

Generation of Higher Fullerenes in Flames

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The presence of fullerenes up to C₁₁₆ was observed in condensable material from a benzene/oxygen flame. The flame material was Soxhlet-extracted with toluene for 363 h, fractionated by means of a silica-based semipreparative HPLC column, and analyzed by HPLC coupled to a mass spectrometer via a heated nebulizer interface using a 2-(1-pyrenyl)ethylsilica stationary phase. UV–vis spectra were measured for C₆₀, C₆₀O, C₆₀•CH₄, C₇₀, C₇₀O, C₇₆, C₇₈, C₈₀, C₈₄, a C₈₄ adduct, C₈₆, C₈₈, C₉₀, C₉₂, C₉₄, C₉₆, C₉₈, C₁₀₀, C₁₀₂, and C₁₀₈. Isomers could be discerned for C₇₈, C₉₀, and C₉₄. A calibration using external standards was performed for C₆₀, C₇₀, C₇₆, C₇₈, and C₈₄. For all other species the relative abundances were estimated based on HPLC peak integration results. Electric arc soot was extracted under similar conditions and the quantification of fullerenes compared to the data obtained with flame-generated condensable material. Except for C₆₀ and C₇₆, the abundances were significantly higher in the case of flame-generated condensable material. Also, striking differences between the two fullerene production methods are seen in the relative abundances of C₇₈ isomers. Considering the present results and the ease with which the experimental setup could be scaled up, flame-generated condensable material represents an excellent starting material for the preparative isolation of higher fullerenes.

Introduction

Shortly after the discovery of fullerenes by Kroto et al.,¹ the presence of charged fullerenes in premixed low-pressure acetylene/oxygen/argon and benzene/oxygen/argon flames was shown by the Homann group.² The generation of extractable amounts of C₆₀ and C₇₀ fullerenes with the condensable material including soot in premixed benzene/oxygen/argon flames was established in 1991 by Howard et al.^{3–5} and confirmed and extended by Richter et al.⁶ Also, the presence of other fullerene compounds such as oxygen- and hydrogen-containing molecules^{7,8} and fullerene nanostructures^{9–11} in samples condensed from sooting flames has been pointed out.

In the present work fullerenes and related compounds like oxides and adducts containing between 60 and 116 carbon atoms were isolated from condensable material generated in a sooting premixed low-pressure benzene/oxygen/argon flame using high performance liquid chromatography (HPLC). UV–vis spectra were measured systematically up to C₁₀₈. Yields of the different fullerenes were determined and compared with data obtained using commercial electric arc soot.

Previously, the presence of fullerenes containing up to 250 carbon atoms in low-pressure benzene/oxygen flames was suggested using on-line mass spectrometry,¹² and direct mass spectrometric measurements of samples condensed from sooting flames showed mass peaks corresponding to fullerenes with up to more than 150 carbon atoms.⁶ Nevertheless, the unambiguous identification and characterization of these compounds require their isolation and purification. Except for C₆₀ and C₇₀ where selective complexation,^{13,14} flash chromatography on activated

carbon or carbon fibers,¹⁵ and fractional crystallization in 1,3-diphenylacetone¹⁶ have been used successfully, chromatographic methods remain the only suitable technique for this purpose. Previously, the separation of fullerenes up to C₈₄ by means of HPLC was described by Jinno et al.,¹⁷ while Diederich et al.¹⁸ separated samples enriched in C₉₀ and C₉₄ using gravity chromatography on alumina. HPLC was used by Kikuchi et al.¹⁹ for the analytical separation and identification of C₉₀ and C₉₆. The presence of compounds with molecular masses corresponding to fullerenes up to C₉₆²⁰ and C₁₀₈²¹ was revealed by Anacleto et al. using HPLC coupled to mass spectrometry (HPLC-MS). In a recent work of our group, different stationary phases and eluents are discussed. Different solvents for extraction were investigated, and the efficiency of toluene was pointed out. Macroscopic amounts of C₈₆, C₉₀, C₉₂, C₉₄, and C₉₆ were isolated and UV–vis spectra measured. The presence of a C₉₀ adduct could be discerned.²²

Experimental Section

Qualitative Analysis. A 5.51 g sample of condensable material was generated in a flat premixed benzene/oxygen/argon flame at a pressure of 5.3 kPa (40 Torr), an atomic C/O ratio of 0.96, 10% argon, and an initial velocity of the fresh gas mixture of 25 cm s^{−1} (at 25 °C) using equipment described previously.^{4,5} This flame was selected because a relatively important set of data concerning its properties is available,²³ even though this flame does not give the highest fullerene yield among the flames investigated in the past.^{4,5}

The condensed material was Soxhlet-extracted with about 600 mL of toluene for 363 h. The efficiency of toluene also for the extraction of fullerenes larger than C₈₄ was shown recently.²² After extraction and filtration, the volume of the solution was reduced to 66 mL, having added 1,2-dichlorobenzene in order to increase the solubility according to Ruoff et al.²⁴ All of this

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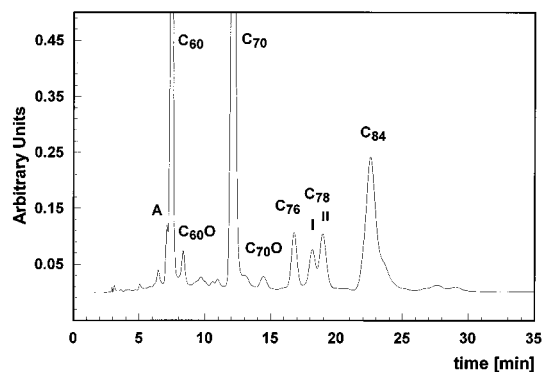


Figure 1. HPLC chromatogram of fraction I (Cosmosil BuckyPrep analytical column, 1 mL min⁻¹ toluene, detection at 330 nm, injection of 20 μ L).

solution was fractionated by means of 13 injections into a silica-based semipreparative column. Two fractions were collected:

fraction I: all compounds eluted after C₇₀ up to the major portion of C₈₄

fraction II: the tail of the C₈₄ peak and all species beyond

After the reduction of the volume, fraction I represents 8.0 mL of a toluene/1,2-dichlorobenzene solution. In the case of fraction II, toluene was entirely replaced by 1,2-dichlorobenzene and 1.4 mL remained. For further HPLC analysis a 2-(1-pyrenyl)ethylsilica stationary phase (Cosmosil BuckyPrep column, 250 \times 4.6 mm) with a toluene flow of 0.5 or 1.0 mL min⁻¹ for elution was used on an Hewlett-Packard Series 1050 instrument equipped with an HP 1040A diode array detector. UV-vis spectra could be measured above 290 nm. Despite baseline subtraction, no reliable spectra could be collected below this wavelength due to the absorption features of toluene. Figure 1 shows the HPLC chromatogram of fraction I obtained at a toluene flow of 1.0 mL min⁻¹ while the chromatogram of fraction II, measured at a toluene flow of 0.5 mL min⁻¹, is represented in Figure 2a,b. In both cases 20 μ L was injected. Unambiguous identification of the peaks could be obtained by means of HPLC/MS.^{8,25} An API-*I* single quadrupole mass spectrometer (Sciex, Thornhill, Ontario, Canada) was coupled via a heated nebulizer interface to the above-mentioned HPLC column using chemical ionization and the positive ion mode. Twenty microliter aliquots of Fraction I and Fraction II were analyzed with this technique. The assignments of the peaks in fraction I are shown in Figure 1 while the peak assignments obtained with fraction II are represented in Figure 2a,b.

The fractionation with the silica-based semipreparative column does not lead to a complete removal of earlier eluting compounds. Relatively important peaks of C₆₀ and C₇₀ could be observed in fraction I as well as in fraction II. C₆₀, C₆₀O, C₇₀, C₇₀O, C₇₆, C₇₈, C₈₀, C₈₂, and C₈₄ could be identified by mass spectrometry in fraction I. C₈₀ is situated between C₇₈ and C₈₄ while C₈₂ cannot be separated and is coeluting with C₈₄. In Figure 1, peak "A" on the left of C₆₀ shows a molecular mass corresponding to C₆₀O while the UV-vis spectrum represented in Figure 3a is clearly different. Referring to Anacleto et al.,⁸ the assignment as C₆₀·CH₄ which corresponds to C₆₀HCH₃ or alternatively C₆₀(CH₂)H₂ seems to be reasonable. The UV-vis spectra of C₆₀ and C₆₀O are also catalogued in Figure 3a while for C₇₀, C₇₀O, and C₇₆ they are represented in Figure 3b. Two HPLC peaks revealing a molecular mass corresponding to C₇₈, labeled "I" and "II", are present in Figure 1. Referring to Jinno et al.,²⁶ the UV-vis spectra as shown in

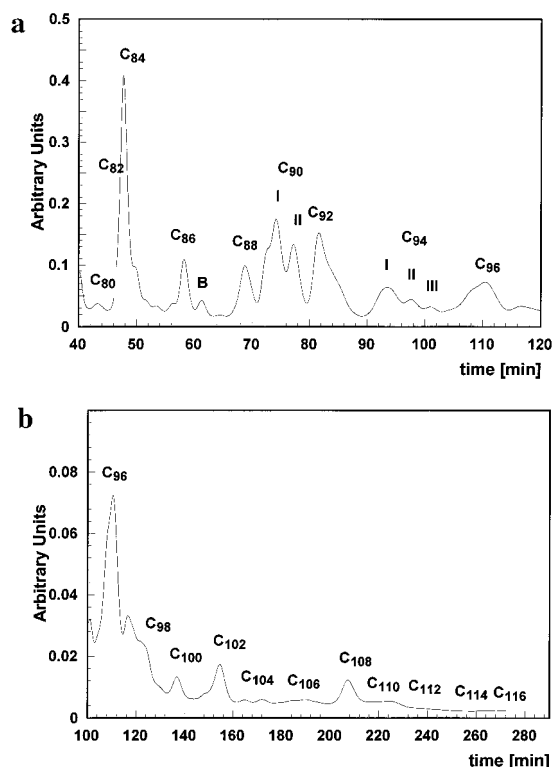


Figure 2. HPLC chromatogram of fraction II (Cosmosil BuckyPrep analytical column, 0.5 mL min⁻¹ toluene, detection at 330 nm, injection of 20 μ L): (a) C₈₀ to C₉₆; (b) C₉₆ to C₁₁₆.

Figure 3c lead to the conclusion that C₇₈ I represents a mixture between the isomers C₇₈-C_{2v} and C₇₈-D₃ while C₇₈ II can be attributed to C₇₈-C_{2v}. The C₈₄ spectrum is shown in Figure 3d. Due to a better quality the UV-vis spectrum of C₈₀ measured with fraction II (Figure 2a) is used for presentation in Figure 3c. Figure 3d also shows the UV-vis spectra of C₈₆ and the compound labeled "B", referred to in Figure 2a, for which the mass determined by HPLC/MS corresponds to C₈₄. The "hump" in the spectrum indicates that a C₈₄ derivative fragmented during the ionization process.²² The UV-vis spectra of C₈₈ and two C₉₀ peaks are summarized in Figure 3e. The C₉₀ spectra are similar, but not identical, so that further studies will be necessary in order to elucidate the differences between these two peaks, which could be two stable isomers. The presence of three different HPLC peaks could be observed in the case of C₉₄. Only C₉₄ I and C₉₄ II are shown in Figure 3f, together with the spectrum of C₉₂. The spectrum of C₉₄ III was too noisy for sufficient reliability. The spectra for the two C₉₄ species are obviously different, and more information will be necessary in order to discern the differences in structure. The UV-vis spectra of C₉₆ and C₉₈ (Figure 2a,b) are represented in Figure 3g. As labeled in Figure 2b, the sequential elution of C₁₀₀, C₁₀₂, C₁₀₄, C₁₀₆, C₁₀₈, C₁₁₀, C₁₁₂, C₁₁₄, and C₁₁₆ could be shown by HPLC/MS, but only the peak heights of C₁₀₀, C₁₀₂, and C₁₀₈ allowed the measurement of reliable UV-vis spectra as represented in Figure 3h. Masses corresponding to C₇₈O, C₈₂O, C₈₄O, C₈₆O, C₈₈O, C₉₀O, and C₉₂O could also be detected by means of HPLC/MS on fraction II, but no reliable UV-vis spectra could be measured due to the low concentrations of these species.

Quantitative Analysis and Comparison with Electric Arc Soot. The amount of the different fullerenes present in the above-described toluene extract of 5.51 g of flame-generated condensable material was determined with a 2-(1-pyrenyl)ethylsilica stationary phase (Cosmosil BuckyPrep column, 250 \times 4.6 mm) using a Hewlett-Packard Series 1050 HPLC instrument. For

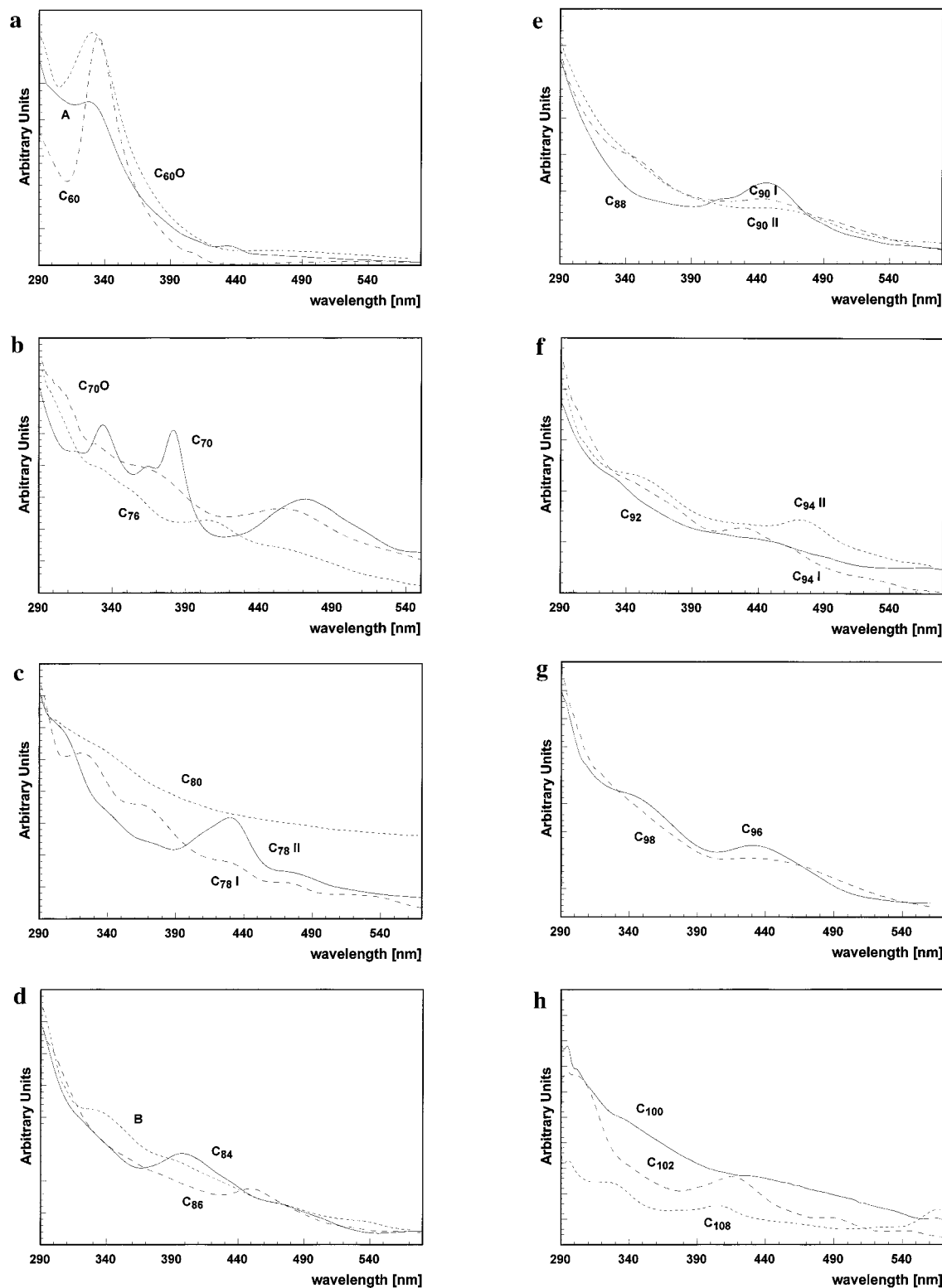


Figure 3. UV-vis spectra of (a) C_{60} , $C_{60}O$, and $C_{60}CH_4$, (b) C_{70} , $C_{70}O$, and C_{76} , (c) C_{78} I, C_{78} II, and C_{80} , (d) C_{84} , C_{84} adduct, and C_{86} , (e) C_{88} , C_{90} I, and C_{90} II, (f) C_{92} , C_{94} I, and C_{94} II, (g) C_{96} and C_{98} , (h) C_{100} , C_{102} , and C_{108}

C_{60} , C_{70} , C_{76} , C_{78} , and C_{84} , external standards were used as described previously.²² For compounds where sufficient quantities are not actually available, the calibration with similar species was used in order to obtain at least an approximate quantification, with C_{60} for $C_{60}O$, C_{70} for $C_{70}O$, C_{78} for C_{80} , and C_{84} for all other compounds. The results are summarized in Tables 1 and 2. For the ease of analysis, fraction II, from which an important part of smaller species had been removed, was used in the case of fullerenes beyond C_{84} . The loss of material due to the removal of smaller fullerenes was checked and was of

about 20%. Generally, a continuous decrease of abundance beyond C_{70} can be stated, especially between C_{98} and C_{116} , but some relatively prominent peaks like C_{84} , C_{90} , C_{92} , C_{96} , C_{102} , and C_{108} must be pointed out.

In order to compare the relative abundances, especially of higher fullerenes, 5.60 g of "as-produced" electric arc soot (MER, Tuscon, AZ) was Soxhlet-extracted with about 600 mL of toluene for 363 h under the same conditions as the flame-generated condensable material. After filtration, 8 mL of the remaining 585 mL was blown down to 0.37 mL in order to

TABLE 1: Relative Abundance of C₆₀, C₆₀O, C₇₀, C₇₀O, C₇₆, C₇₈, C₈₀, and C₈₄ in Flame-Generated Condensable Material and in Electric Arc Soot

compd	% in flame-generated condensable material	% in electric arc soot
C ₆₀	1.60	4.05
C ₆₀ O	0.09	0.07
C ₇₀	1.79	1.13
C ₇₀ O	0.09	0.018
C ₇₆	0.034	0.065
C ₇₈ (C _{2v} + D ₃)	0.0063	0.022
C ₇₈ (C _{2v})	0.035	0.0021
C ₈₀	0.0026	not quantifiable
C ₈₄	0.146	0.057

TABLE 2: Approximative Relative Abundances and Masses of Fullerenes Larger Than C₈₄ in Flame-Generated Condensable Material and Electric Arc Soot

compd	% in flame-generated condensable material	% in electric arc soot
C ₈₄ adduct	0.0031	not detectable
C ₈₆	0.0076	not quantifiable
C ₈₈	0.0097	not quantifiable
C ₉₀ I	0.021	0.0039
C ₉₀ II	0.011	0.0014
C ₉₂	0.023	0.0037
C ₉₄ I	0.010	0.0011
C ₉₄ II	0.0042	0.0023
C ₉₆	0.017	0.0041
C ₉₈	0.0099	not quantifiable
C ₁₀₀	0.0013	not quantifiable
C ₁₀₂	0.0024	not quantifiable
C ₁₀₄	0.00021	not quantifiable
C ₁₀₆	0.00042	not quantifiable
C ₁₀₈	0.0016	not quantifiable

increase fullerene concentration in the solution. The analysis was performed by HPLC as described above for the flame-generated condensed material. The results represented in Tables 1 and 2 show that electric arc soot has a C₆₀/C₇₀ ratio of about 4, which is much higher than for flame-generated condensable material where C₇₀ is often the most prominent fullerene.^{4,5} The comparison of the relative abundances in flame-generated condensable material and electric arc soot shows higher percentages for flame-generated condensable material for each fullerene except C₆₀ and C₇₆. The approximately 5 times higher abundance of C₇₀O in flame-generated condensable material could lead to the use of C₇₀O for further derivatization.

A striking phenomenon is the ratio of the three C₇₈ isomers. In the case of flame-generated condensable material, C₇₈-C_{2v} is about 6 times more abundant than the mixture of C₇₈-C_{2v} and C₇₈-D₃ while in electric arc soot the concentration of the mixture of C₇₈-C_{2v} and C₇₈-D₃ is about 10 times higher than that of C₇₈-C_{2v}. The elucidation of this phenomenon will require a better comprehension of the fullerene formation mechanism in flames and in electric arc systems. Concerning fullerenes beyond C₈₄, no C₈₄ adduct could be observed in electric arc soot, and in the case of C₉₀, C₉₂, C₉₄, and C₉₆, the concentrations in the flame-generated condensable material are about 4–7 times higher than in the electric arc soot. Despite the fullerene concentration being about 2.5 times higher in the electric arc soot extract than in the initial extract of flame-generated condensable material due to the volume reduction before analysis, reliable estimates for the relative abundances of C₈₀, C₈₆, C₈₈, C₉₈, C₁₀₀, C₁₀₂, C₁₀₄, C₁₀₆, and C₁₀₈ were only possible for flame-generated condensable material after the partial removal of smaller fullerenes.

Conclusions

The presence of higher fullerenes up to C₁₁₆ in flame-generated soot could be shown by means of HPLC coupled to mass spectrometry. The partial removal of C₆₀ and C₇₀ allowed to increase the concentrations of higher fullerenes in the solution, so that UV-vis spectra for C₆₀, C₆₀O, C₆₀·CH₄, C₇₀, C₇₀O, C₇₆, C₇₈, C₈₀, C₈₄, a C₈₄ derivative, C₈₆, C₈₈, C₉₀, C₉₂, C₉₄, C₉₆, C₉₈, C₁₀₀, C₁₀₂, and C₁₀₈ could be measured. Besides C₇₈, where the existence of three isomers is well established, some evidence for isomers in the case of C₉₀ and C₉₄ could be found. Despite the general decrease in relative abundance with increasing carbon number, exceptions like C₈₄, C₉₀, C₉₂, C₉₆, C₁₀₂, and C₁₀₈ should be investigated from a thermodynamic and kinetic point of view. A further elaboration of the fullerene formation mechanism in flames based on the work of Pope et al.^{27–29} may help to elucidate this and other striking behavior such as the inversion of the relative abundance of C₇₈ (C_{2v}) and C₇₈ (C_{2v} + D₃) between the flame and the electric arc.

Although it is difficult to make a general comparison of fullerene yields obtained in flame-generated condensable material and electric arc soot based on only one sample from each source, the comparison may nevertheless be meaningful since the substantially higher C₇₀/C₆₀ ratio for flame-generated condensable material observed in this work is consistent with other data reported in the literature for electric arc systems^{30–33} and flame synthesis.^{4–6} Accordingly, the available data indicate that flame-generated condensable material offers an advantage for the generation of higher fullerenes. The optimization of the flame parameters such as pressure, feed gas composition and velocity, and fuel type should allow still larger yields of fullerenes to be achieved. The generation of relatively important amounts of C₇₀O could be of interest because of its potential use as reactant in derivatization chemistry.

Considering the present results and the ease of scaling up the combustion equipment, flame-generated condensable material is an excellent starting material for the preparative isolation of higher fullerenes.

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