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THERMAL DECOMPOSITION OF FULLERENE DERIVATIVES
A synthesis method of new fullerene based molecules

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Abstract

The thermal decomposition of methano-fullerene derivatives such as ethoxycarbonyl methano[60] fullerene and various isomers of bis-(ethoxycarbonyl methano)[60] fullerene leads to new fullerene derivatives, which have been preliminary characterized. The analysis of separated species was performed by UV-VIS, IR, H- and C-NMR, STM, FAB, LDI and MALDI-TOF MS spectroscopy. One of the isolated phases is a C_{122} molecule with a dumbbell-like structure.

Keywords: fullerene dimers, [60]fullerene, thermal decomposition

Introduction

Since the availability of fullerene in macroscopic amounts has been made possible with the method proposed by Kratschmer *et al.* [1] a lot of work has been done in the fullerene chemistry. This interest is justified by the unusual electronic features of the buckminsterfullerene, interesting electronic, optical and catalytic properties [2]. Previous reports on fullerene stability showed that a polymerization reaction can be induced by phonon [3] or electron irradiation [4] and by applying a pressure [5]. We will deal here with another kind of polymerization (although only low molecular mass were obtained) induced by thermal decomposition of fullerene derivatives.

Here, we present the thermal behaviours of some fullerene derivatives such as ethoxycarbonyl methano[60] fullerene noted as **1** and bis-(ethoxycarbonyl methano)[60] fullerene noted hereafter as **2**, **3** and **4**, depending on their structure (Fig. 1). The structures of these compounds consist of cyclopropane derivatives bonded at 6–6 positions (i.e. at the connection between two hexagons) on a fullerene core [6]. These compounds showed a remarkable thermal stability in inert atmosphere. This stability is related to formation, in solid state, of fullerene dimers and other oligomers (up to eight fullerene molecules in a chain as detected by mass spectroscopy). The interest in analyzing such compounds is related to the possibility of synthesis of new fullerene derivatives, by thermal decomposition.

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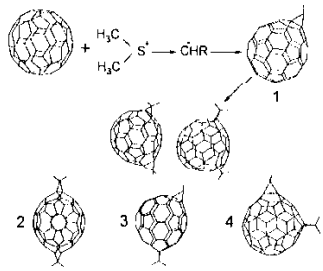


Fig. 1 The synthesis and structures of analyzed compounds

Experimental

The synthesis of compounds **1**, **2**, **3** and **4** were made by a procedure described by Wang *et al.* [7]. The separations were done with a JAI HPLC instrument with JAIGEL 1H/2H columns or by flash chromatography on silica gel. The thermal decomposition curves were recorded on a Ulvac TGD 9600 under static air atmosphere or argon flow (100 ml min^{-1}) at heating rates comprised between 1.25 and 10 K min^{-1}. X-ray powder diffraction experiments were performed with a Mac-Science MXP-18 rotating anode instrument (typically at 40 kV and 150 mA), CuK_α radiation and a graphite diffracted beam monochromator. UV-VIS spectroscopy experiments were performed with a Hitachi U-4000 spectrophotometer, the measurements were done in CS_2 solutions. IR spectra were recorded under ambient conditions for all relevant intermediates with a JASCO FTIR 8900 instrument in the range 4000–400 cm^{-1} on KBr pellets. NMR spectroscopy for H and ^{13}C were performed with a JEOL JM260, 260 MHz for H in $CS_2/CDCl_3$ or CS_2/C_6D_6 solutions. MALDI-TOF MS (Matrix assisted laser – time of flight mass spectroscopy) was used to check the molecular mass for various intermediates with JMS Voyager Elite 337 nm laser. The compounds used were reagent grade. All the solvents were distilled prior to use.

Results and discussion

The thermal decomposition of **1** in static air atmosphere and in argon are represented in Fig. 2. The curves recorded in static air atmosphere showed that after the solvent elimination (at temperatures below 200°C) an exothermic complete decomposition of the analyzed compound takes place. This decomposition takes place presumably by the action of oxygen on the fullerene core and a two step process can be observed on the DTA curve. According to Chen *et al.* [8] the fullerene decomposition in oxygen atmosphere takes place in a two-step process by the formation of a C_{60}–O_{12} which might be a mixture of cyclopentanone-like compounds.

By heating in an argon flow the thermal behaviour was different: after 300°C, an elimination of about 9% (for compound **1**) and 17% in mass (for the compounds **2**,

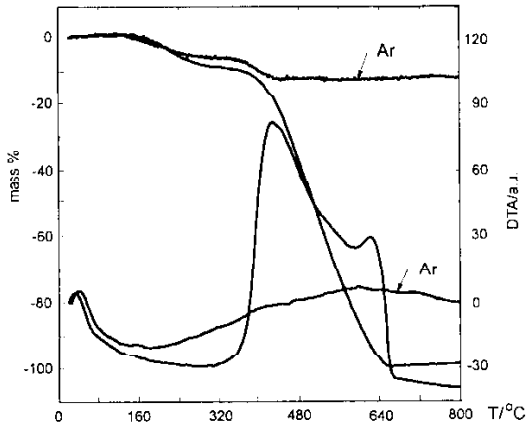


Fig. 2. TG/DTA curves for the decomposition of **1** in oxygen and inert atmospheres

3 and **4**) were recorded. This leads to compounds (noted hereafter as **1'**, **2'**, **3'** and **4'**, respectively) which were stable till about 750°C. The IR spectra for the compounds **1'**, **2'**, **3'** and **4'** showed mainly fullerene absorption lines, indicating that the fullerene core is still intact at these temperatures. XRD patterns for **1'**, **2'**, **3'** and **4'** showed similar features with broad diffraction peaks, suggesting some kind of mesomorphic structures for these intermediates.

Based on the mass loss a decomposition reaction can be proposed:

$$C_{60}(CHCOOEt)_n \rightarrow C_{60}C_n ,$$

where n is equal to 1 for the compound **1** and **2** for the compounds **2**, **3** and **4**, respectively.

MALDI TOF mass spectroscopy (Fig. 3) was undertaken for some of the intermediates isolated at 600°C. These intermediates can be dissolved in CS_2 giving a brown solution. As can be seen from the TOF spectra, various peaks were recorded with an approximate multiples of 720 amu. This suggests that a polymerization occurs conducting to dimers, trimers, etc. and the peaks recorded by TOF-MS can be attributed to these compounds. Definite chemical structures for these compounds are still open to questions, these may be a mixture between various oligomers. H-NMR spectroscopy showed that there are no protons remaining in the structure; the protons connected to cyclopropane rings should appear at about 4.5 ppm as in the parent compounds. Based on these results, we presume that a polymerization occurs by a carbene attack to another fullerene core. The attack position could be one of the reactive 6–6 bonds in fullerene – trans 1, equatorial or the other trans positions – conducting to a mixture of various geometrical isomers (Scheme 1). We suppose that due to steric hindrance effects mainly the trans 6–6 position, either T1 or T2, T3 and T4, would connect to another fullerene core. The separation of the mixture by preparative GPC gave few different compounds, the most interesting being a C_{122} molecule which was also reported recently by Fabre *et al.* [9].

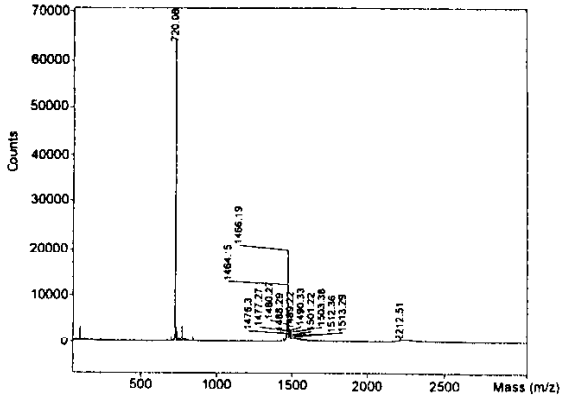
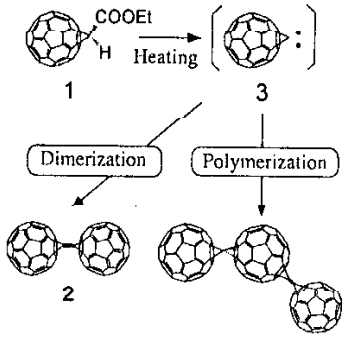


Fig. 3 MALDI TOF MS for the compound **1'**



Scheme 1

In Figs 4 and 5 a MALDI TOF MS for C_{122} are presented. The parent peak is located at 1465.4 amu (calculated for C_{122} 1465.36 amu) with the characteristic isotopic pattern. The IR showed that this molecule is a C_{60} derivative and the same conclusion can be inferred from UV-VIS data which shows two peaks at 430 nm and 700 nm characteristic for dihydrofullerenes.

Concerning these reactions, the thermal analysis calculations (by various methods, integral such as Coats-Redfern [10], Flynn-Wall [11] and Urbanovici-Segal [12] or differential as proposed by Achar *et al.* [13]) gave the results listed in Table 1 (only the CR results are listed, the others gave similar results).

These parameters are describing well the decomposition reaction evolution with a good agreement between the simulated and experimental data. The obtained reaction order is in agreement with a sort of dimerization occurring in the solid state; we note the large activation energy for this reaction, though compensated by a large enough preexponential factor. After 750°C these intermediates start to decompose

with a constant rate, probably by a diffusion limited graphitization of the fullerene core. The isolated residue at 1200°C, noted **1"**, **2"**, **3"** and **4"**, do not exhibit absorption lines in IR and are insoluble in polar and non-polar solvents. The XRD patterns for **1"**, **2"**, **3"** and **4"** show that they are amorphous.

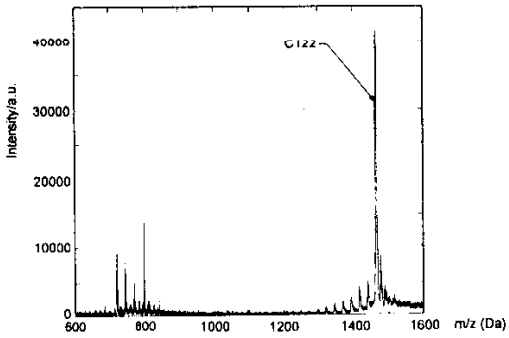


Fig. 4 MALDI TOF MS for the fullerene dimer C_{122}

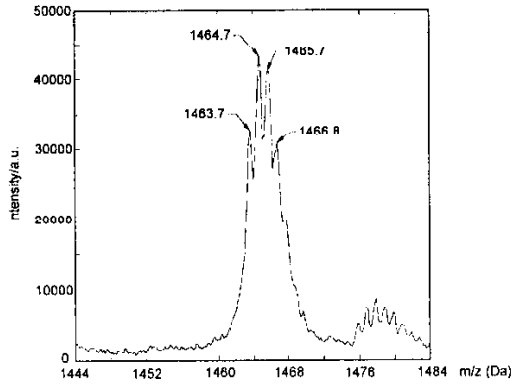


Fig. 5 Details for the dimer peak showing the isotopic distribution

Table 1 Activation parameters obtained by the Coats-Redfern method for the non-isothermal decomposition of **1**, **2**, **3** and **4**

Compounds	1	2	3	4
E/kJ mol^{-1}	214±2	229±4	192±2	227±2
A/s^{-1}	$4.7\pm0.2\cdot10^{13}$	$1.5\pm0.3\cdot10^{16}$	$1.2\pm0.3\cdot10^{13}$	$1.1\pm0.2\cdot10^{16}$
n	1.9±0.1	1.8±0.1	1.8±0.1	1.6±0.1
r	–0.992226	–0.991880	–0.998500	–0.996923

Concerning the values for the reaction orders for the decomposition reactions of **1**, **2**, **3** and **4** we suggest that a diffusional limitation may occur. The dependence between the reaction order and the structure of the starting compounds may be related with a rotation hindrance (Fig. 1).

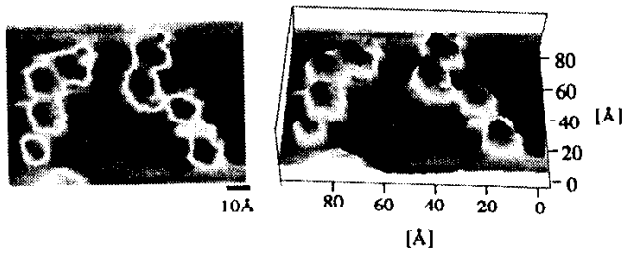


Fig. 6 STM image of pearl-necklace polymer containing C_{60}

The synthesis of fullerene dimers and other oligomers was put in evidence by scanning tunneling microscopy. In Fig. 6 an STM image for a polymer is presented (pyrolytic graphite substrate, 80 K, sample voltage –0.5 V, 0.5 nA).

Conclusions

The fullerene dimerisation was put into evidence in the solid state at a rather low temperature (<600°C). The activation parameters for the decomposition reaction were evaluated and a correlation between the structure and reaction order was proposed. The decomposition reaction of fullerene derivatives can be used for the synthesis of other fullerene derivatives. An all carbon fullerene dimer, C_{122}, with a dumbbell structure was isolated from the reaction products.

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