

Thermoanalytical Investigations of Fullerenes

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Abstract

Based on the results of decomposition studies by means of TG it was possible to show the differences of air oxidation of C₆₀ and C₇₀. Mixtures containing both fullerenes form solid solutions and cannot be distinguished by thermoanalytical methods. It was found that these mixtures adsorb oxygen before they decompose. The effect of the heating rate and atmosphere was investigated. DSC curves of pure C₆₀-Fullerite show a sharp endothermic peak between 200 and 270 K which is due to a phase transition. The shape of the peak and the reversible character of this phase transition depends strongly on the sample preparation and purity. Vapor pressure measurements on C₆₀ samples were carried out by the Knudsen method.

1. Introduction

Fullerenes is the name given to cage-like molecules of carbon in crystalline form. This means they constitute a third form of carbon in addition to the commonly

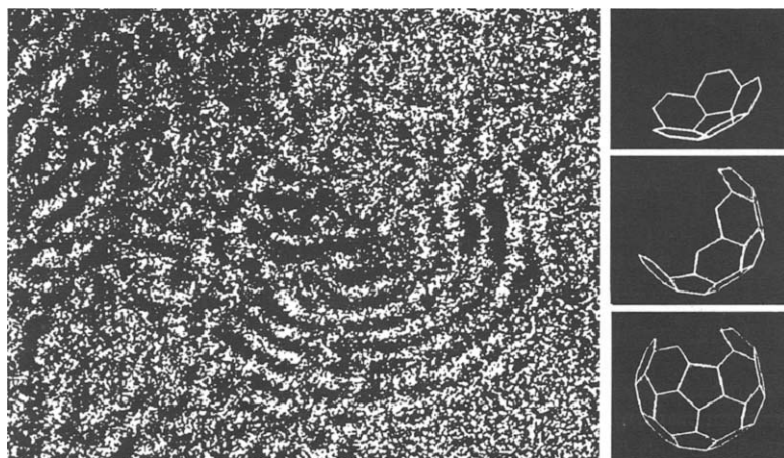


Fig.1 HREM* photograph showing icospiral growth of carbon during charcoal surface graphitization ($6 \cdot 10^6 \times$) compared to the growth of fullerene [1-3]

*High resolution electron microscopy

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known graphite and diamond structures. The archetype of the fullerenes is the C₆₀-Fullerite which is also called buckyball owing to its almost spherical shape. The C₆₀ molecule resembles a single graphite layer wrapped around a sphere with a diameter of 7.1 Å. The growth sequence of such Fullerite can be seen in Fig. 1.

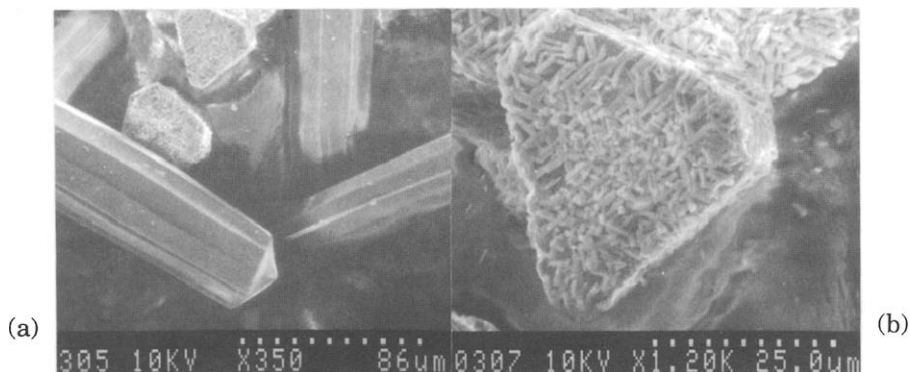


Fig. 2 SEM-photographs of a C₆₀ needle-like crystal (a), and the surface structure of a C₆₀ crystal (b).

Depending on the conditions for synthesis and extraction different purities of fullerenes are found, the main impurity in C₆₀ Fullerite is C₇₀ (usually around 8%), which is also a spherical, crystalline carbon molecule.

The morphology of such C₆₀ crystals can be seen in the SEM-photographs of Fig. 2. The crystals were grown from a toluene solution and show typically three forms: plates, rods and star-like aggregates. These shapes have been described for the first time by Krätschmer [4]. According to its purity C₆₀ probably prefers elongated shapes like needles and rods. Fig. 2 therefore would correspond to pure C₆₀ crystals.

The usual production method of fullerenes by high temperature vaporization of carbon and subsequent condensation of the carbon plasma yields a mixture of C₆₀ and C₇₀. These can be separated from the large amount of soot present in such mixtures by extraction with toluene and vaporization.

Different separation methods are used to produce pure C₆₀ and C₇₀ fullerenes, e.g. by extraction with toluene, by liquid chromatography or by sublimation. In our experimental study we applied various thermoanalytical methods to fullerenes of different purity. Beside commercially available fullerenes also samples obtained from a research laboratory (see acknowledgement) were used. The results obtained so far will be reported in the following.

2. Experimental

The Mettler Thermosystem TA 4000 was used for TG measurements in air and in controlled atmospheres like N₂/H₂ mixtures. As sample containers thin walled alumina and copper crucibles were used. The heating rates were varied from 0.3 to 10 °C/min. The DSC measurements of air oxidation of different fullerenes were carried out in Au crucibles. The Mettler Thermoanalyzer TA1 was used for vapor pressure measurements under isothermal conditions with a copper Knudsen cell [5-6].

3. Results and Discussion

3.1. Air Oxidation of C60

Results of heating experiments of different structures of carbon are summarized in Fig. 3. As expected the oxidation of C60 (Fullerite) occurs at significantly lower temperature than that of graphite and diamond. This is in agreement with the open less dense packed structure of C60.

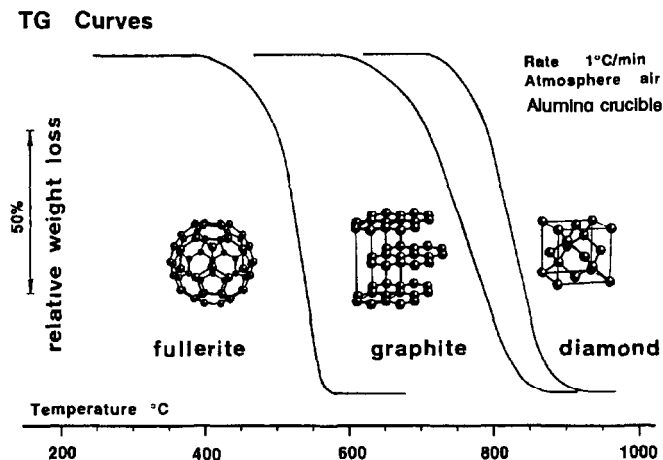


Fig 3 TG curves of the air oxidation of fullerite, graphite and diamond.

The specific density increases in the order C60-graphite-diamond from 1.7-2.3 and 3.5 g/mL. The oxidation of fullerenes in air not only depends on the surface area and the amount of the sample but also on the heating rate. This is shown in Fig. 4

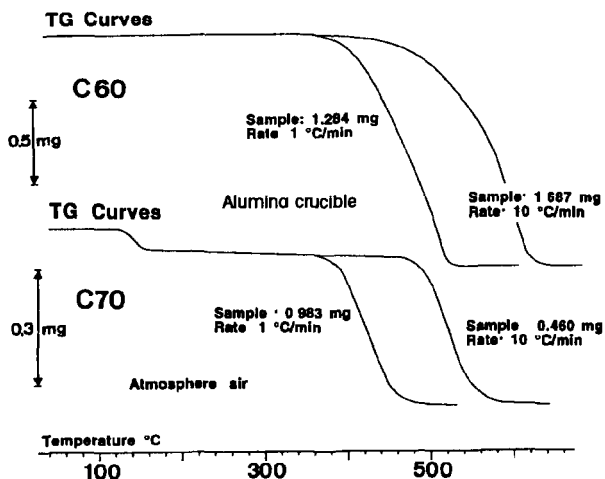


Fig 4 TG curves of C60 and C70 in air at different heating rates [7].

where the faster heating rate (10 °C/min) shifted the oxidation of C60 to higher temperatures as compared to 1 °C/min. In comparison C70 shows the same effect, but a desorption of mainly water in the temperature range of 120 to 170 °C is visible due to the probably higher specific surface of C70. Slow heating rates (0.3 °C/min) applied to mixtures C60/C70 lead to a pronounced adsorption effect of oxygen before the oxidation of the C70 fraction starts (Fig. 5). This oxygen take-up is due to oxygen complex formation on the large BET surface of ~260 m²/g [8]. This effect was not observed during the oxidation of pure C70 (see Fig. 4). The oxidation measurements of C60/C70 mixtures are summarized in Table 1.

Run No	Sample mg	Gas adsorption mg	%	Rate °C/min
1	2.129	0.069	3.26	1
2	2.434	0.1	4.11	1
3	2.647	0.23	8.70	0.3
4	2.820	0.185	8.11	0.3
5	2.803	0.21	7.49	0.3
6	4.103	0.332	8.08	0.3
7	3.982	0.367	9.22	0.3

Since C60 and C70 are oxidized at different temperatures it was tried to separate the more stable C60 from C70 by thermal treatment. The TG curve in Fig. 5 corresponds to the total oxidation of a fullerene mixture (hot extract). The first derivative of the TG (DTG) clearly shows two different rates of oxidation for the C60/C70 mixture in the TG curve (Fig. 5).

From the DTG curve it is possible to estimate the intermediate temperature between C70 and C60 oxidation, where the rate of oxidation has a minimum. Experiments to oxidize preferentially only C70 (by lower temperature heat treatment up to this temperature, 350 °C, TG curve a) were not successful, since the residue (assumed to be pure C60) which was heated up in a separate run (TG curve b) turned out to be a polycondensate of unknown structure. The heat of combustion of this residue was only 7500 J/g as compared to 19700 J/g for pure C60.

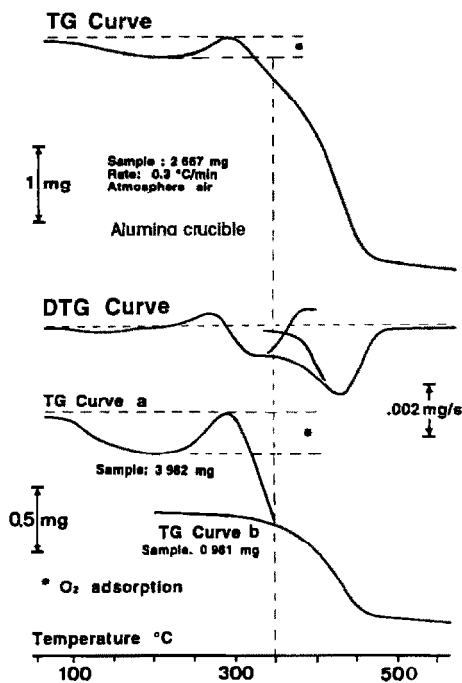


Fig. 5 TG and DTG curves of of C60/C70 mixture (hot extract).

3.2 DSC curves of Fullerenes

Fullerene samples of different purity prepared by hot extraction, cold extraction, and sublimation were investigated by means of DSC and TG/DTG [9,10]. The DSC curves (Fig. 6) show the different peak shapes and the increase of the onset temperature going from the C60/C70 mixture, hot extract, cold extract to the pure C60 (sublimated). TG measurements are less sensitive, the first derivative (DTG) however also shows the differences in the speed of decomposition. The quantities and the temperatures are similar with the DSC results. The onset temperatures and peak temperatures (in °C) of the DSC curves are shown in Table 2

No	T onset	T max
1	419	477
2	439/500	600
3	560	645

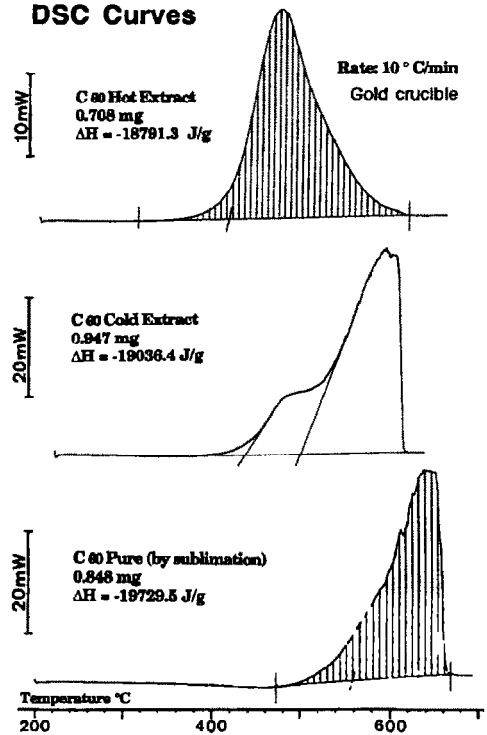


Fig. 6 DSC of air oxidation of fullerene [9]

3.3 Phase Transition of C60

The orientational disorder present in Fullerite (C60) has been investigated by c_p measurements, NMR and Synchrotron X-Ray powder diffraction. Orientational ordering of the molecules takes place when the temperature is lowered trough 249 K. This phase transition can be also seen in the DSC curve shown in Fig. 7 which was measured by Wunderlich [11]. It was found to start gradually at 190 K with an endothermic peak temperature at 259 K.

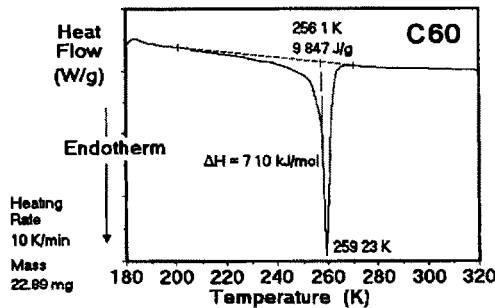


Fig. 7 Thermal analysis of Fullerite (C60) in the transition region [11].

The transition at 259 K is an orientational disordering with an integrated entropy of transition of about 27 J/K·mole [12]. This is in the typical range observed for orientational disordering (20-50 J/K·mole) [13]. A jump-like motion between symmetry-related positions was found at even lower temperature starting at about 110 K by solid state NMR. This jump-motion cannot be seen by thermal analysis since it is not connected with an entropy increase.

The entropy of sublimation is about 111 J/K·mole. Knowing that the crystalline C60 is fully disordered orientationally (plastic crystal) one can estimate the remaining entropy of isotropization as 7-14 J/K mole. Subtracting the isotropization entropy from the sublimation entropy leaves an entropy of vaporization from the liquid state of about 98 J/K·mole. This is in good agreement with Trouton's rule, which states that the entropy of vaporization at the boiling point is approximately constant for various substances, $\Delta S_v = \Delta H_v/T_v$ is equals 90 J/K·mole. For calculating the entropies of evaporation of C60 and C70 the values of the boiling points estimated by Pan [5], 1564 and 1622 K respectively, were used. In a first approximation the enthalpy of sublimation of C60 and C70 given by Pan [5] as -233 J/g was divided by the boiling points and gave the following values for the entropies of sublimation: 107.3 J/K·mole for C60 and 120.7 J/K·mole for C70.

3.4 Vapor Pressure

The Knudsen effusion method was used for measuring the vapor pressure of fullerenes. The orifice of the copper effusion cell was calibrated. Measurements were carried out isothermally between 500-700 K with simultaneous recording of the weight loss as a function of time, temperature and pressure in high vacuum. Preliminary data for the vapor pressure of C60 (Fullerite) were in good agreement with the values given by Pan [5] and gave the value -211 J/g for the enthalpy of sublimation as compared to -233 J/g.

Conclusion

Thermoanalytical methods proved to be useful for distinguishing different types of fullerenes. The data obtained so far are however of a preliminary nature and further investigations will be carried out.

Acknowledgement

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