

Thermal Decomposition of Fullerene Mix Unimolecular Decomposition of ~~C₆₀/C₇₀ Mix~~

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Experiments to determine the cause of fullerene decomposition at temperatures above 973 K were conducted by spectroscopic analysis of samples heated in vacuo. Decay curves of solid fullerene samples display classic unimolecular decomposition character. The decay rates can be fit to an Arrhenius equation yielding an activation energy of 265.6 ± 8.9 kJ/mol and a pre-exponential factor of 1.24×10^9 s⁻¹. X-ray diffraction and Raman spectroscopy indicate that the heated samples are amorphous, though scanning electron micrographs display a distinctly crystalline appearance. Transmission electron microscopy shows that these "crystals" are composed of amorphous carbon, indicating that pyrolysis of the fullerenes without destroying crystal facets.

I. INTRODUCTION

Since fullerenes became available in macroscopic quantities in 1991, there have been numerous studies of the oxidative behavior of C₆₀ and C₇₀²⁻⁷. However, very few investigations of the thermal stability of fullerenes have been reported, particularly at temperatures above 973 K.

Frum et al.⁸ observed thermal degradation of C₆₀ heated to 1223 K while studying its infrared emission spectrum. Subsequent X-ray powder analysis of the remaining sample showed it to be amorphous carbon. Molecular dynamics simulations modeling the process of thermal disintegration of fullerenes have also been reported⁹. Thermal decay studies of gas phase C₆₀ made by examining the time-dependent spectral emission from fullerene heated in shock waves yielded an activation energy of 120 kJ/mol¹⁰. Kolodney et al.¹¹ used mass spectrometry to examine effusive molecular beams of C₆₀ heated up to 102000 K and identified an activation energy of 385.330 kJ/mol for thermal decomposition. In another experimental investigation by Sundar et al.,¹² X-ray diffraction and UV-visible absorption spectra of C₆₀ sealed in evacuated quartz ampoules and heated to temperatures between 773 K and 1173 K for 24 hours showed increasing degradation with higher temperature. However, such a study in which the decomposition is evaluated as a function of time had not been conducted,

11. EXPERIMENTAL PROCEDURE

Because of the large discrepancy in the reports of experimentally determined Arrhenius activation energies for thermal disintegration, we have performed decay measurements to determine the thermal stability of fullerene mix. We pursued a method similar to that of Sundar et al. Quartz ampoules were each filled with approximately 10 mg of fullerene powder. We prepared sets of 5 ampoules at a time, with fullerene extract containing C₆₀ and C₇₀ in a ratio of approximately 85% to 15%. The fullerene mix was Soxhlet extracted with toluene from soot produced by Ulvick industries. Pure C₆₀ from MER Corporation and pure C₇₀ from Term Ltd. were used as standards for compositional analysis.

The fullerene-containing ampoules were placed under dynamic vacuum in the mid 10⁻⁶ Torr range and heated to temperatures between 473 K and 523 K to eliminate solvent and hydrocarbon impurities. Partial pressures of monatomic and diatomic oxygen, CO, CO₂, OH, H₂O, toluene, and benzene were monitored using a MKS model 600A PPT Residual Gas Analyzer. The preheating of the samples lasted anywhere from 6 to 16 hours, depending upon the concentration of solvent impurities in the powder. Upon initial heating, there was a rapid and significant increase in toluene partial pressure, with moderate increases in O₂ and H₂O. C₆₀ epoxide may have been another source of the observed oxygen.

The ampoules were then vacuum sealed and placed in a tube furnace for durations of 5 minutes to 6 hours. We prepared sets of samples heated to 873 K, 973 K, 1073 K, 1098 K, 1123 K, 1148 K, 1173 K, and 1273 K. After removing the samples from the tube furnace, we noted that the fullerene powder had remained in a pile at one end of the ampoule with only a slight coating of soot on the walls. However, samples heated to 1273 K for a few minutes or to 1173 K for one hour formed a thick black coating on the entire inner surface of the ampoules.

11.1. RESULTS AND DISCUSSION

A. UV-VIS Absorption Spectroscopy

Analysis of the samples was performed by UV absorption spectroscopy using a Cary 5E UV-VIS-NIR spectrophotometer and an HPUV 8452A spectrometer. A 1.0 cm path length was used with blank solvent as the reference. The powder samples were placed in 200 ml of methylene chloride or toluene and sonicated. A further dilution of 1:10 was made for analysis. The concentration of C₆₀ and C₇₀ was determined by monitoring the 336 nm and 384 nm absorption features, respectively. The 270 nm peak of C₆₀ was also monitored in the methylene chloride dissolved samples, but was obscured by the strong absorption by toluene at this wavelength. The peak intensity was corrected for initial sample weight, then correlated to remaining fullerene material.

Significant quantities of seemingly insoluble material were observed in the methylene chloride solutions after sonicating for several hours. The solubility of C₆₀ in methylene chloride has been reported¹³ as 0.26 mg/ml. However, we found that some of the residual solid was soluble in toluene. Subsequently, all remaining samples were analyzed in toluene. The main sources of error were the reproducibility of dilution preparation and inhomogeneity of the fullerene mix. Compositional analysis showed that samples varied in C₆₀ composition by as much as 10%. Although we were not able to quantitatively analyze the change in relative concentrations of C₆₀ and C₇₀ due to

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initial sample variation, qualitatively, it appeared that the C₇₀ decomposed at a slower rate than the C₆₀. The amount of higher fullerenes (C_n for n > 70) contained in the samples was not determined.

Figure 1 shows the UV absorption spectrum of mixed fullerene samples heated at 1073 K for 20, 60, 180, and 360 minutes. The solutions were prepared with methylene chloride. Figure 2 shows the degradation rate of the toluene dissolved samples. These curves display purely deceleratory behavior and are typical for unimolecular decay¹⁴.

By fitting the fullerene decay curves shown in Figure 2 to an exponential function, we obtained decay constants, $k(T)$, which were then used to find an Arrhenius plot for the decay via the equations:

$$\ln(k) = \ln(a) + m \ln(T) - \frac{E}{RT}$$

$$E_a = E + mRT$$

$$A = aT^m e^m$$

where E and a are constants, A is the pre-exponential (frequency) factor, E_a is the activation energy, R is the gas constant, and T is the temperature. The exponential temperature dependence, m , was assigned values between 0.0 and 1.5 without significantly varying E_a . Figure 3 shows the Arrhenius plot of the data with the $m=0$ (linear) curve fit. The Arrhenius activation energy was found to be 265.6 ± 8.9 kJ/mol. The pre-exponential factor was 1.24×10^9 s⁻¹.

This activation energy is more than twice as high as the 120 kJ/mol, and approximately 30 percent smaller than the 385.3 kJ/mol previously reported for the thermal decomposition of pure C₆₀ in the gas phase^{10,11}. In exploring this discrepancy, we plotted the published data along with our own. The plot is shown in Figure 4. It is evident that combining our data with that which has been reported previously yields a better picture of the thermal decay behavior of fullerenes due to the large temperature range. Curve fits to the combined data give an activation energy which ranges from 223 kJ/mol to 280 kJ/mol, depending upon which data sets are included in the fit. It should be noted that we have not accounted for possible differences in the data sets due to the presence of C₇₀ in our experiment. Further, we have not determined whether a kinetic compensation effect¹⁵ may be applicable to this system.

The frequency factor is related to the entropy of activation for a reaction. For unimolecular decay, it is typically 10^7 to 10^{14} s⁻¹ for simple molecules, yet it is 4 to 5 orders of magnitude smaller here. However, because of the many possible ways for energy to be distributed among the degrees of freedom in a C₆₀ molecule, it is reasonable to expect that the probability of the molecule achieving the transition state is low, resulting in a smaller reaction rate.

In addition to reconciling our results with prior experimental findings, we sought to compare a thermal disintegration temperature like that defined by B. I. Zhang et al.⁹ with our data. Zhang et al. used a molecular dynamics simulation with velocity scaling for temperature control. They heated a C₆₀ molecule at a rate of 3.57×10^{14} K/s and then at 0.7×10^4 K/s when the molecule neared dissociation. Therefore, the timescale for the onset of bond-breaking at 5500 K in C₆₀ was on the order of tens of picoseconds. However, all of the experimental results described here show that breakdown occurs on the order of microseconds at 5500 K - much longer than the time observed by Zhang et al, necessary for disintegration.

The problem may also be illustrated by finding a rate equation for C , the amount of material present:

$$\frac{dC}{dt} = ae^{mT} e^{(-\frac{E_a}{RT})} C$$

and finding C in terms of the exponential integral $E_n(x)$:

$$\ln\left(\frac{C}{C_0}\right) = ae^m \int_0^t T^m e^{(-\frac{E_a}{RT})} dt$$

$$\ln\left(\frac{C(T)}{C_0}\right) = -\frac{a}{b} e^m \int_{T_1}^{Tf} T^m e^{(-\frac{E_a}{RT})} dT$$

allowing the temperature to scale as a function of time, $T=bt$ and setting $u = T/Tf$, we get

$$\ln\left(\frac{C}{C_0}\right) = -\frac{a}{b} e^m T_f^{m+1} \int_1^{\infty} \frac{e^{(-ku)}}{u^{m+2}} du$$

where $k = E_a/RT_f$. With $m=0$, the expression becomes

$$\ln\left(\frac{C}{C_0}\right) = -\frac{a}{b} T_f E_2\left(\frac{E_a}{RT_f}\right)$$

when C/C_0 is on the order of $1/e$, we obtain the transcendental equation:

$$\frac{b}{aT_f} = E_2\left(\frac{E_a}{RT_f}\right)$$

Using the value of 3.57×10^{14} K/s for b would indeed yield a thermal disintegration temperature, T_f , of approximately 5500 K if a were on the order of 10^{13} s⁻¹. However, we have shown experimentally that a is at least four orders of magnitude smaller than this.

B. Diffuse Reflectance FTIR Spectroscopy

To verify that the observed decomposition was not a result of catalysis with impurities, diffuse reflectance Fourier Transform Infrared spectroscopy was also used to analyze the (ic.composed material. Figure 5(a,b,c) shows three spectra: (a) untreated fullerene mix, (b) a sample heated to 1073 K in vacuum for 1 hour, and (c) a sample heated for 18 hours at 523 K in nitrogen and air. Note the appearance of cyclic anhydride features in the 1800-1000

cm^{-1} region of Figure 5(c) similar to those reported elsewhere.³ However, no oxidation products are evident in the 1073 K sample, although only 50% of the material remained as fullerene. Small amounts of hydrocarbon impurities are evident in all of the samples. Also, there is a possibility that at these temperatures, any intermediate compounds will have decomposed, leaving only CO_2 and CO as reaction products and catalysts. We have not attempted to determine whether these gases are present in the sealed ampoules after heating.

C. Microscopy

Samples that had been heated to temperatures greater than 1273 K were completely insoluble in toluene. This material was examined with an X-ray diffractometer, which showed no diffraction peaks. Raman spectroscopy also failed to show evidence of an ordered structure. Although all indications were that the fullerenes had decomposed into amorphous carbon, the material appeared distinctly crystalline. Scanning-electron-microscope images of this material are shown in Figure 6(a,b). A selected area diffraction pattern of one of the "crystals" in a Phillips 301 transmission electron microscope produced only rings (Figure 7) from graphite polycrystals. Figure 8 is a bright field image of the "crystal". Note the granularity of the constituent carbon. The fullerite appears to have pyrolyzed without destroying the crystal shape.

IV. CONCLUSIONS

We have found an activation energy of 265.6 ± 8.9 kJ/mol for the thermal decomposition of a fullerene mix. This result is consistent with the previously published experimental data. SEM images of the decomposed sample show a crystalline structure, though X-ray diffraction, Raman spectroscopy, and TEM all show that the material is amorphous. Diffuse reflectance FTIR spectroscopy does not detect the presence of intermediate compounds. The integrity of the fullerite crystal shape after decomposition makes it unlikely that the reaction mechanism is catalysis with impurities or quartz surfaces. The decay curves of the fullerene are purely deceleratory. Hence, we attribute the degradation to solid state unimolecular decay.

This result makes the existence of a liquid phase of C_{60} ^{16,17} highly unlikely. It also places bounds on the range of operating temperatures of fullerene vapor sources and ionization techniques for producing fullerene plasmas.

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Figure 1. UV-VIS absorption spectrum of mixed fullerene samples heated at 1073 K for 20, 60, 180, and 360 minutes. The solutions were prepared with methylene chloride.

Figure 2. Degradation rate of the toluene dissolved samples heated to 1098 K, 1123 K, 1148 K, and 1173 K. Data points are experiments, lines are exponential curve fits.

Figure 3. Arrhenius plot of the thermal decay of a fullerene mix.

Figure 4. Arrhenius plot of fullerene thermal decay with data from the present study and from von Gersum et al.¹⁰

Figure 5. Diffuse Reflectance FTIR spectra of fullerene mix (a) heated to 523 K for 12 hours under vacuum, (b) heated to 1073 K for 1 hour under vacuum, and (c) heated for 18 hours in nitrogen and air.

Figure 6. SEM micrographs of carbon powder obtained from heating mixed fullerenes to 1273 K for one hour (a), (b).

Figure 7. Diffraction pattern of decomposed fullerene material showing rings attributed to graphite polycrystals.

Figure 8. Bright-field TEM micrograph of a decomposed fullerite "crystal",









