisional activation with a

$$M(CO)_x \rightarrow M + xCO \qquad (1)$$

$$M + Z \rightarrow M^* + Z \qquad (2)$$
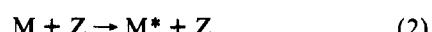
third body (e.g., Z = Ar, solvent vapor, CO, or $M(CO)_x$). A less
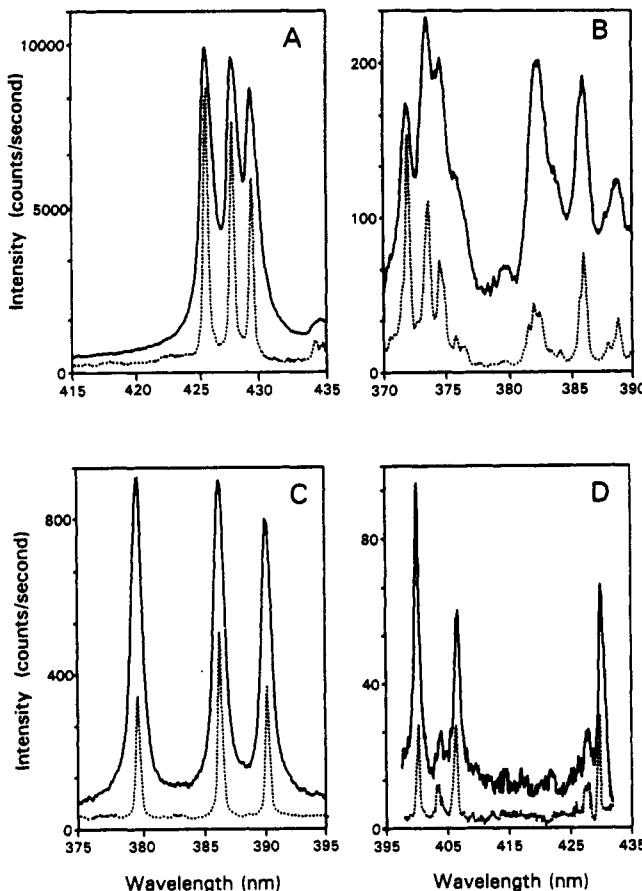
Figure 2. Sonoluminescence spectrum from the ultrasonic irradiation of 0.0025 M solutions of metal carbonyls in silicone oil. The same metal atom emission from a hollow cathode lamp is shown as a dotted line. (A) $Cr(CO)_6$, (B) $Fe(CO)_5$, (C) $Mo(CO)_6$, and (D) $W(CO)_6$. Solution temperatures were 70 °C for (A), (B), and (C) and 80 °C for (D). Under the conditions used in this study, no emission above background was observed from the silicone oil (Dow-Corning 200 Fluid, molecular weight ≈5000). Spectrograph resolution was 0.4 nm.

likely scenario would produce the excited-state metal atom directly from the organometallic precursor. After the cavitation event, the metal atoms coalesce and form an amorphous powder.[10]

In Figure 2 (and confirmed in other very high-resolution spectra not shown), one may note that the sonoluminescence line widths are quite broad compared to typical gas-phase spectra. Assuming that the broadening is homogeneous, the large line width of the metal emission is probably the result of the short excited-state lifetimes from collisional deactivation (i.e., pressure broadening). Consistent with this, Putterman and co-workers[20] have recently reported that the emission lifetime of sonoluminescence from single cavitating bubbles in water is less than 50 ps, which is ≈100 times shorter than typical lifetimes of excited metal atoms in low-pressure argon plasmas.[16]

In addition, our sonoluminescence line widths were unaffected by changes in solvent vapor pressure (decane, dodecane, or silicone oil) or dissolved inert gas (Ar or He), both of which alter the pressure and temperature of the cavitation event.[3,11] From sonochemical studies of nonvolatile substrates, it has been shown that there are two reaction zones formed during acoustic cavitation:[8,21] first, a gas-phase hot spot, and second, an *initially* liquid region, presumably from the layer surrounding the cavitating bubble or possibly from liquid droplets thrown into the bubble by surface waves. There are two plausible explanations for the lack of variation in line width: either the excited-state emission is coming from the initially liquid reaction zone, or the emission of the excited state is *not* thermally equilibrated with the gas in the hot spot. Further work on analysis of the metal atom sonoluminescence line widths is in progress.

The emission spectra from $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are by far the most intense sonoluminescence that we have yet seen. In contrast, emission from solutions of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were too weak to be observed, in spite of their sonochemical ligand substitution reactions.[7,9] The observed relative intensities of emission from ultrasonic irradiation of the metal carbonyls (Cr > Mo > Fe > W ≫ Mn, Co) reflect a combination of factors. Among these are the intrinsic emissivity of the metal atoms, the relative vapor pressure of the metal carbonyl (i.e., its concentration in the cavitating bubble), the extent of self-absorption of the solution in the spectral region of the emission, and the sonochemical rates of production of the excited states. For example, the relative emission from Cr, Mo, and W excited states is due, at least in part, to the relative volatilities of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. On the other hand, self-absorption from $Fe(CO)_5$, even in very thin layer emission cells, strongly diminishes its apparent sonoluminescent intensity.

References and Notes

(1) Frenzel, H.; Schultes, H. *Z. Phys. Chem.* **1934**, *27B*, 421.

(2) Chambers, L. A. *J. Chem. Phys.* **1937**, *5*, 290.

(3) Verrall, R. E.; Sehgal, C. Sonoluminescence. In *Ultrasound: Its Chemical, Physical, and Biological Effects*, Suslick, K. S., Ed.; VCH: New York, 1988.

(4) (a) Suslick, K. S.; Flint, E. B. *Nature* **1987**, *10*, 553. (b) Flint, E. B.; Suslick, K. S. *J. Am. Chem. Soc.* **1989**, *111*, 6987.

(5) Flint, E. B.; Suslick, K. S. *J. Phys. Chem.* **1991**, *95*, 1484.

(6) (a) Flint, E. B.; Suslick, K. S. *Science* **1991**, *253*, 1397. (b) Jeffries, J. B.; Copeland, R. A.; Flint, E. B.; Suslick, K. S. *Science* **1992**, *256*, 248.

(7) (a) Suslick, K. S.; Goodale, J. W.; Wang, H. H.; Schubert, P. F. *J. Am. Chem. Soc.* **1983**, *105*, 5781. (b) Suslick, K. S.; Schubert, P. F.; Goodale, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 7324.

(8) (a) Suslick, K. S.; Cline, R. E., Jr.; Hammerton, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 5641. (b) Suslick, K. S.; Hammerton, D. A. *IEEE Ultrason. Symp. Proc.* **1985**, *4*, 1116. (c) Suslick, K. S.; Hammerton, D. A. *IEEE Trans. Ultrason. Ferroelec. Freq. Cont.* **1986**, *33*, 143.

(9) Suslick, K. S.; Schubert, P. F. *J. Am. Chem. Soc.* **1983**, *105*, 6042.

(10) (a) Suslick, K. S.; Choe, S. B.; Cichowlas, A. A.; Grinstaff, M. W. *Nature* **1991**, *353*, 414. (b) Grinstaff, M. W.; Cichowlas, A. A.; Choe, S. B.; Suslick, K. S. *Ultrasonics* **1992**, *30*, 168.

(11) (a) Suslick, K. S. *Science* **1990**, *247*, 1439. (b) Suslick, K. S. *Sci. Am.* **1989**, *260*, 80. (c) Suslick, K. S., Ed. *Ultrasound: Its Chemical, Physical, and Biological Effects*; VCH: New York, 1988. (d) Apfel, R. E. In *Ultrasonics*; Edmonds, P. D., Ed.; Academic Press: New York, 1981; pp 356–413. (e) Neppiras, E. A. *Phys. Rep.* **1980**, *61*, 159.

(12) (a) We note in passing that a new electrical theory has been proposed for sonochemical phenomena[12b] but that there remain experimental observations difficult to explain from electrical microdischarge.[12c] (b) Margulis, M. A. *Adv. Sonochem.* **1990**, *1*, 39. (c) Suslick, K. S.; Dokytcz, S. J.; Flint, E. B. *Ultrasonics* **1990**, *28*, 280.

(13) (a) Sugar, J.; Corliss, C. *J. Phys. Chem. Ref. Data* **1977**, *6*, 317. (b) Reader, J.; Sugar, J. *J. Phys. Chem. Ref. Data* **1975**, *4*, 353.

(14) Ultrasonic irradiation was accomplished with a titanium immersion horn (Heat Systems, Model W375) operating at 20 kHz and ≈85W/cm². Solutions were sparged with argon for 10 min prior to and during ultrasonic irradiation. The sonoluminescence spectra were collected with a Princeton Instruments IRY 512N diode array detector on a Thermo Jarrell-Ash MonoSpec-18 0.25-m spectrograph, as previously described.[4]

(15) (a) Jackson, R. L.; Tyndall, G. W. *Chemtronics* **1989**, *4*, 127. (b) Tyndall, G. W.; Jackson, R. L. *J. Chem. Phys.* **1988**, *89*, 1364. (c) Karny, Z.; Naaman, R.; Zare, R. N. *Chem. Phys. Lett.* **1978**, *59*, 33.

(16) (a) Wagatsuma, K.; Hirokawa, K. *Spectrochim. Acta* **1988**, *43B*, 831. (b) Long, G. L.; Bolton, J. S. *Spectrochim. Acta* **1987**, *42B*, 581. (c) Uchida, H.; Kosinski, M. A.; Omenetto, N.; Winefordner, J. D. *Spectrochim. Acta* **1984**, *39B*, 63.

(17) Baxter, D. C. *Spectrochim. Acta* **1988**, *43B*, 129.

(18) Watanabe, H.; Kendall, K. K. *Appl. Spectrosc.* **1958**, *9*, 132.

(19) Shackleford, W. L.; Penner, S. S. *J. Chem. Phys.* **1966**, *45*, 1816.

(20) Barber, B. P.; Hiller, R.; Arisaka, K.; Fetterman, H.; Putterman, S. *J. Acoust. Soc. Am.* **1992**, *91* (5), 3061.

(21) (a) Riesz, P.; Berdahl, D.; Christman, C. L. *Environ. Health Perspect.* **1985**, *64*, 233. (b) Henglein, A. *Ultrasonics* **1987**, *25*, 6.