$Me_2C{=}CH_2$. Similarly, CMe_4 was observed in addition to $SiMe_4$ and $Me_2C{=}CH_2$ in the CVD of WC thin film from $(Me_3SiCH_2)_3W{\equiv}CCMe_3$, **3**. The unexpected presence of $SiMe_4$ and CMe_4 in the CVD from **2** and **3**, respectively, suggests the previously unobserved interconversion of alkyl and alkylidyne groups in $R_3W{\equiv}CR'$. A kinetic/mechanistic study in solution at 100 °C has demonstrated such an exchange and further that the hydrogen atom transfer occurs via an intramolecular mechanism.[15]

A crossover CVD experiment was performed with **1** and $(Me_3CCD_2)_3W{\equiv}CSiMe_3$, **2**-$d_6$. The precursors (1:1 ratio) were placed in two separate sample holders and vacuum transferred simultaneously to the deposition chamber. Mass spectral analysis of gaseous components collected during CVD showed a molecular ion peak of $Me_3SiCD_3^+$ (m/e = 91). No detection of ion peak corresponding to $Me_3SiCD_2H^+$ (m/e = 90) was observed above the isotopic purity of **2**-d_6 (>98% D). Lack of Me_3SiCD_2H in the gas phase is significant in two aspects. First, it shows that $SiMe_4$ production does not proceed significantly through γ-hydrogen elimination. Second, it indicates that unimolecular decomposition is the principal mechanism of tetramethylsilane production in the CVD process.

α-Elimination has been observed in the CVD of TiC thin film from $Ti(CH_2CMe_3)_4$.[16] Our results here are consistent with intramolecular α-elimination as the primary route of decomposition. Considering the alkyl/alkylidyne exchange, we propose the early steps in the CVD production of WC from precursor **2** shown in Scheme I.

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Registry No. $(Me_3CCH_2)_3W{\equiv}CCMe_3$, 68490-69-7; $(Me_3CCH_2)_3W{\equiv}SiMe_3$, 129960-83-4; WC, 12070-12-1.

Supplementary Material Available: Yields of hydrocarbon produced on thermal conversion to WC (1 page). Ordering information is given on any current masthead page.

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[14] Chisholm, M. H.; Huffman, J. C.; Klang, J. K. *Polyhedron* **1990**, *9*, 1271.

[15] Caulton, K. G.; Chisholm, M. H.; Xue, Z. submitted for publication.

[16] Rogers, D. M.; Jensen, J. A.; Girolami, G. S. to be submitted for publication.

Thermal and Oxidative Analyses of Buckminsterfullerene, C_{60}

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Recent developments in the preparation of the fullerene C_{60}[1,2] and discussions of its stability relative to other polycarbon molecules[3] have prompted us to examine its thermal and oxidative behavior. Haufler et al.[3] have proposed that the stability of the fullerene spheroid, relative to a graphitic structure, is due to the absence of dangling bonds typical of those formed along the edges of graphitic layers. This suggestion is consistent with semiempirical[4] and ab initio[5] calculations that conclude that the icosahedral C_{60} molecule is more thermodynamically stable than a graphitic structure. In addition, numerous studies of the kinetics and oxidation mechanism of synthetic graphite have shown that reaction occurs at the edges of layer nets where the atoms are least strongly bonded into the lattice.[6,7] We reasoned, therefore, that the absence of edges and dangling bonds in C_{60} would be expected to impart greater thermal and oxidative stability than is characteristic of graphite. Preliminary reports by Haufler et al.[2] indicate that C_{60} does burn in oxygen; however, to the best of our knowledge, a controlled combustion or oxidation study has not been done.

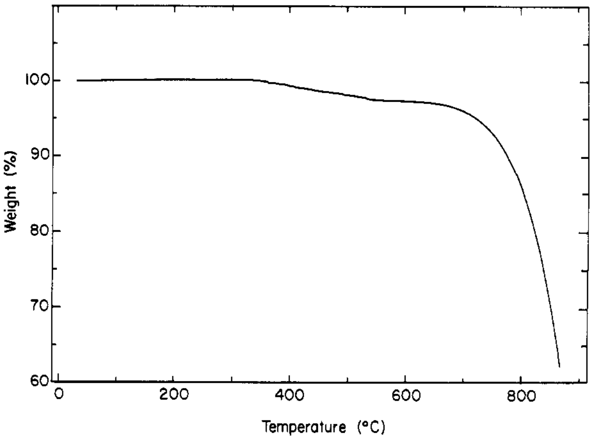

Figure 1. TGA of C_{60} heated at 10 °C/min to 860 °C under N_2 at a flow rate of 50 cm^3/min. Sample had been predried by heating at 300 °C for 0.5 h.

C_{60} was prepared and isolated following the procedures described by Haufler et al.[3] and Aije et al.[8] The C_{60}:C_{70} ratio was greater than 99:1 as determined by negative-ion chemical ionization mass spectrometry. Fisher Scientific G-67 Grade 38 graphite powder was used for comparative studies.

Thermal analyses were performed with a Du Pont Model 2100 thermal analysis system equipped with a thermogravimetric analyzer (TGA). We studied powdered samples (10–12 mg) in air and nitrogen atmospheres at a flow rate of 50 cm^3/min. Initially, samples were dried by heating under nitrogen to 300 °C at a rate of 20 °C/min and holding for 30 min. Subsequent treatment of C_{60} to 860 °C under nitrogen at a heating rate of 10 °C/min demonstrates loss of a volatile component between 300 and 600 °C corresponding to 3–5 wt % (Figure 1). In an effort to identify the volatile component, a sample of C_{60} heated

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[1] Krätschmer, W.; Lamb, L.D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

[2] Haufler, R. E.; Chai, Y.; Chibante, L. P. F.; Conceicao, J.; Jin, C.; Wang, L.; Maruyama, S.; Smalley, R. E. *Mater. Res. Soc. Symp. Proc.*, in press.

[3] Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

[4] Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469.

[5] Lüthi, H. P.; Almlöf, J. *J. Am. Chem. Soc.* **1987**, *135*, 357.

[6] Dawson, I. M.; Follett, E. A. C. *Proc. R. Soc. London, Ser. A* **1963**, *274*, 386.

[7] Walker, P. L.; Rusinko, F.; Rakszawski, J. F.; Ligget, L. M. *Proc. 3rd Conf. Carbon*; Pergamon Press: New York, 1959.

[8] Aije, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sensharma, K.; Whetten, R. L. *J. Phys. Chem.* **1990**, *94*, 8630.

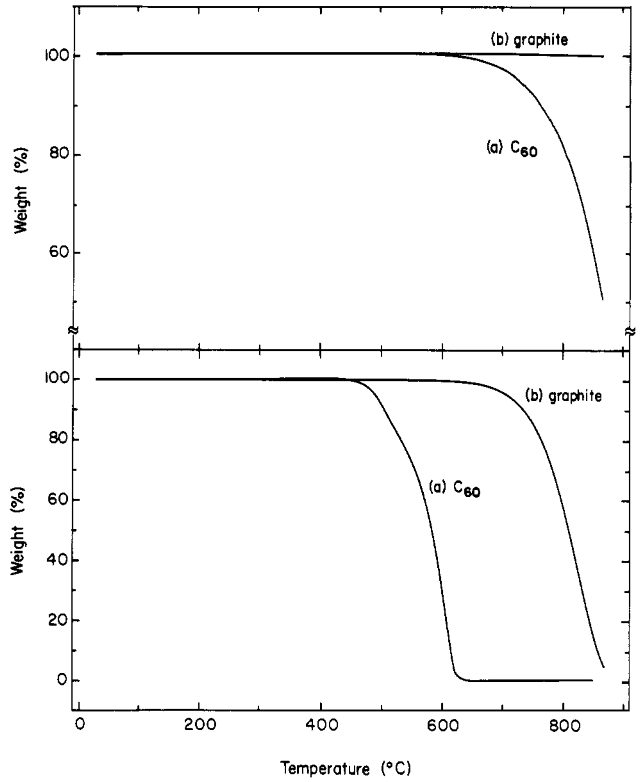

Figure 2. Top: TGA of (a) C_{60} and (b) graphite. Samples were heated at 10 °C/min to 860 °C under N_2 at a flow rate of 50 cm^3/min. C_{60} had been predried by heating at 210 °C for 16 h in a dynamic vacuum. Bottom: TGA of (a) C_{60} and (b) graphite. Samples were heated at 10 °C/min to 860 °C in air at a flow rate of 50 cm^3/min. C_{60} had been predried by heating at 210 °C for 16 h in a dynamic vacuum. A small effect from residual toluene can be observed.

in the TGA under nitrogen at 300 °C for 30 min was analyzed by using thermal desorption mass spectrometry. This analysis indicated the presence of appreciable amounts of toluene (m/z = 92 and 91, a prominent fragment ion) in the sample, suggesting that the volatile component observed in the TGA is toluene.

TGA studies were carried out to ascertain the heat treatment necessary for complete removal of toluene from the C_{60}. Surprisingly, the toluene was eliminated in a stepwise manner, as determined from heat treatments at various temperatures up to 600 °C. For example, when a sample of C_{60} was heated for 0.5 h at 350, 400, and 450 °C, the observed weight loss corresponded to approximately 1.0, 1.0, and 1.0%, respectively. Weight loss was rapid, occurring during the first 5 min at a particular temperature. To effectively remove all toluene, it was necessary to heat the sample at 600 °C for approximately 0.5 h. While attempting to prepare standard solutions of C_{60} that had been heated to 600 °C in the manner described above, we found that the material would no longer completely dissolve in toluene. This change in solubility suggested to us that some decomposition or transformation of C_{60} occurs when it is heated to 600 °C. To avoid this problem, toluene was removed by heating the C_{60} at 210 °C for 16 h in a dynamic vacuum. The C_{60} heated in this manner was completely soluble in toluene.

The thermal and oxidative properties of C_{60} predried to 210 °C in the manner described above were compared to those of graphite. Powdered samples of each were heated from 30 to 860 °C at 10 °C/min in nitrogen and air atmospheres at a flow rate of 50 cm^3/min. The upper panel of Figure 2 shows the thermal stability of C_{60} and graphite. When heated to 860 °C, graphite and C_{60} retain 100% and 40% of their weight, respectively. Moreover, C_{60} commenced to lose weight at ~600 °C. The lower panel of Figure 2 shows the comparative oxidative stability of C_{60} and graphite in air. When heated as described previously, a sample of C_{60} began to lose weight at ~480 °C with complete weight loss occurring at ~650 °C. Graphite commenced losing weight at ~700 °C and had lost 95% of its weight at 860 °C.

We presume that the weight loss observed when C_{60} is heated in nitrogen (Figure 2 upper panel) is due to sublimation. Krätschmer et al.[1] have reported that C_{60} sublimes in a vacuum at ~400 °C. Using Knudsen effusion mass spectrometric measurements, Pan et al.[9] have determined the heat of sublimation of C_{60} from a polycrystalline mixture of C_{60} and C_{70} to be 40.1 kcal/mol at the average temperature of 434 °C.

The TGA results presented in the lower panel of Figure 2 indicate that reaction of C_{60} with air does occur. If the weight loss of C_{60} in air were due to sublimation, the data should be identical with those observed in nitrogen. We conclude, therefore, that C_{60} is less stable than graphite powder when heated in air.

The tenacity of C_{60} for toluene was an unexpected observation. We expected complete degassing of toluene at 300 °C; however, TGA and mass spectral data suggest that toluene remains adsorbed at temperatures up to 600 °C. This behavior, however, is consistent with C_{60}–solvent interactions observed during crystal studies.[10] Two possible explanations for this solvent interaction come to mind: (1) toluene is a trapped impurity from the separation process and/or (2) some molecular interaction exists between C_{60} and toluene. In either case, the strong retention and stepwise elimination of toluene observed in the TGA suggests that different binding sites for toluene exist in C_{60}. We are continuing to investigate this phenomenon.

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Registry No. C_{60}, 99685-96-8; graphite, 7782-42-5; nitrogen, 7727-37-9; toluene, 108-88-3.

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(9) Pan, C.; Sampson, M. P.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem.*, in press.

(10) Fleming, R. M.; Siegrist, T.; Marsh, P. M.; Hessen, B.; Kortan, A. R.; Murphy, D. W.; Haddon, R. C.; Tycko, R.; Dabbagh, G.; Mujsce, A. M.; Kaplan, M. L.; Zahurak, S. M. *Mater. Res. Soc. Symp. Proc.*, in press.

Magnesium Methoxide Derived Catalysis of Transesterification, Hydrolysis, and Condensation of Si(OMe)$_4$ in the Sol–Gel Syntheses of Magnesium Silicates

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In recent work in our laboratories, the preparation of sol–gel precursors for synthetic forsterite, Mg_2SiO_4,[1] and enstatite, $MgSiO_3$,[2] were achieved by the H_2O_2-assisted

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(1) (a) Beeman, M.; Burlitch, J. M.; Kohlstedt, D. L. *Sol-Gel Routes to Olivine-Based Ceramic-Glass Composites*; 905th Annual Meeting of the Amer. Ceram. Soc., Cincinnati, OH, 1988; Abstract No. 159-B-88. (b) Burlitch, J. M.; Beeman, M. L.; Riley, B.; Kohlstedt, D. L., to be submitted for publication.

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