

SOME APPLICATIONS OF THERMAL ANALYSIS TO FULLERENES

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Thermal analysis is a convenient means of characterizing the soot used as a source of the carbon clusters, the extracted mixture of fullerenes, and the individual clusters themselves. TG in an inert atmosphere will rapidly assay the volatile fractions, presumably the lower molecular weight clusters. TG in oxygen indicates – a slight weight gain for the soots and clusters prior to their combustion.

DSC in oxygen is used to determine the heat of combustion for the separated C₆₀ and C₇₀ materials. The combustion occurs around 300°C for the clusters. There is a small exothermic peak before this which is attributed to the oxidation associated with the slight weight gain. The heats of combustion measured are –18.7 and –21.0 kJ·mol⁻¹ for the C₆₀ and C₇₀ respectively.

MS-EGA indicates the loss of small amounts of water and argon at temperatures around 250°C in vacuum and of solvent at about 350°C prior to sublimation.

Keywords: fullerenes, heat of combustion for C₆₀ and C₇₀

Introduction

Tremendous interest has been generated in the carbon clusters based on the soccer ball style cage-like structures. These materials, commonly referred to as ‘fullerenes’, form a significant fraction (5–20%) of the carbon soot generated from the electrical arcing between graphite rods in a reduced pressure of Ar [1]. The fullerenes are separated from the soot by sublimation in an inert atmosphere or extraction with various organic solvents, e.g., benzene, toluene, etc. The individual clusters are then separated from each other via chromatography [2].

Mass spectroscopic examination of various chromatographic fractions revealed the presence of many other fullerenes beyond the major components, C₆₀

and C₇₀ [3]. Trichlorobenzene proved superior at extracting both more and a wider range of fullerenes from the soot. It appears [2, 3] that there is approximately 16 wt% of lower molecular weight fullerenes, which are very predominantly C₆₀ and C₇₀, and 2% of higher molecular weight fullerenes, C₉₈ to C₂₁₂. One other very interesting extractable species that has been observed [3, 4] is C₇₀O.

Results and discussion

Thermogravimetry (TG)

One of the major contributions of TG is to assay the potential yield of fullerenes in the various sources of soot. Figure 1 shows TG curves, taken at 20 deg·min⁻¹ in flowing Ar that has been gettered with hot Ti, for graphite and two sources of soot. The graphite is stable to above 1200°C in this atmosphere. The lower fullerenes are volatile in the 600° to 800°C range and the higher fullerenes become volatile at about a 1000°C. Clearly the soot, S1, made 'in house' has a higher content of the lower fullerenes than the commercial sample, S2. A

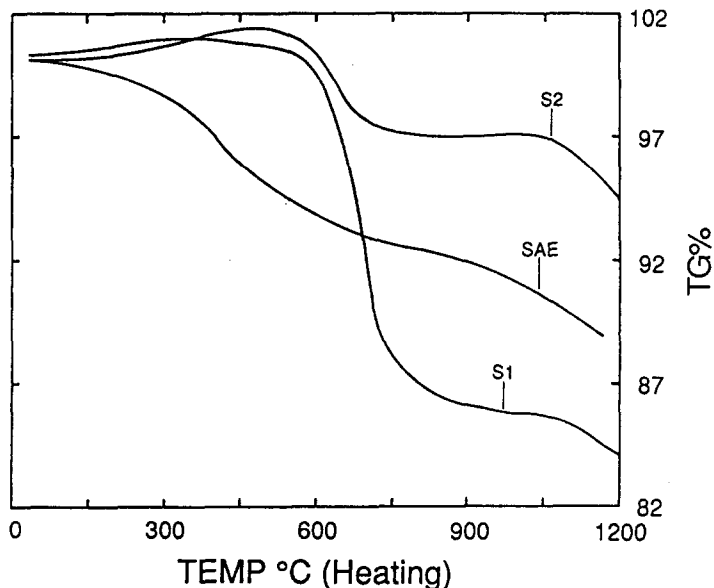


Fig. 1 TG curves in gettered flowing (100 ml·min⁻¹) Ar at 20 deg·min⁻¹ for two sources of soot. a) S1, prepared at OSU by Dr. James V. Coe, *et al.* b) S2, purchased from Texas Fullerenes, Inc. c) S1, after extraction with benzene

value of 15 wt% is typical of the reported values. The sample after extraction shows less weight loss but indicates that the initial extraction procedure was incomplete.

Milliken *et al.* [5], report TG data for C₆₀ in flowing N₂ and air. They indicate the onset of weight loss in N₂ at a heating rate of 10 deg·min⁻¹ is about 600°C. This seems consistent with the sublimation conditions proposed [1] for separation of >400°C in vacuum for some length of time. The most interesting aspect of TG results is that 4–5 wt% are lost in the temperature region of 400° to 600°C prior to sublimation. It was suggested [5] that this weight loss is due to tenaciously held solvent, toluene, which does not desorb until 400° C and above. Such adducts can be formed, however, it is claimed that the presence of a catalyst, e.g., FeCl₃ or Br₂, is required during digestion with the solvent [6].

From the data of Milikan *et al.* [5], the onset of weight loss in air is about 400°C. This is approximately 200°C lower the onset of weight loss for graphite. The combustion process for C₆₀ was complete by 600°C. The rate of the combustion process, however, is highly dependent on the surface area and the accessibility of the oxygen to the carbon surface. Great variability, therefore, is to be expected from one investigation to the next.

The mixed C₆₀ and C₇₀ fraction from the OSU soot, S1, extracted with benzene was heated at 20 deg·min⁻¹ in gettered Ar and oxygen. The TG curves are presented in Fig. 2. There is a loss of several wt% in Ar below 600°C consistent

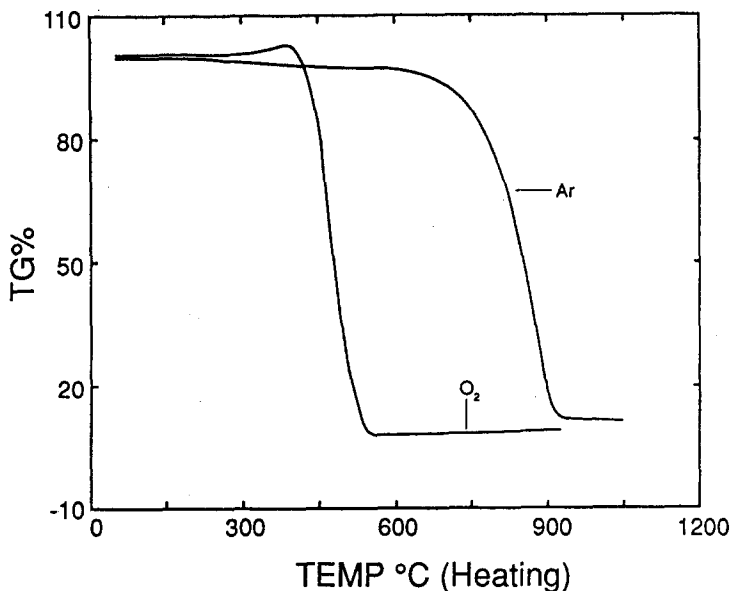


Fig. 2 TG curves at 20 deg·min⁻¹ of a solid isolated from the benzene extract of the OSU soot (S1). a) In flowing (100 ml·min⁻¹) gettered Ar. b) In flowing (100 ml·min⁻¹) O₂

with Milliken *et al.* [5]. Unfortunately, the sample size was only 1.0 mg so that passing the exhaust into a heated FTIR cell was not sufficiently sensitive to determine the volatile species during any portion of the experiment. MS-EGA results are presented later which help to clarify the low temperature weight loss.

The combustion of the mixed sample in oxygen is interesting in that the small initial weight might be due to the formation of some oxides, such as the $C_{70}O$ described earlier [3, 4]. The combustion process begins around 400°C for this sample under these experimental conditions. This is at a somewhat lower temperature than that observed by Milliken *et al.* [5], in air.

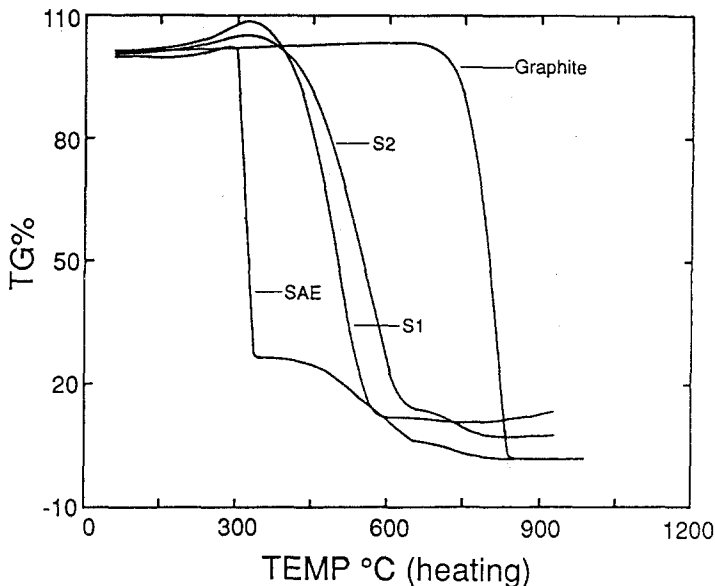


Fig. 3 TG curves at 20 deg·min⁻¹ in flowing (100 ml·min⁻¹) O₂. a) Graphite b) S1, Soot, OSU, J. V. Coe, *et al.* c) S2, Soot, Texas Fullerenes, Inc. d) S1, after extraction with

Combustion of the raw materials is compared with graphite and a soot after extraction in Fig. 3. Graphite is clearly the most stable of the materials with respect to oxidation. The two soots behave similarly and also reveal the small weight gain attributed to formation of a solid oxide prior to the combustion. The soot after extraction is surprisingly reactive, presumably due either to an enhanced surface area and porosity or residual solvent.

Evolved Gas Analysis (EGA)

Samples of both soots and separated C_{60} and C_{70} materials, chromatographically isolated [7] from the extract of the OSU soot, were heated to 1000°C in an MS-EGA apparatus [8, 9] under vacuum, 10^{-6} Torr, at 20 deg·min⁻¹. In our earlier

results [10] on an unseparated extract, only water vapor was detected by the quadrupole MS up to 150 Daltons. Curves for C_{60} are presented in Fig. 4. There is in-

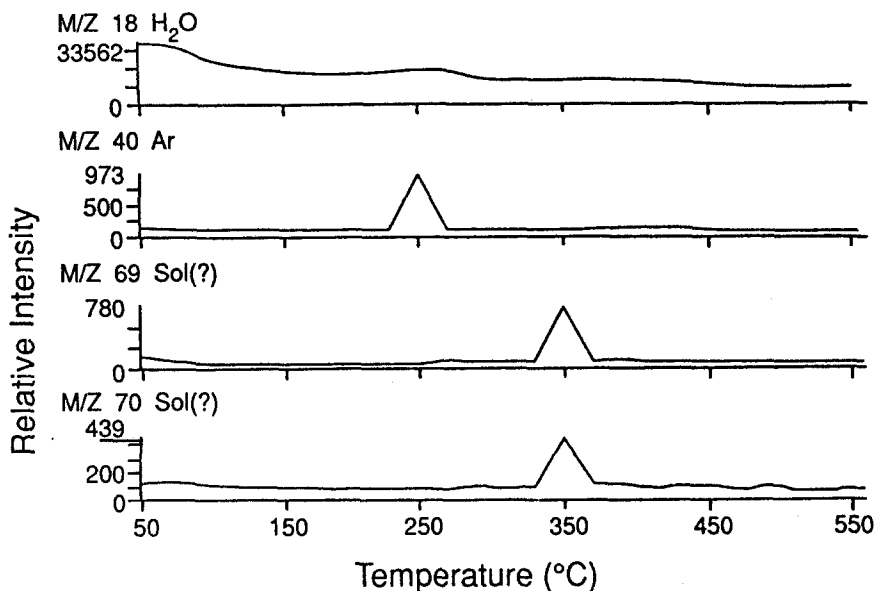


Fig. 4 MS-EGA curve of water for C_{60} extracted from S1 heated in vacuum at $20 \text{ deg}\cdot\text{min}^{-1}$

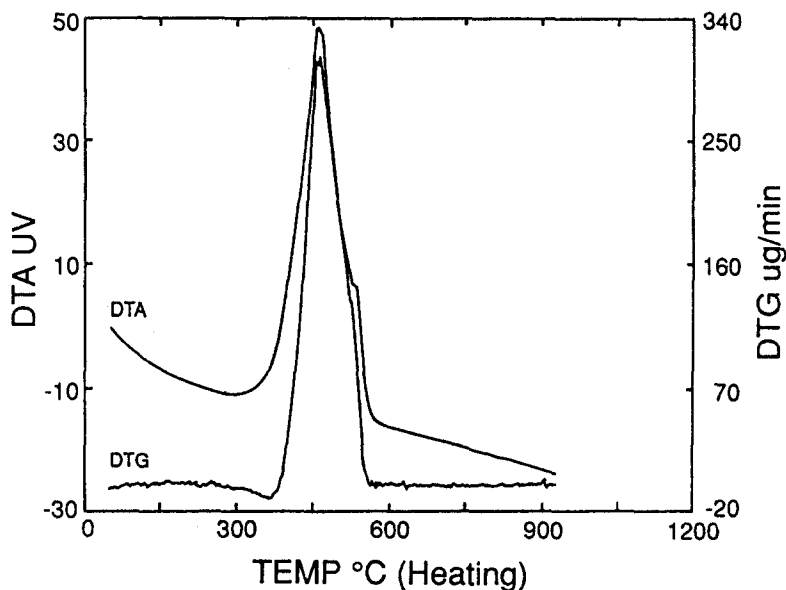


Fig. 5 Simultaneous DTG and DTA curves for the extracted material heated in flowing ($100 \text{ ml}\cdot\text{min}^{-1}$) oxygen at $20 \text{ deg}\cdot\text{min}^{-1}$

dication of water and argon around 250°C. Around 350°C there are peaks in the 65 to 105 range indicative of some residual solvent. Similar results were observed for C₇₀ except that the temperature ranges were about 100°C lower. Further work is underway on these materials.

Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)

The TG experiments in the previous section were performed by simultaneous TG/DTA using a Seiko, Model 5200 instrument. The TG curve for the oxidation of the C₆₀-C₇₀ mixture shown in Fig. 2 was very closely paralleled by the exothermic DTA signal. The very close correspondence of the differential TG (DTG) curve and the DTA curve is indicated in Fig. 5. There is a clear indication of overlapping events, presumably the separate oxidation of the C₆₀ and C₇₀.

This difference in oxidation rates offers another opportunity to assay the soots in advance for their contents of fullerenes. To more closely examine this possibility, the soots were examined by DSC and compared with graphite. The DSC curves determined in oxygen are shown in Fig. 6.

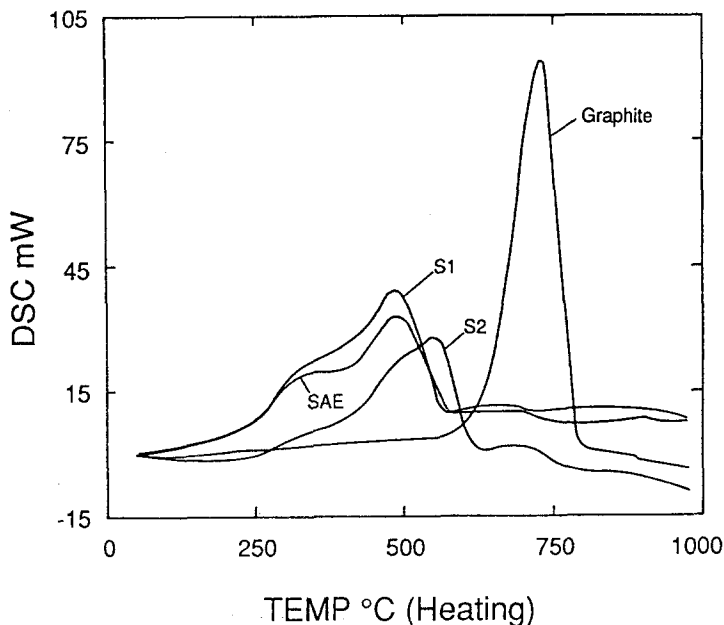


Fig. 6 DSC curves for various soots and graphite in flowing (100 ml·min⁻¹) oxygen at 10 deg·min⁻¹. a) Graphite b) S1, OSU soot c) S2, Texas Fullerenes, Inc. d) SAE, S1 soot after extraction with benzene

As predicted by the TG curves in Fig. 3 and the work of Millikan *et al.* [5], the exothermic peak associated with the graphite combustion occurs at a much higher temperature than for the soots. The area under the DSC curve for graphite gives an observed heat of combustion of $-32.3 \text{ kJ}\cdot\text{g}^{-1}$. This is in excellent agreement with the reported value of $-32.8 \text{ kJ}\cdot\text{g}^{-1}$ [11].

The combustion of the soots are virtually complete by the temperature that the graphite combustion begins. The DSC curve for the graphite is reasonably symmetrical, however, the curves for the soots suggest the presence of overlapping events. It is speculated that the lowest temperature process corresponds to the combustion of the fullerenes and the heat from this process combined with higher surface areas of the soots initiates the combustion of the remaining soot at a relatively low temperature. It must be recalled that there is an initial weight gain observed for this process and the early portion of the DSC curve should reflect this event.

The measured heats of combustion for the three soots are much lower than for graphite. They are -26.6 , -23.6 , and $-22.5 \text{ kJ}\cdot\text{g}^{-1}$ for the S1, S2, and SAE materials respectively. This implies a considerably lower heat of combustion for the fullerenes or the volatilization of significant amounts of material. The reported enthalpy of sublimation for the lower fullerenes is around $233 \text{ J}\cdot\text{g}^{-1}$ [12]. Even in oxygen it may be possible for the material to volatilize sufficiently that the heat of combustion is not released within the confines of the DSC detector.

The DSC curves for the separated C_{60} and C_{70} are presented in Fig. 7. There are small exothermic peaks around 275°C which are attributed to the oxidation as-

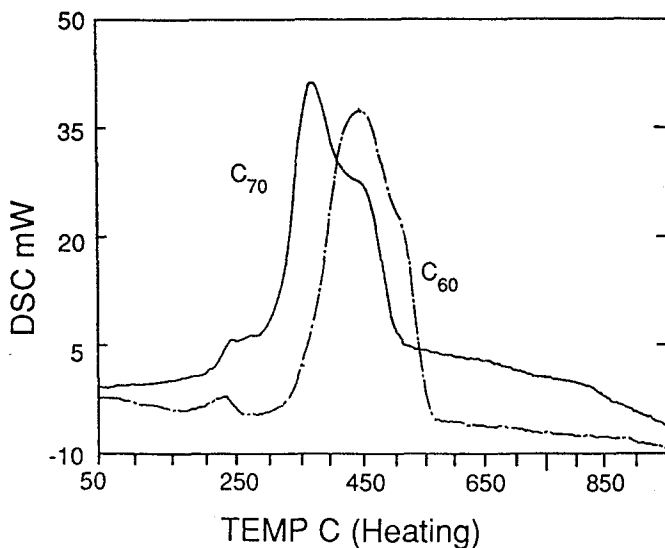


Fig. 7 DSC curves for C_{60} and C_{70} extracted and separated from S1 and heated at $10 \text{ deg}\cdot\text{min}^{-1}$ in flowing ($100 \text{ ml}\cdot\text{min}^{-1}$) oxygen

sociated with slight weight gain described earlier. These amount to -0.3 to $-0.5 \text{ kJ}\cdot\text{g}^{-1}$. The major oxidation peaks are asymmetrical beginning around 300°C and ending around 520°C . The heats of combustion of the C_{60} and C_{70} calculated from the areas are -18.7 and -21.0 , excluding the small peak, and -19.1 and $-21.5 \text{ kJ}\cdot\text{g}^{-1}$, when including the combined exotherms, respectively. While these heats are somewhat lower than those observed for the soots, they are still too large to explain alone the observed difference in the heat of combustion of the graphite and soots. Using the observed heats of combustion for graphite and C_{60} , a value of $-13.2 \text{ kJ}\cdot\text{g}^{-1}$ is calculated for the conversion of graphite to C_{60} .

Conclusion

Thermoanalytical methods are a powerful, relatively fast, and versatile class of techniques. TG is particularly suitable for assaying the relative fullerene contents of soots. At this time neither TG nor DSC is able to clearly resolve the relative amounts of C_{60} vs. C_{70} . The TG curves show a small weight gain in oxygen prior to the combustion of carbon suggesting the formation of an oxide. It would be interesting to halt a TG curve at that point and measure the C_{70}O content by chromatographic methods.

Sealed containers may be necessary to accurately measure the heat of combustion of the fullerenes because of their volatility. The combustion of the soots appears virtually complete by the temperature that normal graphite begins to oxidize. The fullerenes and soots adsorb significant moisture during normal storage and this is probably responsible for most of the low temperature weight loss in an inert atmosphere. There are, however, small amounts of argon and solvents incorporated into these materials.

Thermal analysis will continue to play a major role in the characterization of these interesting materials and the processes in which they are involved.

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Zusammenfassung — Thermoanalyse ist ein praktisches Hilfsmittel zur Charakterisierung von Ruß als Quelle für Kohlenstoffcluster, extrahierte Gemische von Fullerenen und die individuellen Cluster an sich. TG in einer inerten Atmosphäre ergibt schnell die flüchtigen Fraktionen, wahrscheinlich die niedermolekularen Cluster. TG in Sauerstoff zeigt einen leichten Gewichtszuwachs für Ruß und Cluster vor ihrer Zersetzung.

DSC in Sauerstoff wurde angewendet, um die Verbrennungswärme der getrennten C₆₀ und C₇₀ Materialien zu ermitteln. Die Verbrennung erfolgt für die Cluster bei etwa 300°C. Davor kann ein kleiner exothermer Peak beobachtet werden, welcher der Oxidation in Verbindung mit dem geringen Gewichtszuwachs zugeschrieben wird. Die gemessenen Verbrennungswärmen betragen -18.7 und -21.0 kJ·mol⁻¹ für C₆₀ bzw. C₇₀.

MS-EGA zeigt den Verlust von geringen Mengen an Wasser und Argon bei Temperaturen von etwa 250°C in Vakuum und von Lösungsmittel bei etwa 350°C, bevor die Sublimation eintritt.