



Transformation of [60] Fullerene to a Derivative C₁₂₀O by Shock-Compression

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For study on the transformed behaviour of C₆₀ under the high temperature and pressure, C₆₀ fullerene powder was impacted by shock wave at 14.3 gigapascals, generated by a high-speed flyer, in helium. For toluene extraction, the mixtures were isolated using high performance liquid chromatography. The targets, which were obtained from mixtures, were examined with Mass spectrum and other methods. The results showed that most of the C₆₀ were decomposed, a small part transformed to C₁₂₀O and other carbon cluster under the shock wave. The C₆₀ powder transformed to dimeric fullerene oxide C₁₂₀O were also discussed.

Key Words: C₆₀, Shock wave, C₁₂₀O, Transformation.

INTRODUCTION

Since the discovery and large-scale production of fullerene, there has been much interest in high temperature and pressure. Up to now, most of the researches have been devoted to its chemical physical properties. Solid C₆₀ has a closely packed face-centred cubic crystal lattice under the standard conditions, but it transforms to the simple cubic phase between 252 and 258 K¹⁻⁸ and even generates a new crystal lattice^{9,10}. Various carbon materials can be fabricated from C₆₀ fullerene under different temperatures and pressures. Endohedral fullerenes were prepared from C₆₀ and noble gas by Saunders and co-workers¹¹⁻¹⁴ using hydrostatic pressure. Nanocrystalline diamond ceramics were fabricated from a C₆₀ thin film by Hirai and co-workers^{15,16} used a rapid-cooling technique from graphite sheets shock-compressed to 65 gigapascals and 3700 K. Tomotaka Homae, *et al.*¹⁷⁻²⁰ transformed the C₆₀ fullerene powder into highly ordered graphite, giant carbon hollow spheres and other special carbon materials by shock-compression to 57 gigapascals. The aggregate structure prepared under high pressure and temperature using fullerene powder²¹⁻²⁸. He@C₆₀ and He₂@C₆₀ were prepared from C₆₀ and noble gas by Peng and co-workers²⁹ by an explosive method.

In this paper, we used the flyer, which can promote the detonation shock wave impacting on the C₆₀ powder and succeeded in isolating C₁₂₀O that were characterized and investigated with several spectroscopic methods. In addition, the yield of the polymer and the recovery rate of C₆₀ is discussed.

EXPERIMENTAL

C₆₀ (purity 96.5 %, C₆₀O 3.48 %) was prepared. Helium (purity 99.99 %), toluene and other commercial available reagents are at the level of analytical pure.

Design and fabrication of explosion-based experimental apparatus: It consists of a high-strength steel cylindrical (12 mm thick i.d. 52 mm) reaction vessel. A PBX-HMX plug (10 mm thick i.d. 10 mm), whose density is 1.86 g/cm³, beneath which is attached a steel plate (1.0 mm thick 'flying plate'), the distance between the flying plate and C₆₀ is about 10 mm. An electric detonators and explosives were connected by stents of detonator and the reaction vessel was nestled inside an airtight, helium filled obturator.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization (ESI) mass spectrometry were performed on the institute of Chemistry of Chinese Academy of Sciences and the Institute of Chemical Materials of Chinese Academy of Engineering Physics, respectively.

Chromatography were measured on a Elite P230p using a buckyprep column (4.6 mm i.d., 250 mm length, Nacalai Tesque Co.) as the stationary phase and toluene as the mobile phase (flow rate 1 mL/min). Injection volume was 20 μL. HPLC detection of the eluting material was accomplished using UV absorption at 330 nm.

Absorption spectra were obtained with a resolution of 1 nm and using a computer-controlled UNICO, UV-2102PCS spectrophotometer. The wavelength range was 300-900 nm.

Transient absorption spectra in the FT-IR region ($3300\text{--}450\text{ cm}^{-1}$) were measured using a Nicolet 800.

C_{60} powder loading shock wave. 400 mg C_{60} fullerene powder was spread evenly in the bottom of the reaction vessel. The explosive, flying plate, stents of detonator, detonator and reaction vessel was assembled according to Fig. 1. The obturator was evacuated to 400 pascals, then 0.6 millionpascals helium was loaded into the obturator. The obturator was evacuated to 400 pascals and 0.6 millionpascals helium was loaded into the obturator again. After the detonation, the reaction were completed. The soot in the reaction vessel were recovered as a toluene-soluble residue.

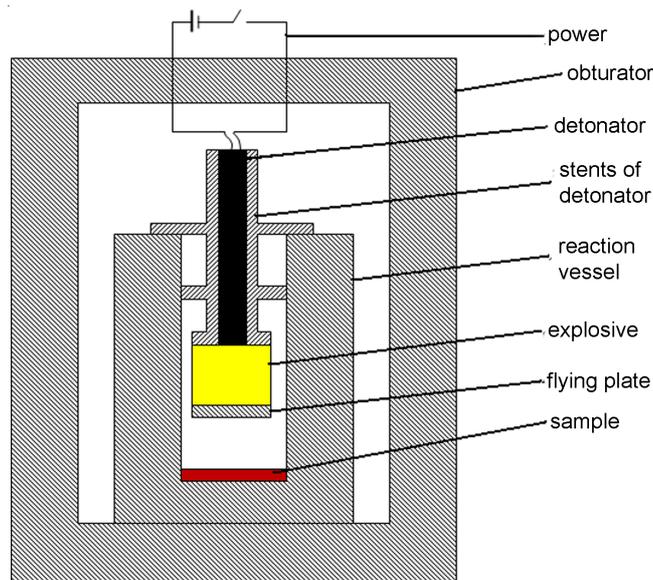


Fig. 1. Experimental setup

Separation of products: The resulting materials were dissolved in toluene and filtered with micron membrane. According to high performance liquid chromatography (HPLC), the solution included unreacted C_{60} , which was about 54 mg, C_{70} , dimer $C_{120}O$ (Fig. 2). No other peaks were observed up to a retention time > 100 min. the recovery rate of C_{60} that is 13.4 % determined by the standard curve. The dimer $C_{120}O$ was separated from C_{60} with respect to the starting materials by six-stage HPLC, respectively. Powder samples of dimer $C_{120}O$ (purity > 99 %) were a yield of 0.13 wt. %.

RESULTS AND DISCUSSION

Chromatography: To demonstrate the changes in sample components after the experiment, the starting materials were detected by HPLC method. The absorption spectra are shown in Fig. 3.

The HPLC chromatogram shows, essentially, C_{60} powder contained only small amount of C_{70} and a small amount of $C_{60}O$, but not other impurities (Fig. 2). The chromatogram of C_{60} powder shows a product peak at a retention time of 18 min and a small shoulder behind of it at 21 min, in addition, a peak of unreacted C_{60} at 8.2 min (Fig. 2). Under similar conditions, if the retention times for C_{60} is 7.4 min that dimer C_{120} and trimer C_{180} are, 14.8 and 29 min³⁰⁻³², respectively. Therefore, this trend suggests that the peak at 18 min is C_{60} dimer, not a

trimer. The peak of $C_{60}O$ almost disappeared in Fig. 2. Therefore, we speculate that dimer $C_{120}O$ was formed with $C_{60}O$ and C_{60} .

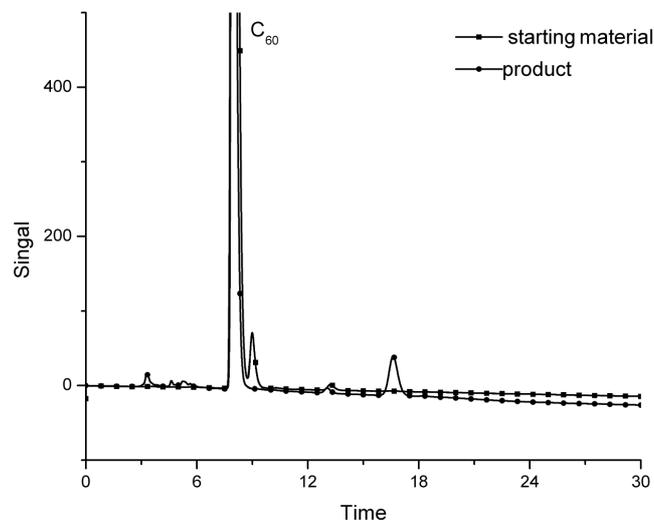


Fig. 2. HPLC patterns of sample before and after shock (Buckyprep column, elution with toluene, optical detection at 330 nm)

Absorption spectra: The absorption spectrum of the dimer $C_{120}O$ in toluene at room temperature ($22\text{ }^{\circ}\text{C}$) was shown in Fig. 3 and was compared with those of the C_{60} . The UV-visible absorption spectra of each of the isomers of $C_{120}O$ were similar to that of C_{60} . Different to the C_{60} , the dimer $C_{120}O$ has a weak absorption peak at *ca.* 700 nm^{31,32}. The absorption bands are at around 288 nm and 328 nm, which are shifted, a slight shoulder at around 433 nm³³. These differences may result from the less symmetrical structure of $C_{120}O$ and broader conjugated system.

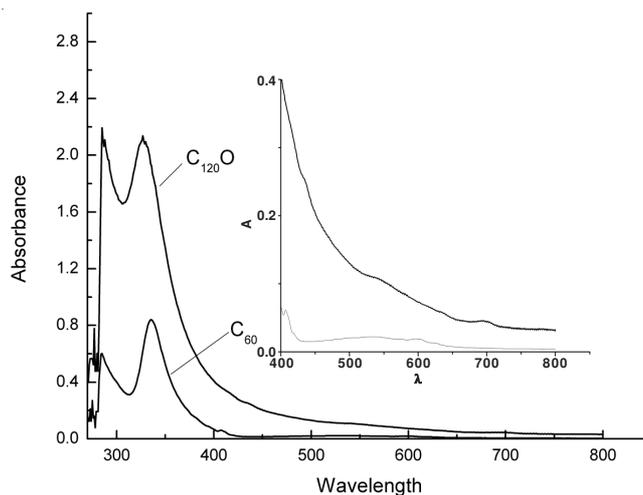


Fig. 3. Absorption spectra of $C_{120}O$ in toluene. Shown in the inset are the absorption spectra of C_{60} in the same solvents for comparison

Mass spectrometry: Several mass-spectral techniques including matrix-assisted laser desorption/ionization and electrospray ionization (ESI) in both positive and negative ion modes showed only one molecular ion peak of $C_{120}O$ at m/z 1,457 (M^+), we increased the laser power in the mass spectrometer to the point where it will partially decompose $C_{120}O$.

The resulting mass spectrum (Fig. 4), shows a strong peak of C₁₂₀O. Two weak peaks of C₆₀ at m/z 721 (M⁺) and C₆₀O at m/z 737 (M⁺) were also observed. The peaks at m/z 721 and 737 indicate a fragmentation of C₁₂₀O into C₆₀ and C₆₀O. Evidently, C₁₂₀O is completely decomposed into the molecules/ions under the MS conditions. On the other hand, the dimeric fullerene oxide C₁₂₀O, with stronger cage-to-cage furanoid links readily yield dominant parent ion peaks in the mass spectra. Taking into account the other experimental data we proposed a structure as shown Fig. 5³³.

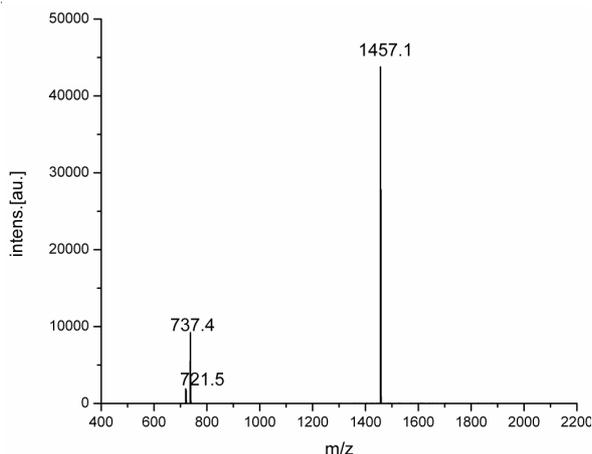


Fig. 4. Positive-ion electrospray ionization two stage mass spectrum of the C₁₂₀O. The fragment corresponds to a C₆₀ loss from C₁₂₀O

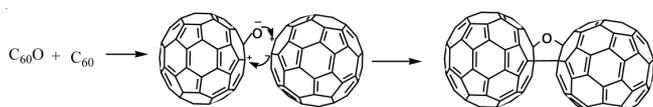


Fig. 5. Proposed reaction mechanism for the formation of C₁₂₀O

Vibrational spectroscopy: FT-IR spectra were obtained with a resolution of 3 cm⁻¹ from powder samples (pressed in pellets embedded in KBr pellets for the IR measurements) on a Nicolet 800 spectrometer. The spectrum of C₁₂₀O (Fig. 6), shows a different of the original C₆₀ vibrations spectroscopy. In particular, the bands between 1100-1000 cm⁻¹ are near the characteristic region of the C-O-C stretching vibration of cyclic ethers.

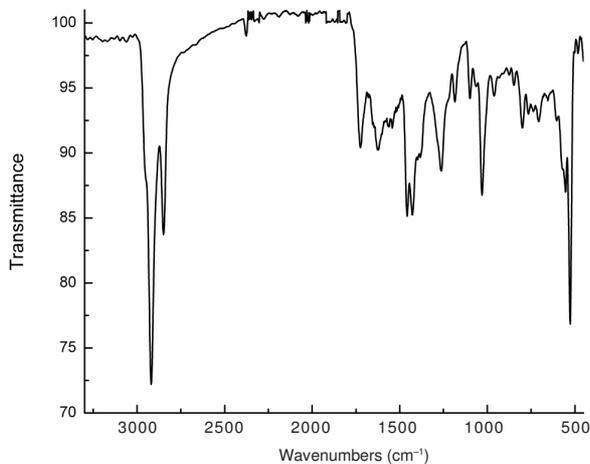


Fig. 6. FT-IR absorption spectra of C₁₂₀O in KBr all are measured at room temperature

Different conditions: In this study, the flight distance of flyer, quality of explosives and flyer was limited and then the intensity of the shock wave in the sample was controlled. The results were shown in Table-1.

TABLE-1
RECOVERY RATE OF C₆₀ AND THE YIELD OF C₁₂₀O UNDER DIFFERENT CONDITIONS

Order	Size of explosive (mm)	Size of flyer (mm)	Distance (mm)	Experimental environment	Recovery rate of C ₆₀ (%)	Yield of C ₁₂₀ O (%)
1	φ10×10	φ10×2	5.0	Frozen water	26.30	13.64
2	φ10×10	φ10×2	5.0	Helium	16.31	0.35
3	φ10×20	φ10×2	5.0	Helium	14.62	0.13
4	φ10×20	φ10×2	10	Helium	7.13	0.05
5	φ10×20	φ10×1	10	Helium	6.07	0.03

As can be seen from Table-1, the recovery of C₆₀ range from 6.07 to 26.30 % and the yield of C₁₂₀O range from 0.03 to 13.64 %. On the other worlds, the most of C₆₀ was decomposed, a small part is on the formation of polymers and other products. If shock wave is the certain intensity, the yield of C₁₂₀O is the highest in the experiments environment of frozen water. This may be the thermal stability of C₁₂₀O, the role of shock wave within a few microseconds, but the explosion will produce a high temperature environment then the C₁₂₀O that generated not long can be broken down. The frozen water can lower the overall system temperature quickly, which improve the yield of C₁₂₀O and the recovery of C₆₀ greatly. In the helium environment, the 2nd to 5th experiment, the recovery of C₆₀ from 16.31 to 6.07 % and the yield of C₁₂₀O from 0.35 to 0.05 %. The recovery of C₆₀ and the yield of C₁₂₀O decreases with the increase of the shock wave strength. As the shock strength increases, the temperature and pressure of sample increases too, the C₆₀ and the C₁₂₀O were destructed enhanced. Compared the recovery of C₆₀ to the yield of C₁₂₀O, the thermal stability of C₆₀ is more than C₁₂₀O.

Conclusion

In this study, a novel explosion-based method that C₆₀ powder transformed to dimeric fullerene oxide C₁₂₀O was developed. The work were experimentally studied at different shock wave. The chromatograph of C₆₀ powder have been changed in composition. The C₁₂₀O were purified by HPLC and examined by some methods. The targets were dissected and supported.

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