Production of Metallo-Carbohedrenes in the Solid State

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Macroscopic quantities of the metallo-carbohedrenes Ti_8C_{12} and V_8C_{12} have been synthesized with an arc discharge technique. Mass spectroscopy of raw soot samples generated in both an alternating and direct current arc between two metal-graphite powder composite electrodes establishes that the titanium and vanadium analogs of the metallo-carbohedrenes have been produced. An estimated yield of ~1 percent is obtained, and significantly, the products are stable in air.

Recently, our group reported evidence for the existence of stable metal-carbon clusters of the stoichiometry M_8C_{12} (M = Ti, V, Zr, and Hf) (*1–3*), termed metallo-carbohedrenes (Met-Cars). A pentagonal dodecahedral structure of T_h symmetry, with eight equivalently bonded metal atoms, was proposed to account for the unusual stability of this class of molecular clusters. Further studies by our group provided evidence supporting the proposed structure when magic numbers in mass spectra corresponding to multicage Zr_mC_n clusters were observed (*4*). Subsequent investigations conducted by experimentalists (*5*) and theoreticians (*6*) have both reemphasized the unusual stability of these Met-Cars, as well as extended our knowledge about the range of metals capable of forming these species.

We have pursued a means by which to prepare macroscopic quantities of Met-Cars, as can be done for fullerenes (*7*). Met-Cars can be produced in the gas phase, not only by hydrocarbon-metal reactions in a plasma, but also from the supersonic expansion of laser-ablated titanium and graphite powders (*8*). We report the successful bulk production of Met-Cars in the solid state.

The production method relies on a modification of the common arc-discharge technique used in the production of fullerenes (*9*). Within the discharge reaction chamber, through which helium flows, an arc resulting in a plasma is generated at ~70 V ac between a sharpened cathode and the anode. As the electrodes are consumed, they are kept at a distance no greater than 4 mm and the current is typically ~20 A. However, we have also produced the Met-Cars by using dc voltages and higher currents. The 6-mm diameter metal-graphite composite electrodes are pressed in a hardened steel dye under a force approaching 20,000 pounds and are affixed to machined graphite holders by means of graphite cement (Dylon Industries, GC grade, Berea, Ohio). These are baked at 150°C for up to 4 hours prior to use. We have been successful in producing Met-Cars from composite electrodes over a range of compositions, with those richer in carbon yielding fullerenes as well. After the plasma is terminated, the deposited black soot is gently scraped off the cooled collecting surfaces of the vessel and stored in air.

A critical aspect in reporting our successful synthesis of Met-Cars is establishing the existence of macroscopic quantities in the solid state. Subsequent to removal from the reactor, a portion of the soot is packed into a boron nitride laser-desorption sample holder and analyzed by laser-desorption time-of-flight mass spectrometry (TOF-MS). Briefly, the method is as follows. A desorption laser (Nd:YAG laser, second harmonic, 532 nm), kept at a low power (<15 mJ per pulse), is focused to a spot size of approximately 1 mm in diameter onto the sample supported directly behind the TOF acceleration lens. After desorption, the potentials on the TOF lens are pulsed so that the desorbed ions are accelerated into a field-free region. The ions are subsequently collected by a multichannel plate detector and the signal is averaged and stored with a digital oscilloscope. Proper timing of the high-voltage pulses applied to the acceleration grids following laser desorption is critical. The spectrometer was calibrated by using various known samples containing C_{60} and C_{70}. The laser-desorption technique was found to be a sensitive analytical method. However, because all of the ions within the TOF lens are accelerated simultaneously, the method lends itself to only moderate resolution.

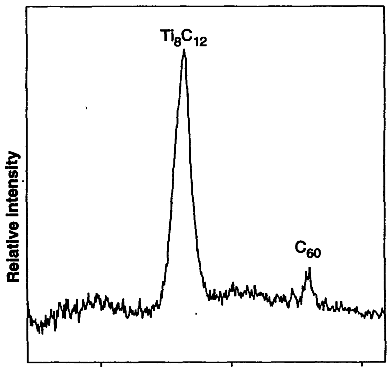

Fig. 1. Laser-desorption time-of-flight mass spectrum of soot generated in an arc between two composite Ti-C electrodes (5:1 metal to carbon mass ratio) in the mass range from 300 to 800 amu. The Met-Car Ti_8C_{12} and, to a lesser extent, C_{60}, are both present in the desorbed vapor.

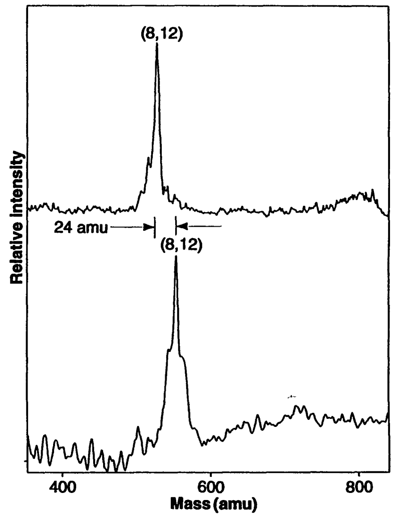

Fig. 2. Mass spectrum of laser-desorbed soot produced in an arc-discharge: top, Ti/C; and bottom, V/C. Note the 24-amu shift between Ti_8C_{12} and V_8C_{12}.

The result of the TOF-MS analysis of one sample of raw soot is shown in Fig. 1. This soot sample was produced from a discharge between titanium (−325 mesh, 99%, Aesar, Ward Hill, Massachusetts)–graphite (1 to 2 μm, Aldrich) composite electrodes and shows the presence of both Ti_8C_{12} and C_{60}. Although C_{60}, and less often C_{70}, are inconsistently present in our various soot samples in the low mass range (<150 amu), our spectra are consistently reproducible and display peaks assignable to the pure metal, metal oxides and metal-carbon species depending upon the system. The top mass spectrum in Fig. 2 is the 400- to 800-amu mass range of the soot produced in the manner described above. Significantly, in the mass range from 300 to 1500 amu, only one peak (528 amu) is observed, which corresponds to the parent peak of Ti_8C_{12}. In the expanded view of this spectrum (Fig. 3), the designated shoulders are at 504 amu and 516 amu, which correspond to the Ti_8C_{11} and Ti_8C_{10} fragments of Ti_8C_{12}.

In order to confirm our successful production of Met-Cars, we also generated a soot sample from vanadium (−325 mesh, 99.5%,

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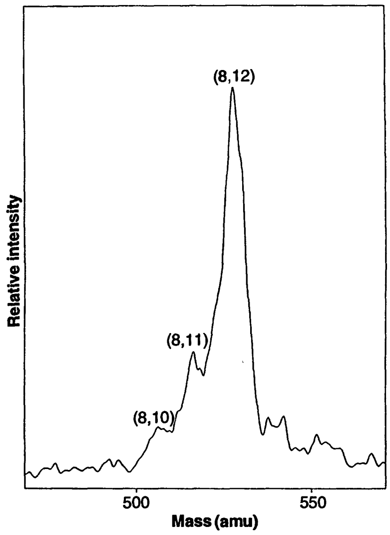

Fig. 3. Expanded view of Ti_8C_{12} spectrum shown in Fig. 2, top. The shoulders on the dominant Ti_8C_{12} peak are assignable as the fragments Ti_8C_{11} and Ti_8C_{10} produced during the desorption.

Aesar)–graphite composite electrodes and analyzed it in the same manner (Fig. 2, bottom spectrum). There is an obvious mass spectral shift of 24 amu from 528 to 552 amu, establishing the presence of the vanadium analog of V_8C_{12} in the sample. Moreover, we can assign the 540- and 564-amu species to V_8C_{11} and V_8C_{13}, respectively. These species are also observed in molecular beam studies of the vanadium derivatives of the Met-Cars (*3*, *10*).

These Met-Car–containing soot samples are stable in air. This finding is an important clue to the electronic nature of these clusters as well as an affirmation of their predicted stability. These soot samples are inhomogeneous and C_{60}, and to a lesser extent C_{70}, are, not surprisingly, commonly present in our soot. Because our soot samples are inhomogeneous, and oxidation of the soot does also sometimes occur, we do not detect Met-Cars in every sample analyzed from the same run. However, under favorable circumstances we can estimate our Met-Car abundance from the mass spectral data to be approximately 1%.

In considering the results of our analyses, we are aware that laser desorption can generate a range of products depending on the sample. However, we establish through the following arguments that we are actually desorbing Met-Cars from the raw soot. First, it is highly unlikely that we are producing M_8C_{12} (M = Ti, V) molecules within the sample with one laser pulse and desorbing them with subsequent pulses. The Met-Car signal is observed immediately (<ten laser shots) and the signal intensity thereafter decreases with time, neither of which would be expected if we produced Met-Cars in the soot sample with the desorption laser. Second, if the Met-Cars were generated during desorption via gas phase growth processes, we would expect to see their characteristic building pattern as is observed in the molecular beam experiments (*3*, *10*) and in the mass distribution of the laser desorption experiments of pure graphite samples in which fullerenes are produced (*11*). We see no evidence of these processes occurring during desorption. Additionally, as there are comparatively few collisions above the surface relative to the number of collisions in the plasma of either the laser vaporization source used in the gas phase experiments (*1*–*6*, *8*, *10*) or of the arc discharge used to produce the species in the present work. If either of these scenarios were the case, we would expect to see M_8C_{12} from a mixed sample of pure metal and graphite powders studied over a wide range of desorption laser powers; we have not seen any masses corresponding to Met-Cars in these test experiments. Similar tests were performed with baked titanium carbide with no indication that Met-Cars are formed by the desorption process. Third, we are certain that we are not merely fragmenting C_{60} to smaller fullerenes which have mass coincidences with Ti_8C_{12} (C_{44}) and V_8C_{12} (C_{46}). Besides the fact that no other fragments are observed, it is highly unlikely that C_{44} would be the most abundant fragment from the Ti/C soot with C_{46} then being the most abundant in the V/C soot. Finally, we observe the significant diminution of Met-Car abundance upon baking the soot samples, which is further evidence of their existence in the soot rather than being a product of the desorption process.

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Metastability of Superconducting Compounds in the Y-Ba-Cu-O System

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Precision isothermal solution calorimetry was used to determine the standard-state enthalpy of formation of a number of phases in the Y-Ba-Cu-O system. An analysis of the data indicates that $YBa_2Cu_4O_8$ is thermodynamically metastable under ambient conditions. Taken together with the results from previous investigations, these data show that all of the superconducting compounds in the Y-Ba-Cu-O system are thermodynamically metastable at low temperatures.

Since the discovery of the phenomenon of superconductivity in mercury at 4 K, by Onnes in 1911, researchers have attempted to synthesize superconducting materials with higher transition temperatures. Superconductivity in the temperature range from 1 to 23 K is observed in more than 1000 metal-metalloid compounds (*1*, *2*). However, superconductivity above the boiling point of liquid nitrogen (~77 K) is a recent observation and has been found in only a very small class of cuprate-based oxide superconductors. The

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