

Joint Synthesis of Small Carbon Molecules (C_3 - C_{11}), Quasi-Fullerenes (C_{40} , C_{48} , C_{52}) and their Hydrides

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Abstract Earlier small carbon molecules C_2 - C_{13} as cations and anions in hot carbon plasma and flame gases were detected only. From large amount of quasi-fullerenes ($C_{20 < n < 60}$) revealed in mass spectra of carbon vapor only C_{20} and C_{36} were synthesized. Therefore problem of creation of new methods for synthesis of carbon molecules is considered extremely important. By us new reactionary conditions of pyrolysis of hydrocarbons, in particular benzene is developed. A main distinctive feature of this pyrolysis is opportunity of separate localization of condensed products and soot. Mass spectra of toluene and ethanol solutions of obtained products contain intensive peaks with m/z values appropriate anions of small molecules ($C_3 - C_{20}$), them hydrides (C_5H_2 , $C_{10}H_4$, $C_{14}H_4$, $C_{16}H_8$, $C_{18}H_2$) and cations of molecules (C_6 , C_7 , C_{15} , C_{17}). For the first time in products of pyrolysis quasi-fullerenes C_{40} , C_{48} , C_{52} , C_{54} , C_{56} and C_{58} are found out. Thus, small carbon molecules and quasi-fullerenes in reactionary conditions excluding carbon evaporation can be formed.

Keywords: small carbon molecules, quasi-fullerenes, hydrides, synthesis, pyrolysis, benzene

1. Introduction

After discovery of fullerene C_{60} [1] and its higher homologues (C_{70} , C_{76} , C_{78} , C_{84} and more) [2,3] the synthesis of quasi-fullerenes $C_{20 < n < 60}$ (in which isolated pentagons are absent) and small carbon molecules $C_n < 20$ is considered as the basic challenge to modern chemical community. The fate of small carbon molecules C_2 - C_{20} and quasi-fullerenes found out simultaneously with clusters C_{60} and C_{70} in carbon vapors [1,2] by means of a mass spectrometric method [4] has appeared less bright in comparison with fullerenes C_{60} and C_{70} . Only C_{20} [5] of many quasi-fullerenes detected in mass spectra [6,7] in preparative amounts was synthesized. Quasi-fullerenes C_{28} and C_{50} are obtained only as their derivative: endohedral metallofullerene (MC_{28}) [8] and decachlorofullerene ($C_{50}Cl_{10}$) [9]. The fate of quasi-fullerene C_{36} synthesized by Piskoti [10] by arc-discharge method is still unclear because in [11] by the same reactionary conditions only the hydrides ($C_{36}H_4$, $C_{36}H_6$) and oxyhydrides ($C_{36}H_4O$, $C_{36}H_6O$) as main products were revealed. Despite intensive signals in mass spectra [6,7] molecular clusters C_{26} , C_{30} , C_{34} , C_{38} , C_{42} , C_{46} , C_{48} , C_{52} , C_{54} , C_{56} , C_{58} and their endohedral derivatives were not found out yet. Moreover, assumed as most stable clusters C_{32} and C_{44} , as well as C_{50} , which are referred to the category «magic» in a molecular form also are not synthesized yet.

The small carbon molecules such as C_2 and C_3 , C_4 and C_5 together with polyynes (HC_nN) ($n \leq 11$) only in the circumstellar medium [12] are found out. In laboratory conditions these carbon molecules only in solid argon

about 15 °K [13,14,15,16,17] were isolated. However a time of life of such frozen clusters is extremely small (~ 10 ms). Even and odd ions of small carbon molecules in laboratory conditions in mass spectra of carbon vapour are detected only. It is considered [18] that the hot carbon plasma contains linear chains $C_1 - C_{10}$, where C_3 cluster is contained in the greatest amount (~ 70 %) [19]. These chains C_1 - C_{10} as a chemical radicals to radical polymerization are extremely inclined and can be stabilized owing to the interaction of trailer atoms of carbon with H, N or CN with formation of relatively more stable polyynes or cyanopolyynes [18,20]. Therefore problem of creation of a new method for synthesis of carbon molecules is considered extremely important. The absence of appreciable progress in synthesis C_n ($n < 20$) and quasi-fullerenes is probably determined by domination of hypothesis that the atoms of carbon are necessary always for growth of carbon molecules and their generating is possible only under carbon sublimation.

Here we first represent a new method of generation of small carbon molecules and quasi-fullerenes as well as their hydrides in which the stage of high-temperature sublimation of carbon is completely excluded. In mass spectra of products of benzene pyrolysis the ions of all kinds of carbon molecules are found out:

- small carbon molecules ($C_3 - C_{20}$);
- quasi - fullerenes C_{21} , C_{23} , C_{33} , C_{40} , C_{48} , C_{52} , C_{54} , C_{56} and C_{58} ;
- hydrides of small carbon molecules, for example, C_5H_2 , $C_{10}H_4$, $C_{14}H_4$, $C_{16}H_8$ and $C_{18}H_2$;
- hydrides of quasi - fullerenes ($C_{25}H_2$, $C_{27}H_2$, $C_{31}H_4$, $C_{33}H_4$, $C_{37}H_6$, $C_{39}H_6$, $C_{43}H_8$, $C_{45}H_8$, $C_{47}H_{10}$ and $C_{49}H_{10}$).

2. Materials and Methods

Experiments on the typical apparatus for pyrolysis of hydrocarbon vapors were carried out. Tests by means of changing of temperature in the most highly temperature zone A of reactionary space, the concentration and flow rate of introduced in the horizontal tubular quartz reactor reagent (benzene (ESSO Deutschland GmbH)) were realized. The maximum (T_2) and minimum (T_1) temperatures in zone A were 1100 and 1000 °C respectively. Concentration of reagent (benzene) was varied in the range of 0.05-0.2% and the flow rate of carrier gas (Ar) range 100-300ml / min. Products B and C condensed and deposited in low temperature zones B and C respectively reactionary space for the study were used. The temperatures in the zones B and C were 400 and 70 °C, respectively. Products of several (8-10) tests obtained at given temperature taken from zones B and C were mixed. Condensed substances by toluene from products zone B were extracted. Product of zone C in ethanol was dissolved. By a method of matrix-activated laser (nitrogen, 337nm) desorption/ionization (MALDI) (Bruker Daltonics flexAnalysis) obtained extracts were investigated. The extract on a metal substrate is located and after evaporation of the solvent to a laser irradiation was exposed.

XPS valence-band and core-level spectra of the product synthesized were measured using the UHV-Analysis-System assembled by SPECS Surface Nano Analysis Company (Germany). The system is equipped with a PHOIBOS 150 hemispherical analyzer. A base pressure of a sublimation ion-pumped chamber of the system was less than 5×10^{-10} mbar during the present experiments. The Mg $K\alpha$ radiation ($E=1253.6\text{eV}$) was used as a source of XPS spectra excitation. The XPS spectra were measured at the constant pass energy of 25eV. The energy scale of the spectrometer was calibrated by setting the measured Au $4f_{7/2}$ and Cu $2p_{3/2}$ binding energies to $84.00 \pm 0.05\text{eV}$ and $932.66 \pm 0.05\text{eV}$, respectively, with regard to E_F . For investigated sample, all the spectral features are attributed to the constituent element core-levels or Auger lines.

The composition of volatile products of thermal decomposition of product B_2 was investigated by a method temperature-programmed desorption mass spectrometry (TPDMS). Thermodesorption measurement was carried out on monopole mass spectrometer MX-7304A (Sumy, Ukraine) with impact electron ionization (EI). A sample at the bottom of molybdenum-quartz ampoule was evacuated at room temperature up to $5 \cdot 10^{-5}$ Pa. The linear heating of a sample up to 650 °C was carried out with speed $0.15\text{K} \cdot \text{s}^{-1}$. The volatile thermolysis products passed through a high-vacuum valve (5.4mm in diameter) into the ionization chamber of the mass-spectrometer. The ion currents of the desorption and thermolysis products were recorded with a secondary-electron multiplier VEU-6. Mass spectra were registered in a range 1-210amu.

3. Results and Discussion

Shortly after discovery [1] and synthesis C_{60} by the electro-arc method [2] method of heat treatment of hydrocarbons was used as an alternative [21,22]. However

fullerenes under usual method of pyrolysis (continuous flow pyrolysis, CFP) [22] and under burning of hydrocarbons [21] in small amounts are formed only. Products obtained at heat treatment ($< 1200\text{ }^\circ\text{C}$) of naphthalene $C_{10}H_8$, its dimer and corannulene [22,23] as well as benzene, cyclopentadiene [24], ethylene and acetylene [25], up to $\sim 1\%$ C_{60} contain only. Besides fullerene C_{70} at the presence of metallic (nickel) catalyst is formed only [26]. Hence, known methods of hydrocarbons pyrolysis are low effective. Though the obtained experimental results convincingly demonstrate that the formation of C_{60} and C_{70} can be realized in the absence of atoms (or clusters) of carbon from hot carbon gas.

Earlier by us [27,28] it was proposed the polycondensation mechanism of carbon molecules and nanostructures growth at hydrocarbons pyrolysis according to which the escalating of bonds C-C with formation of graphene net can be fulfilled due to a reaction of dehydropolymerization (polycondensation) mainly of benzene molecules and products of their partial decomposition. The curvature of graphene net is created at the expense of trailing, peripheral sp^3 - hybridization atoms of carbon. At pyrolysis (as well as at cracking) of hydrocarbons the escalating of bonds C-C is realized also according to reaction of polymerization with formation of polyaromatic hydrocarbons. The reactions of polycondensation and polymerization are competitive in the given process and, therefore, one of them is obviously possible for optimizing by means of a variation of reactionary conditions.

By the systematic investigation [27,28,29,30] we have studied the influence of various technological parameters and reactionary factors on obtained product composition and, in particularly, on the composition of condensed products. As a result of these researches the new method of heat treatment of organics vapours was developed. This method differs from two already of known processes of pyrolysis which are used long ago and for different purposes. Flash vacuum pyrolysis (FVP) [31,32] is used mainly to prepare small size, highly reactive objects. Continuous flow pyrolysis (CFP) [22,31] is employed for obtaining both carbon nanostructures of different morphologies and large polyaromatic molecules. Novel method of pyrolysis allows obtain simultaneously not only carbon nanostructures but also fullerene C_{60} and fullerenes hydrides [30,33,34,35].

Distinctive feature of our method is the possibility of partial division of products of deposition and condensation, their subsequent localization in different zones of reactionary space. A part of condensation substances and pyrolytic soot are taken out in a gas reactionary flow from a zone A and are located in more low temperature zone B. Other part of vapour-like products (sometimes along with very small amount of pyrolytic soot) is condensed in the special zone C cooled reactionary space. The composition of products zones B and C and their amounts on temperature in a zone A depend on essentially. The results of study of two products (B_1 and B_2) and one product C condensed in zones B and C respectively are presented. A product B_1 at more low temperature in a zone A, then product B_2 was obtained. The reaction of polymerization in comparison with competitive reaction of polycondensation in the thermodynamic relation should be more preferable at lower temperature. Therefore according to the

mechanism, assumed by us, the product B_2 should contain mainly carbon clusters and product B_1 are hydrides of carbon clusters.

Toluene extract from B_1 by method of mass spectrometry matrix-assisted laser desorption/ionization (MALDI) was investigated. It is visible (Figure 1) that mass spectra of positive and negative ions cardinaly differ.

In group of positively charged clusters (Figure 1 (b)), beginning from the cluster with value m/z 228 and finishing by cluster with value m/z 696, there is a precise periodicity in growth of their size. Every subsequent cluster on 24 or 26 units grows only. Clusters with values m/z 228, 252, 276, 624, 648, 672 and 696, probably,

correspond to molecules C_{19} , C_{21} , C_{23} , C_{52} , C_{54} , C_{56} and C_{58} . (Usually believe that clusters C_{52} , C_{54} and C_{56} , C_{58} which detected in mass spectra of C_{60} are products of its decomposition) [36]. Peaks with m/z from 302 up to 598 can belong both as a little hydrogenated odd ($C_{25}H_2$ - $C_{27}H_2$ - ... - $C_{31}H_4$ - $C_{33}H_4$ - ... - $C_{37}H_6$ - $C_{39}H_6$ - ... - $C_{43}H_8$ - ... - $C_{45}H_8$ - ... - $C_{47}H_{10}$ - $C_{49}H_{10}$) as even clusters, but with the large contents of hydrogen ($C_{24}H_{12}$ - $C_{26}H_{12}$ - ... - $C_{48}H_{22}$). Closing one in the given group of peaks is a cluster with m/z 748 which corresponds to hydride $C_{60}H_{28}$. It is possible, that positively charged cluster with m/z 123 correspond to hydride ($C_{10}H_4$) of small molecule C_{10} .

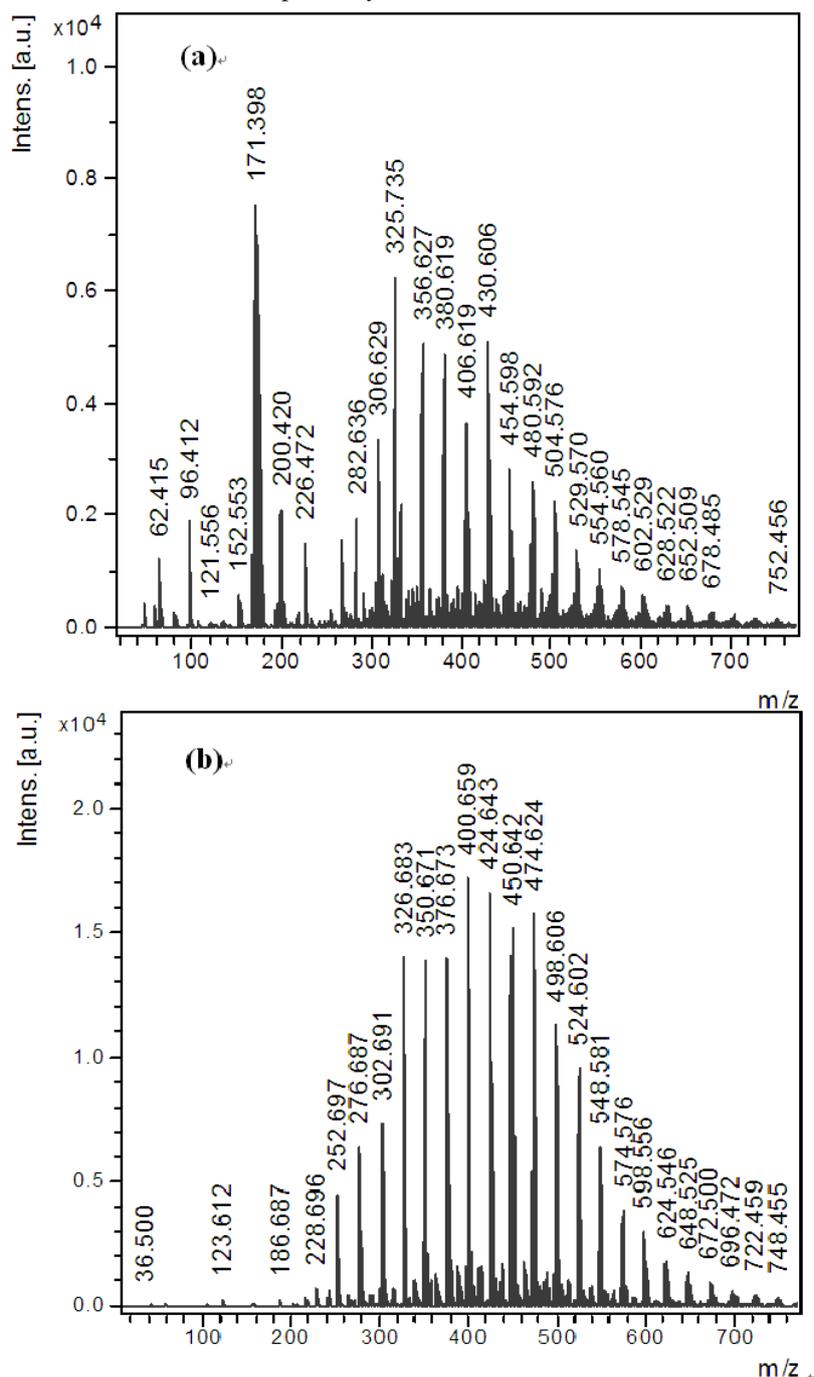


Figure 1. Mass spectra of toluene extract from the product B_1 : negative ions (a), positive ions (b)

In a spectrum of negative ions (Figure 1 (a)) peaks with m/z 172 and 326 considerably dominate and they can correspond to partially hydrogenated molecules $C_{14}H_4$, and $C_{27}H_2$. The less intensive peaks with m/z 62, 200 and

96, probably, also display presence of hydrides C_5H_2 , $C_{16}H_8$ and molecule C_8 at a product B_1 . At a spectrum also there is a group of peaks, m/z values which differ on 24 or 26 units. Among them there is a distinct peak with value

m/z 480 that can correspond to quasi-fullerene C_{40} . Only cluster $C_{27}H_2$ is detected in both spectra. Positively charged cluster C_{52} (m/z 624) is shown in a spectrum of negative ions as hydride $C_{52}H_4$ (m/z 628). Remarkable, that negatively charged clusters ($C_{30}H_{20}$ and $C_{34}H_{22}$) are, as a rule, more hydrogenated than appropriate positively charged ($C_{30}H_{16}$ and $C_{34}H_{16}$).

From a product B_2 obtained at the more high temperature T_2 in a zone A soluble in toluene substances were extracted and deposited by ethanol. Deposited powder B_2 was again dissolved in toluene and mass spectra of this solution are submitted in **Figure 2** (anions) and **Figure 3** (cations). In a spectrum of negative ions

(**Figure 2**) there is a group of peaks, in which the periodicity of change of m/z values makes 12 units. Such m/z values as 36, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, 168 and 180 (**Figure 2** (b)), undoubtedly, concern to small carbon molecules C_3 , C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} , C_{11} , C_{12} , C_{13} , C_{14} and C_{15} accordingly. It is considered [37], [38] that in the carbon vapour formed line and ring C_n ($2 > n < 20$) clusters with carbon atoms in the sp -hybridization. Clusters with m/z 193, 205, 217, 229, 241, 255 and 326 can correspond to anions $C_{16}H$, $C_{17}H$, $C_{18}H$, $C_{19}H$, $C_{20}H$, $C_{21}H_3$, $C_{27}H_2$ which at ionization by laser of minimally hydrogenated cyclic molecules (or linear polyynes [39] $C_{16}H_2 \dots C_{27}H_2$ are formed.

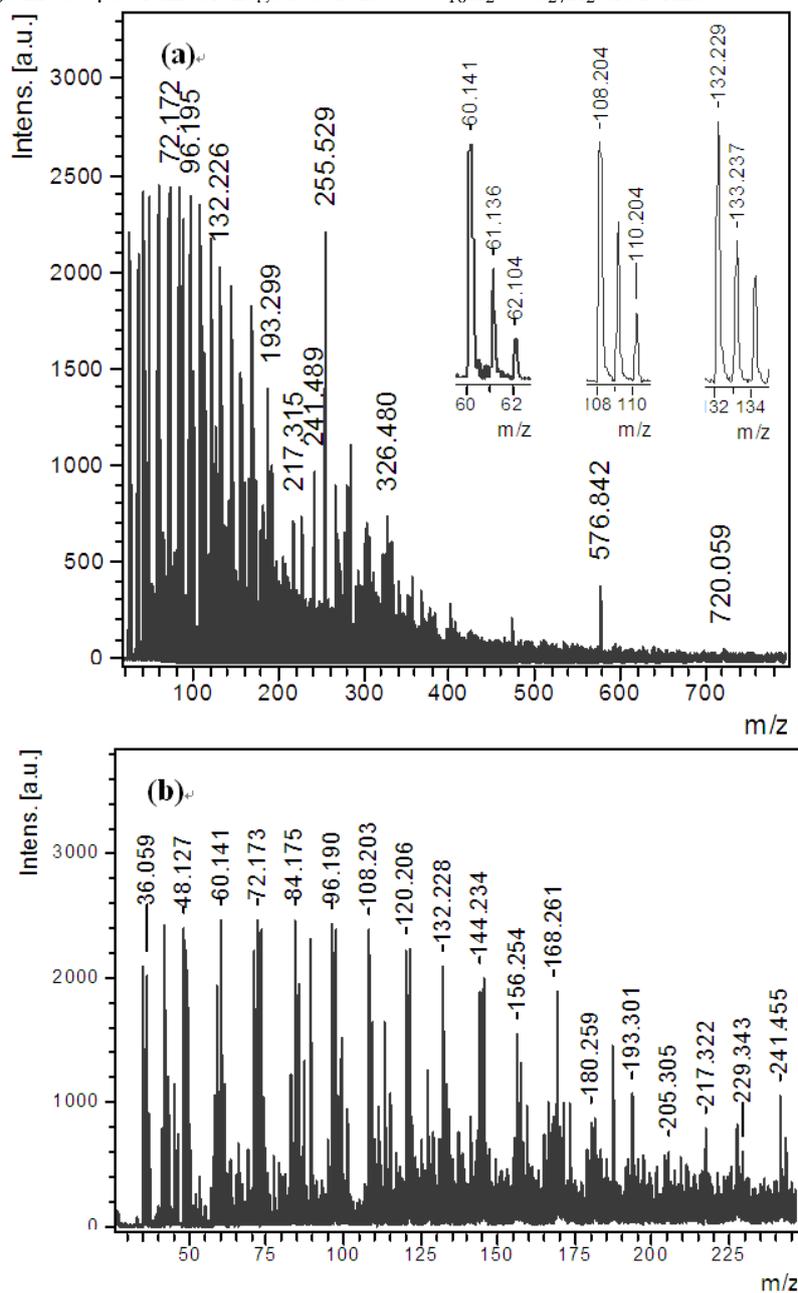


Figure 2. Anions mass spectrum of toluene extract from the product B_2 with the expansions around the m/z 60, 108, 132 peaks in the inset (a); m/z 25-245 region (b)

In the spectrum of negative ions the peaks with m/z 720 and 576 are present, which may correspond to fullerene (C_{60}) and quasi-fullerene C_{48} . The peak with m/z 326 ($C_{27}H_2$) was also detected in the mass spectrum of the product B_1 (**Figure 1**). Note, that in the mass spectrum of high-resolution (**Figure 2** (a), inset) it can be seen that the

molecules C_5 , C_9 and C_{11} are hydrogenated, because for these molecules the ration, that is characteristic for the natural isotopic distribution of carbon [40], is a garbled. The formation of small carbon clusters as a result of degradation of C_{60} is unlikely. It is likely that the clusters C_3 - C_{15} and their hydrides are new products of the

pyrolysis of benzene, which are formed at a temperature of 1000 °C, eliminating the evaporation of carbon.

Spectrum of positive ions (Figure 3) contains three intensive peaks with m/z 84, 133 and 219, which can

display molecules C_7 , C_{11} (or $C_{11}H$) and $C_{18}H_3$. Just these clusters detected by mass spectrometric method as cations as anions, are, probably, most stable among small carbon molecules.

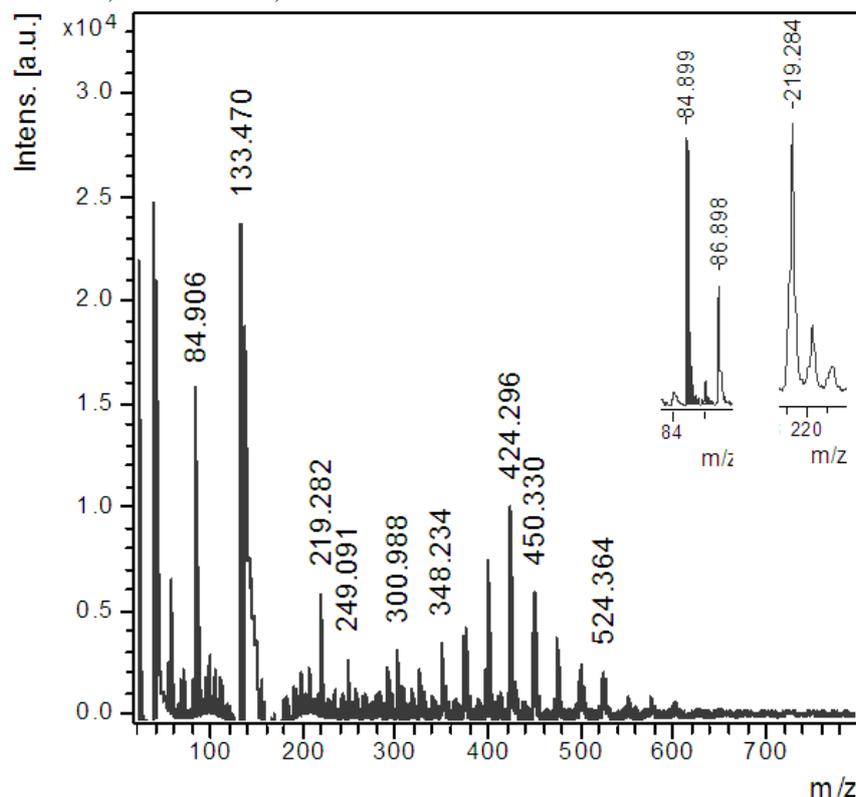


Figure 3. Cations mass spectrum of toluene extract from the product B_2 with the expansions around the m/z 84, 219 peaks in the inset

Cation mass spectra of high resolution (Figure 3, inset) demonstrates that odd cluster C_7 partially hydrogenated up to C_7H_2 but cluster with even number carbon atoms ($n=18$) is only hydrogenated.

So, the products B_1 and B_2 deposited together with soot contain small carbon molecules from C_3 up to C_{15} , quasi-fullerenes C_{21} , C_{23} , C_{40} , C_{48} , C_{52} , C_{54} , C_{56} , C_{58} , fullerene C_{60}

and hydrides of carbon molecules of different sizes, particularly, $C_{14}H_2$, $C_{16}H_8$, $C_{18}H_2$, $C_{20}H_2$. If the small carbon molecule can only be a cyclic structure with polyynic (even molecules C_{2n}) or cumulenonic bonds, the dihydrides of these molecules can be both cyclic and linear (polyynes) structures.

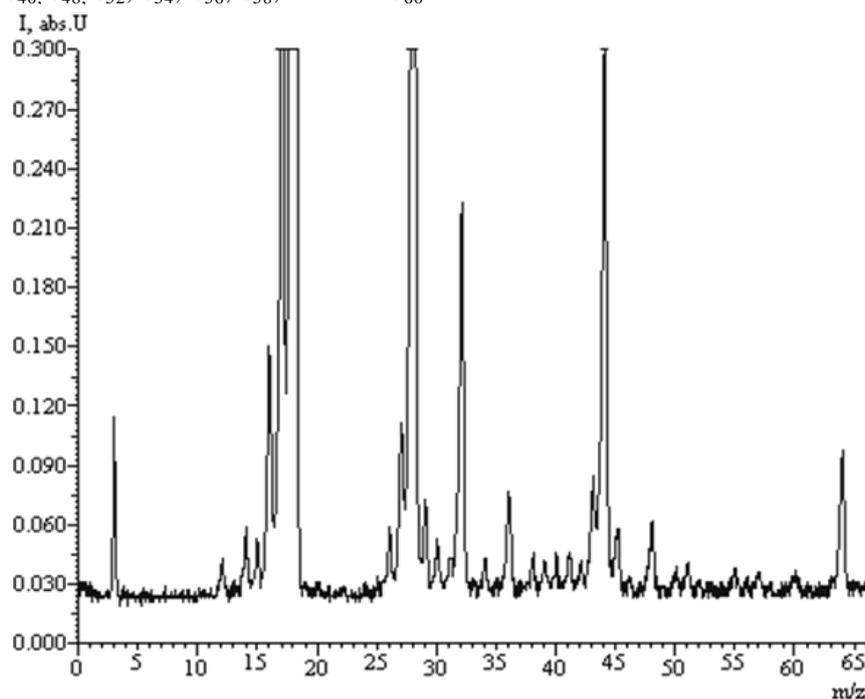


Figure 4. Representative thermodesorption mass spectrum (EI) at 200 °C of the powdery product B_2

The hydrogen as can see from a curve of thermodesorption begins allocation from a powdery product B₂ already at room temperature (in vacuum) and in enough large amount. It is improbable that PAHs in a similar way can be decomposed. Mass spectrum (EI) at 200 °C of a powdery product B₂ on Figure 4 is presented. Intensive peaks with 18, 28 and 44 amu correspond to molecular ions desorbed water, nitrogen and carbon

dioxide, respectively. Ions with 31 and 45 amu as fragments of decomposition of molecules of the solvent (ethanol) are characteristic for EI mass spectra. The basic products of thermodesorption are carbon clusters C₃, C₄ and C₅H₂ with molecular mass 36, 48 and 64 accordingly. It is possible that detected on MALDI mass spectra of a product B₂ carbonaceous and hydrogenated molecules are thermo unstable already at low temperatures.

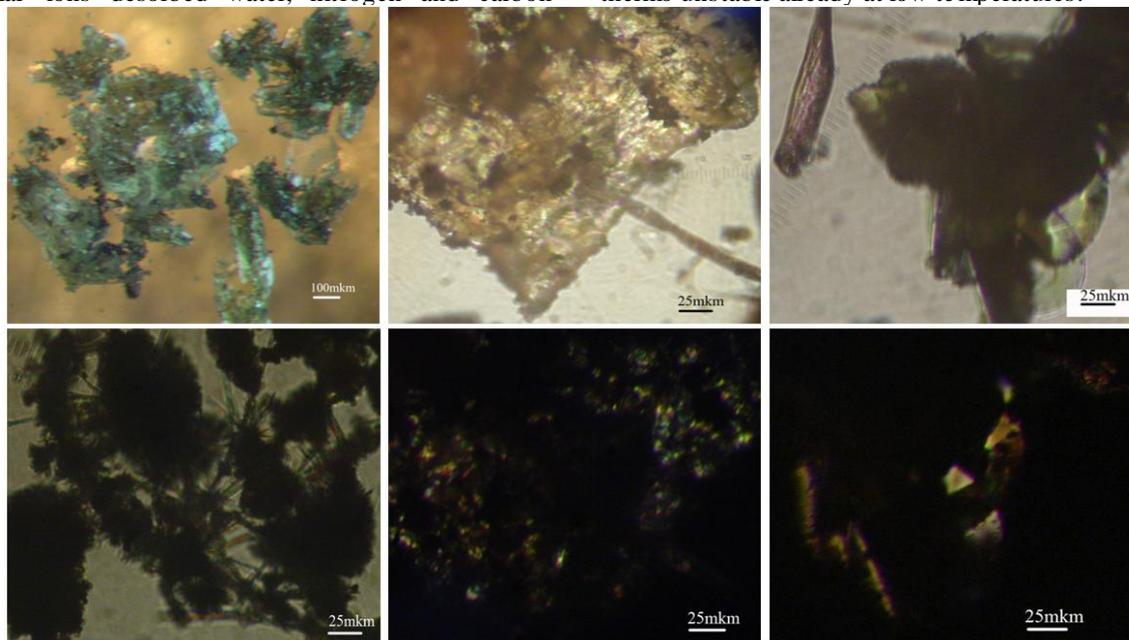


Figure 5. (Color online) Optical microscopy images in polarized light of the white transparent crystalline plates of product C

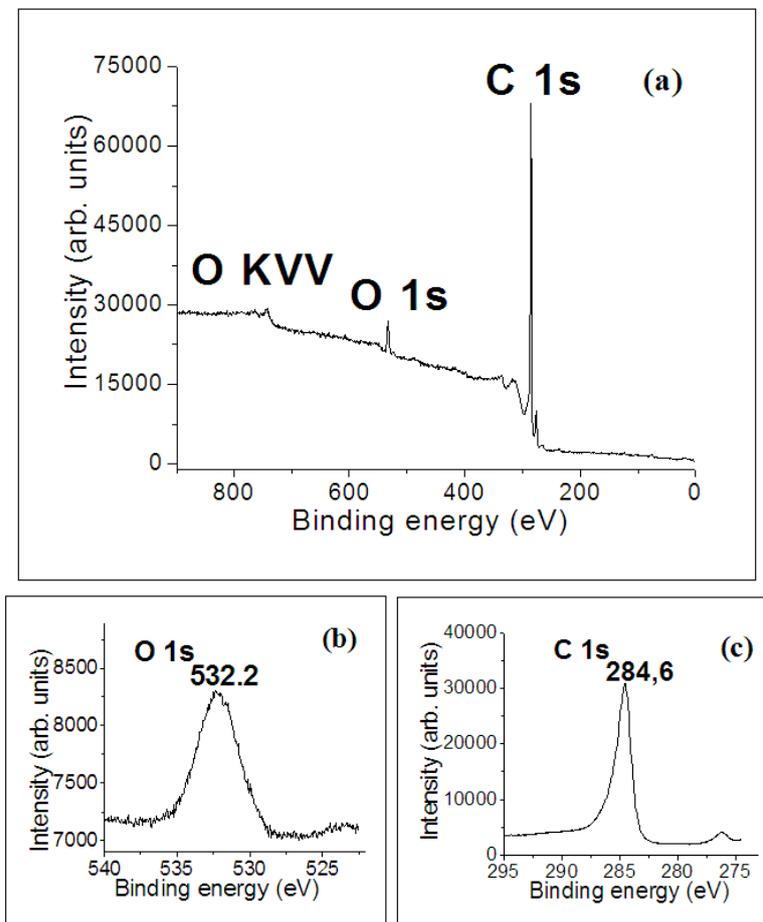


Figure 6. XPS survey (a) and core level O 1s (b), C 1s (c) spectra of white transparent crystalline plates into product C

Product of C represents of white crystalline transparent plates (Figure 5) which are formed at any regime of heat treatment of benzene vapors. Sometimes these plates are located on a surface of deposited in a reactionary C zone soot and are taken with the help of optical microscope.

White plates are easily dissolved in many solvents (ethanol, benzene, acetone). A study of white plates by the XPS method was shown (Figure 6 (a, b, c)) that they consist of carbon (96.5%) only. Broadened peak of oxygen at 532.2eV indicates on its adsorbed state.

Mass spectra of an ethanol solution of this product are submitted in Figure 7 (anions) and Figure 8 (cations). It is

visible, that the spectrum of negative ions (Figure 7 (a, b)) contains mainly a group of the most intensive peaks, which, as well as in mass – spectrum of a product B₂, correspond to anions of small carbon molecules from C₃ up to C₂₀. In a spectrum peak with m/z 576 distinctly also is seen, which thin structure (Figure 7 (a), inset) a somewhat differs from isotopic distribution of carbon. Probably, this cluster as quasi-fullerene C₄₈ partially hydrogenated up to C₄₈H₂. There is a peak with m/z 846, characteristic for C₇₀H₆ at a spectrum also.

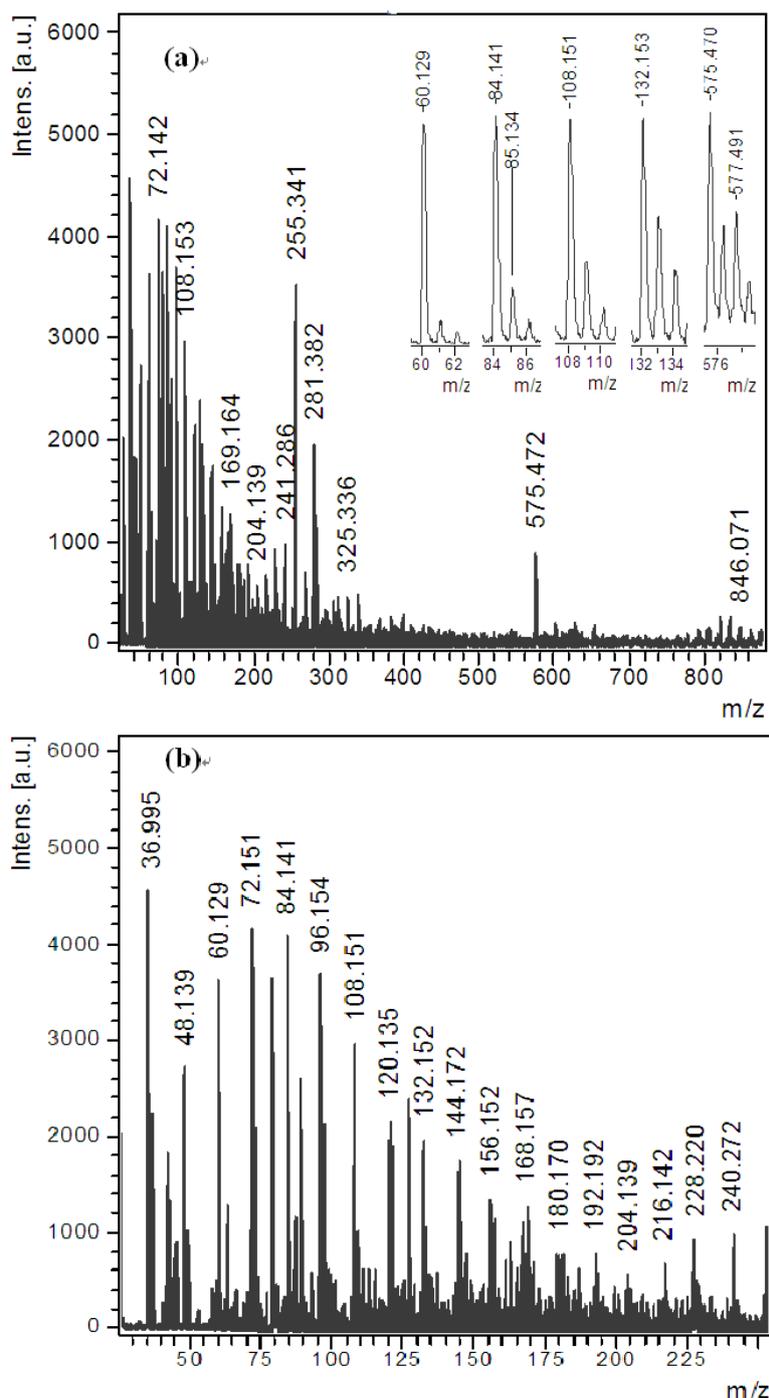


Figure 7. Anions mass spectrum of ethanol extract from the product of low temperature C zone with the expansions around the m/z 60, 84, 108, 132, 576 peaks in the inset (a), m/z 25-250 region (b)

At mass spectrum of positive ions (Figure 8 (a, b)) peaks with m/z 85, 97 and 109 are present, which can correspond to ionizing by proton molecules C₇, C₈ and C₉.

Four distinct peaks at m/z 72, 120, 180 and 204 correspond to molecules C₆, C₁₀, C₁₅ and C₁₇. Note, that in the mass spectrum of high-resolution (Figure 8 (a), inset)

it can be seen that the molecules C_{15} and C_{17} are minimally hydrogenated, because for these molecules the ration, that is characteristic for the natural isotopic distribution of carbon [40], is a bit garbled. Thin structure of C_{18} (Figure 8 (a), inset) demonstrate that this molecule

is hydrogenated only. Hence, the small carbon molecules are detected mainly as anions but their hydrides are as cations. Only molecules C_6 , C_{10} , C_{15} and C_{17} are detected in both spectra.

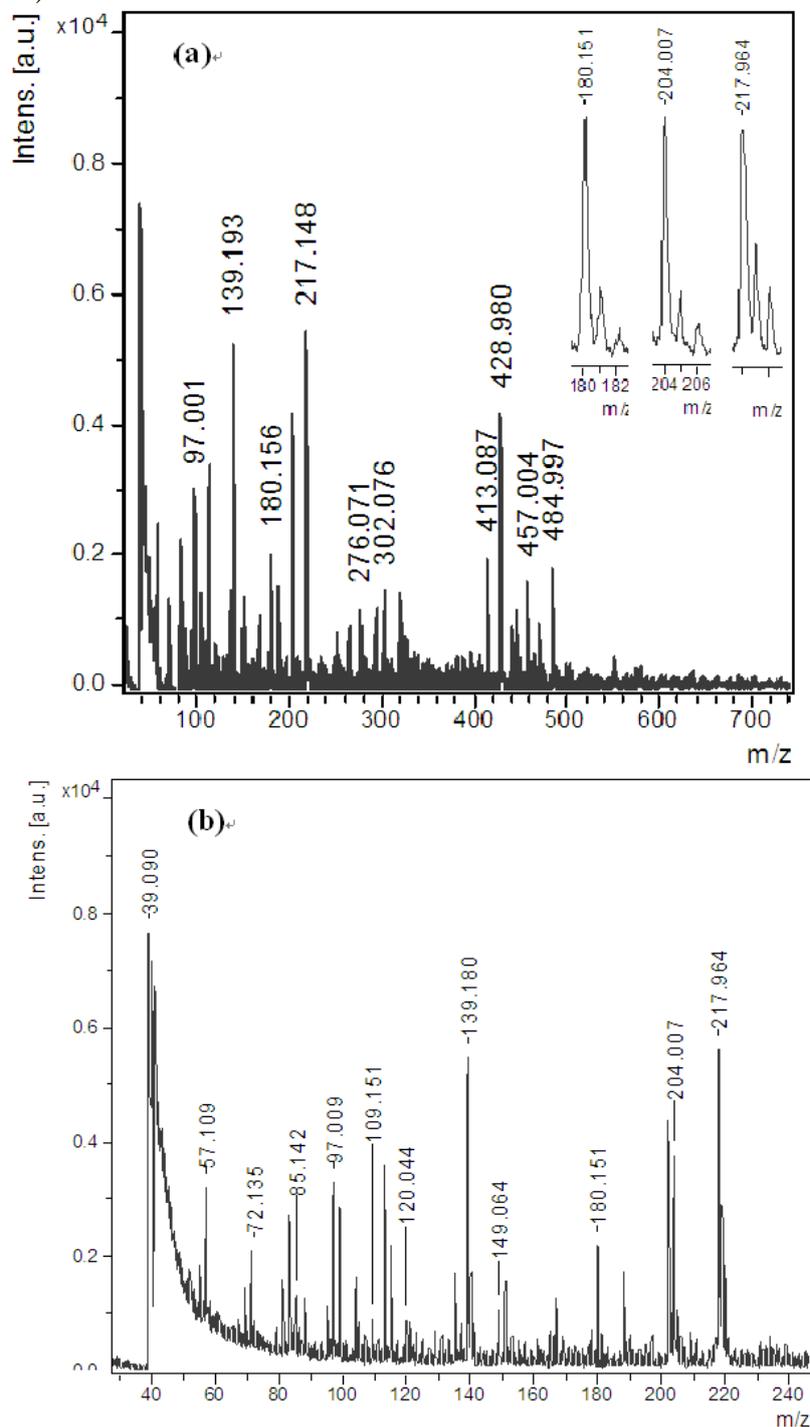


Figure 8. Cations mass spectrum of ethanol extract from the product of low temperature C zone with the expansions around the m/z 180, 204, 217 peaks in the inset (a), m/z 25-245 region (b)

It is unlikely that in the products B_2 and C contain practically the full spectrum of small carbon molecules. It is possible that the product B_2 contains mainly molecule C_7 , C_{11} and C_{18} , which are recorded in the mass spectra in the form of cations (Figure 3) and anions (Figure 2). Under the impact of the laser from these molecules anions mostly of smaller molecules of carbon are formed. In a product C mainly molecules C_{15} , C_{17} , C_{18} and C_{20} can break up at laser ablation.

4. Conclusions

In this paper, we report the experimental results obtained at realization a new method of benzene pyrolysis which for the first time are demonstrate that the small carbon molecules ($C_3 - C_{20}$), quasi-fullerenes C_{40} , C_{48} , C_{52} , C_{54} , C_{56} and C_{58} can be obtained in reactionary conditions

excluding evaporation of carbon. Earlier such carbon molecules as ions in hot carbon plasma and in flame gases under burning of hydrocarbons were detected only.

First the method of joint synthesis of carbon molecules and their hydrides is developed. Usually the hydrides fullerenes exclusively by hydrogenation of carbon molecules are obtained.

First solid substances are synthesized, which mass-spectra clusters, appropriate to small carbon molecules contain. Before such molecules in circumstellar medium and in a matrix of solid argon at the temperatures ~ 15 -24 K were detected.

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