Eur. Phys. J. D **9**, 373–376 (1999)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences
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Springer-Verlag 1999

The endohedral fullerene formation process with a laser furnace apparatus

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Received: 1 September 1998 / Received in final form: 5 November 1998

Abstract. In order to elucidate the formation processes of empty and endohedral fullerenes, we produced fullerenes and endohedral fullerenes by changing La concentration as well as furnace temperature. The yields of these products were systematically investigated by ultraviolet-visible (UV-VIS) absorption spectroscopy and electron spin resonance (ESR) and high-performance liquid chromotography (HPLC) analyses. As a result, it was found that the C_{60} yield decreases monotonically when La concentration increases, while the LaC_{82} yield shows a maximum at 0.25 atom %, and then decreases monotonically by increasing La concentration as like as C_{60}. From the HPLC analysis it was also found that the yield of higher fullerenes decreases more rapidly because of the presence of La.

PACS. 36.40.-c Atomic and molecular clusters – 81.05.Tp Fullerenes and related materials; diamonds, graphite

1 Introduction

Since the discovery of fullerenes and endohedral metallofullerenes [1–3], their formation mechanism has been an intriguing issue. A "laser furnace" technique, which was first applied to the production of endohedral fullerenes [3] and single-wall carbon nanotubes [4] by Smalley and coworkers, has characteristic advantages. Several physical parameters such as laser fluence, the temperature of the reaction region, foreign gas pressure, etc., are well controlled independently. Through the use of these advantages, a laser furnace technique has been successfully applied to the investigation of the formation process of higher fullerenes, showing that the formation of some particular isomers of C_{78} (C'_{2v}–C_{78}) is strongly enhanced by elevation of the temperature of the electric furnace [5].

On the other hand, for the formation mechanism of endohedral fullerenes, very little information has been available so far. Ying *et al.* reported that the increase of La atom concentration in the composite rods results in the decrease in the number of fullerenes [6]. They also found the relationship between the intensities of C_n and LaC_n species by using of a Fourier-transform ion-cyclotron-resonance mass spectrometer, indicating that only C_{60} and C_{70} remain in a sublimed film when La atom concentration is very high. A preliminary investigation of solvent extractable materials in the arc-burning soot using a La/carbon composite rod suggested that at low He pressure, neither LaC_{82} nor some particular isomers, such as C'_{2v}–C_{78}, are produced [7].

In the present work, using the laser furnace technique, we systematically investigated the correlation between the formation of endohedral fullerenes and empty higher fullerenes by using an electron spin resonance (ESR) technique for the detection of the endohedral fullerene LaC_{82} and a high-performance liquid chromatography (HPLC) technique for the separation of solvent extractable higher fullerenes. Results obtained with different temperatures of the electric furnace and different La atom concentration are summarized and discussed.

2 Experimental

We have described the laser furnace apparatus used here in a previous paper [5], and its design is essentially the same as that described by Haufler *et al.* [8]. A home-made La/carbon composite rod was prepared and put at the end of the molybdenum rod in a quartz (or ceramic) tube, which was heated with a slow flow of Ar gas in the electric furnace. The Ar pressure was fixed at 200 Torr throughout the experiments. The ceramic tube was used at 1150 °C and above, since a quartz tube is easily damaged in this temperature range. The La atom concentration used in this work are 0.05, 0.1, 0.25, 0.5, 0.76, 1.0, 1.5 and 2.0 atom %. The detail of the preparation of the composite rods is essentially the same as described elsewhere [3].

The target rod was evaporated by 1.8×10^4 shots of a second harmonic of Nd:YAG laser (532 nm; 300 mJ/pulse). After laser vaporization, all the sooty materials deposited on a quartz (or ceramic) tube were washed out with CS_2. So that the relative yield of the endohedral fullerene LaC_{82} could be estimated, the ESR spectrum was measured using this crude extract. Since the yield of LaC_{82} in the crude ex-

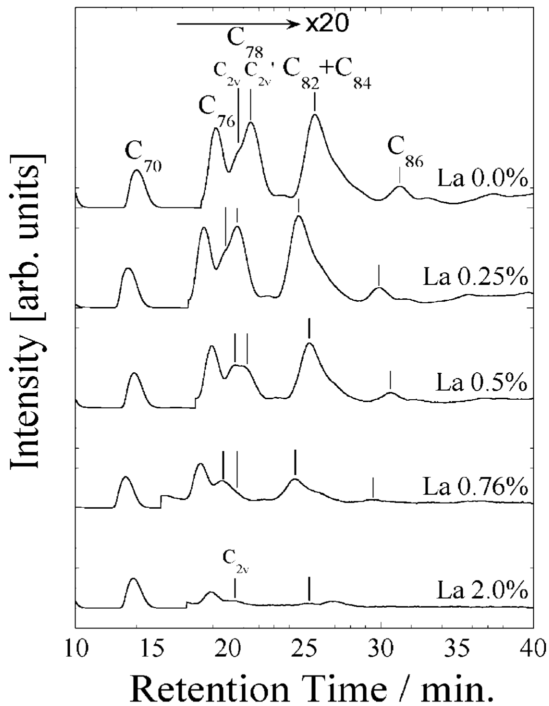

Fig. 1. HPLC chromatograms of crude extracts obtained from laser-vaporized soots of carbon and C/La composite rods with various La concentration. In each spectrum, the intensities are normalized by the C_{60} yield (not shown), and enlarged twenty times after 17 min.

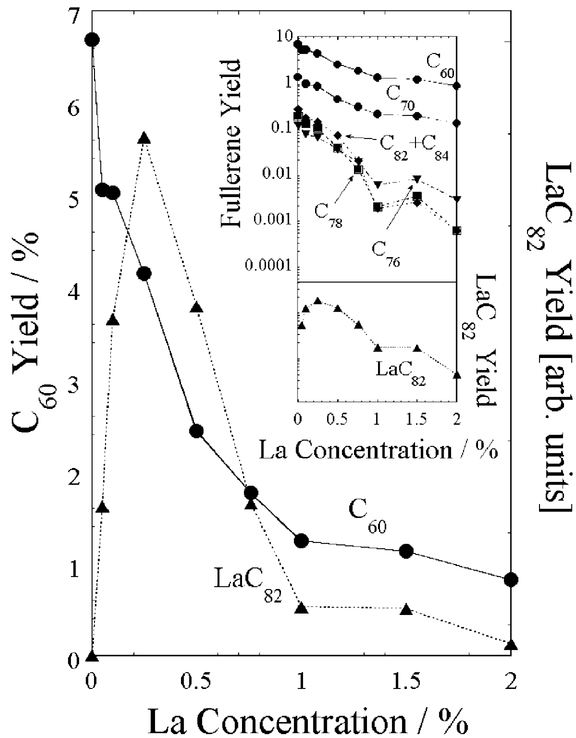

Fig. 2. La-concentration dependence of yield of C_{60} and LaC_{82}. Inserted figure shows La-concentration dependence of the yield (logarithm scale) of fullerenes C_{60}–C_{84} and metallofullerene LaC_{82}.

tract was quite low, only the relative yield was estimated from the measured ESR signal intensity. The total (absolute) C_{60} yield of the crude extract was estimated from the intensity of ultraviolet-visible (UV-VIS) absorption by Lambert–Beer's law. Finally, for the estimation of relative yields of C_{70} and other higher fullerenes to that of C_{60}, an HPLC technique was applied to the crude extract obtained with several different La atom concentration and temperatures of the electric furnace. The yields of C_{70} and higher fullerenes were determined by comparison between the fraction area corresponding to C_{60} and each of those corresponding to other fullerenes. The typical HPLC chromatograms are shown in Fig. 1.

3 Results and discussion

3.1 Lanthanum concentration dependence of fullerene and metallofullerene yields

Figure 2 shows the variation of the yield of C_{60} and LaC_{82} as a function of the concentration of La atoms, and the inserted figure shows the yield (logarithm scale) of fullerenes up to C_{84} and LaC_{82}. During laser vaporization, the ambient temperature was fixed at 1100 °C. The yield of C_{60} decreases drastically and monotonically as the La concentration increases. These results show that the effect of lanthanum is a sort of inhibitor of formation of empty fullerenes. It should be noted that the toxicity of the La atom is quite strong for the higher fullerenes. For example, the addition of only a 0.5% concentration of La atoms in the composite rod changes the yield of C_{60} to 1/3 of that in the pure-C case (0.0%), and in the presence of 2.0 atom % of La, the C_{60} yield changes to 1/10 of that in the pure-C case. The yield of higher fullerenes decreases more significantly than that of C_{60} as the La atom concentration increases. As shown in the inserted figure, the relative yield of C_{76} is about 1/60 of that of C_{60} in the pure-C condition, while it is about 1/300 at 2.0% of La atom concentration. The yield of $C_{82}+C_{84}$ changes more sharply. It is about 1/25 of C_{60} yield at pure-C condition, but only 1/1500 at 2.0% of La atom concentration.

In our previous paper, we have reported that even the relative ratio of a specific isomer is strongly influenced by inert gas temperature [5]. By decreasing temperature, the number of C'_{2v}–C_{78} decreases more rapidly than that of other species. In the present study, the intensity of the isomer C'_{2v}–C_{78} was found to decrease faster than other species when the concentration of La increased, as can be seen in Fig. 1. This indicates that the effect of temperature is similar to that of adding La atoms.

The plot of the yield of metallofullerene LaC_{82} against the La concentration in the target rod is also shown in the Fig. 2. The plot rises sharply from 0 to 0.25% of La atom concentration, and then decreases as the La concentration increases further. The former is readily acceptable since a certain number of La atoms are necessary for the formation of LaC_{82}. However, the yield of LaC_{82} decreases again for La concentrations higher than 0.25%. The logarithmic plot inserted in Fig. 2 clearly shows that the tendency of the decrease is very similar to those in the higher fullerene cases. This indicates that the metallofullerene LaC_{82} has a formation process similar to the ones the empty higher fullerenes have.

3.2 Temperature dependence of fullerene and metallofullerene yields

In the previous section, we pointed out the similarity between the effects of La addition and temperature-lowering on fullerene formation. The effect of ambient temperature for the formation of empty fullerenes has been studied in more detail [5]. Roughly speaking, the yield of empty fullerenes increases as the ambient temperature of the furnace increases up to 1200 °C, and then decreases beyond that temperature. The role of the ambient temperature could possibly be interpreted as follows. In order to explain the furnace-temperature role on fullerene formation, here we tentatively assume that fullerene cages grow up via an open-cage-like precursor, first suggested by Smalley [9]. We further assume that the precursor considered here can be formed only when a thermal reaction of laser-vaporized carbon species takes place at the temperature above ≈ 500 °C. In the lower temperature region, the hypothetical precursor would not be sufficiently formed, probably due to the activation barrier for forming the precursors from the intact species by laser irradiation of a graphite. On the other hand, in the temperature region higher than the optimum conditions, some kinds of competing processes may appear which disturb the fullerene formation; for example, (1) the too rapid growth of precursors to very large particles, (2) the thermal fragmentation of the precursors, and (3) the thermal destruction of the fullerene itself.

So that the effect of the ambient temperature and La addition could be sorted out, the fullerene yields were measured under various temperatures through the use of pure and composite carbon rods. The plots of the yields of C_{60}, C_{76} (as typical higher fullerenes), and LaC_{82} against the ambient temperature are shown in Figs. 3a, 3b, and 3c, respectively. In Figs. 3a and 3b, the yields of C_{60} and C_{76} obtained for the samples with different La concentrations, 0%, 0.25%, and 0.76%, are shown. Temperature dependence of the yield of LaC_{82} shown in Fig. 3c was obtained by the use of the rod with the La concentration of 0.25%. The common feature of these plots is that the yield increases with the temperature up to 1000–1200 °C and then decreases. When the yields of empty fullerenes (3a and 3b), are compared, it is strongly indicated that the temperature dependence of the fullerene yield is almost the same over the broad temperature range.

For the metallofullerene, the yield shows a rise at about 800 °C and a peak at about 1200 °C. This trend is very similar to that of the empty fullerenes, especially higher fullerenes. That is, the optimum temperatures for these three fullerenes are essentially the same, whereas the onset for LaC_{82} and C_{76} is higher than C_{60}. This behavior is consistent with the assumption described in the preceding section that there exist common processes for the formation of empty fullerenes and metallofullerenes.

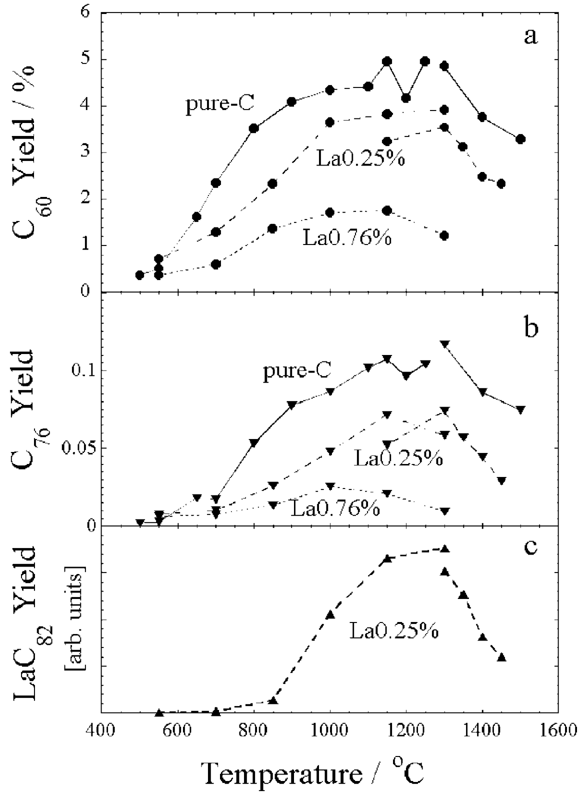

Fig. 3. Temperature dependence of the yields of C_{60} (a), C_{76} (b), and LaC_{82} (c). In the case of 0.25% La atom concentration, a quartz tube was used in the range of 550–1300 °C, and a ceramic tube was used in the range of 1150–1450 °C.

3.3 The effect of La on the formation of higher fullerenes

The experimental finding that the yield of higher fullerenes effectively decreases as La atom concentration increases is rationalized in the following way. The high yield of C_{60} and C_{70} as compared with other higher fullerenes is explained in terms of kinetic factor. In the previous study, we showed that the nominal activation energies for the formation of C_{60} and C_{70} have a smaller value than those for other, higher fullerenes; this suggests that higher fullerenes have more complicated reaction paths, in which each reaction step has basically some activation barriers, resulting in the requirement of the higher activation energy as a whole process [5]. The most probable reaction process accompanying the activation energy might be a sort of annealing process in the rare gas atmosphere in which the formation of a six-membered ring network is more pronounced, competing with the production of a five-membered ring network. It should be noted here that if the so-called isolated pentagon rule (IPR) totally governs the fullerene cage formation process, then C_{60}, with icosahedron symmetry, is the fullerene cage which introduces five-membered rings as quickly as possible. As a matter of fact, if the annealing process tends to form a six-membered ring instead of introducing a five-membered one, the size of fullerene cage becomes larger than those of C_{60} and C_{70}. If the formation of higher fullerenes requires more annealing steps than that of C_{60} in order to accomplish closing the cage, it is deduced that an La atom has a better chance of attacking the annealing intermediate species during the formation of higher fullerenes. As a result, the presence of La atom would disturb the formation of both C_{60} and other, higher fullerenes, but would more effectively disturb the formation of higher fullerenes.

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