

New Method of Generation of Carbon Molecules and Clusters

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ABSTRACT

Firstly the method of joint synthesis of carbon molecules and their hydrides is developed. The stage of high-temperature sublimation of carbon in a new method of generation of carbon molecules is completely excluded. By mass spectrometric method the condensation products of new method of pyrolysis (NMP) benzene are studied. Firstly clusters (C_3 - C_{17}), typical for carbon vapour, in substances obtained under pyrolysis of hydrocarbons were detected. Fullerene C_{60} and its hydrides, quasi-fullerenes C_{48} and C_{33} in products of benzene pyrolysis are detected also. Firstly it is shown what clusters C_3 - C_5 can be generated at so low (100°C - 200°C) temperatures of decomposition of substance. Obtained experimental results firstly demonstrate that the small carbon molecules can be generated in reactionary conditions excluding evaporation of carbon. Dehydrogenation and destruction of hydrocarbon molecules is the first stage on a route of the transformation of benzene to carbon molecules.

Keywords: Pyrolysis; Benzene; Fullerene; Quasi-Fullerene; Small Molecules; Mass Spectra; Carbon Clusters

1. Introduction

It is considered, that precursor of formation of carbon molecules are carbon clusters, generated at high-temperature evaporation processes of carbon or materials on its basis. One year early to discovery of fullerene C_{60} by Kroto *et al.* [1], Rofling [2] obtained the unique mass spectrum of carbon clusters that were created at laser evaporation of graphite in a flow of inert gas. In mass spectrum alongside with even and odd carbon clusters of the small sizes C_n ($1 < n < 30$) were detected even clusters C_n ($n > 30$), including clusters, appropriate to fullerenes opened later. Kroto *et al.* [1] have created the special conditions of increased collision (clusterization) of carbon clusters and firstly have obtained mass spectrum of carbon vapour, which contained mainly clusters C_{60} and C_{70} . Isolation of many others clusters, observable in Rofling mass spectrum [2], from carbon vapour has appeared immeasurably more difficult task. Only after 6 years (in 1990) after detection of fullerenes C_{60} and C_{70} by mass spectrometric method, Kretschmer [3] succeeded to create conditions of the arc-discharge, which have allowed to fulfill not only the clusterization of generated carbon vapour with primary formation of C_{60} and C_{70} , but also to locate them in appreciable amounts in obtained fullerene soot. The research by mass spectro-

metric method of a powder [3], obtained at evaporation of benzene extract from fullerene soot, has shown presence of positive ions with m/z 60 and 70 in the ratio 10:1 in mass spectrum.

The further researches of benzene extracts from fullerene soot have shown [4] that in carbon vapour generated by the arc-discharge method can be realized raising clusterization with the formation of larger than C_{60} and C_{70} molecules. It was possible to allocate fullerenes C_{76} , C_{84} , C_{86} , C_{90} and C_{94} [5], and also C_{78} [6] from *o*-xylene (or *o*-dichlorobenzene) extracts of fullerene soot by a chromatography method (Al_2O_3 , toluene). However some of "high" fullerenes such as C_{74} and C_{80} is not possible to isolate because of extremely high propensity of the given molecules with not coupled electrons [7] to polymerization.

In [8] carbon clusters, earlier detected only in carbon plasma, were found out in gases of a flame of incomplete combustion of benzene by means of mass spectrometric method. This method has appeared most effective for obtaining of fullerenes [9]. Presence of C_{60} and C_{70} is found out also in mass spectra of products of heat treatment of benzene and acetylene [10], naphthalene $C_{10}\text{H}_6$ and corannulene [11-13].

Thus, from large amount clusters generated at super high temperatures of the evaporations and burning of carbon and benzene accordingly are synthesized only

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fullerene C_{60} and its homologues as more stable molecules with isolated pentagons. Only C_{36} was synthesized from smaller carbon molecules with adjacent pentagons, quasi-fullerenes [14]. (Though in [15] there is information about obtaining by an arc-discharge method hydrides ($C_{36}H_4$, $C_{36}H$) and oxy-hydrides ($C_{36}H_4O$, $C_{36}H_6O$) only, but not molecules C_{36}). Unsuccessful attempts to synthesize quasi-fullerenes are explained by their low stability because of presence of adjacent pentagons at the structure. However quasi-fullerene C_{20} , which molecule consists of only pentagons, is easily formed at an irradiation of polythene by a beam of ions Ar^+ [16] and laser ablation of diamond [17]. On the other hand, quasi-fullerenes C_{28} and C_{50} with smaller number of adjacent pentagons are formed only as their derivative: endofullerene $M@C_{28}$ ($M=Ti, Zr, Hf$ or U) [18] and decahlorofullerene $C_{50}Cl_{10}$ [19].

As to ions of small clusters C_n ($n < 20$), which always present in carbon plasma [2] and flame of a benzene/oxygen stream [8,9], the molecules, appropriate to them, for example C_2 and C_3 , C_4 and C_5 are found out only in circumstellar medium [20]. From carbon vapour the chains C_1 - C_{10} stabilize in solutions of methanol or acetonitrile due to a connection to trailer atoms of carbon H , N or CN with formation of relatively more stable polyyynes [21] or cyanopolyyynes [22]. The technology of matrix isolation of carbon vapour in solid argon (or neon) at 25 - 14 K [23] allows to keep carbon chains, but time of life of such frozen clusters is extremely small (~ 10 ms) [24].

The results of study by a mass spectroscopic method of the condensed products of a new method of pyrolysis (NMP) of benzene are presented and discussed in the report. Firstly in mass spectra of several solid products of condensation as and in carbon plasma (or in flame gases) small carbon clusters, new carbon molecules (quasi-fullerenes) as well as fullerene C_{60} and its hydrides are detected simultaneously. The stage of high-temperature sublimation of carbon in a new method of generation of carbon molecules of the different size is completely excluded.

2. Experimental Results and Discussion

Earlier [25-28] we have been systematically studied the influence of various technological parameters on composition of obtained products and, in particular, condensed substances formed at heat treatment of hydrocarbons. On the basis of the experimental results the new method of pyrolysis (NMP) of organic vapours was developed [28-31]. This method differs from two already known processes of pyrolysis [32]. Flash-pyrolysis (FP) [32,33] is used for obtaining of highly active objects of very small size. Flowing continuous pyrolysis (FCP) [32,34] is applied to obtain carbon nanostructures and polyaro-

matic hydrocarbons (PAH). NMP allows obtaining simultaneously not only carbon nanostructures but also practically all carbon clusters detected in carbon plasma. Distinctive feature of NMP is an opportunity of partial division of products deposition and condensation. The time of stay of reagents in the most high temperature ($\sim 1000^\circ C$) zone A of reaction can be changed in a wide interval that allows generating of intermediate products. A part of condensed substances and pyrolytic soot are taken out from a zone A and are located in more low-temperature zones B and D. Vapour-like products (sometimes together with traces of soot) also is condensed in the special zone C of cooled reactionary space. Products of several (8 - 10) experiences obtained at given temperature taken from zones B, C and D were blended. Results of study of the condensed products B, C and D of the heat treatment of benzene vapours by a method of matrix-assisted laser (nitrogen, 337 nm) desorption/ionization (MALDI) (Bruker Daltonics Flex Analysis) are submitted here. The extract (ethanol, toluene or water) was located on a metal substrate and after evaporation of the solvent was exposed to a laser irradiation.

2.1. Products of Zone B

From a product, located in a zone B, condensed substances were extracted serially by toluene B_1 and then ethanol B_2 . After evaporation of ethanol from a solution B_2 a deposit B_3 have obtained as conglomerates from transparent white crystals. The deposit B_3 is easily dissolved in water B_4 . In mass spectrum of negative ions of a water solution B_4 (Figure 1) there are peaks which correspond to values m/z (48, 60, 72, 84, 96, 108, 120 and 132) differing precisely on 12 units (Figure 1, inset). The similar periodicity is connected to different number of atoms of carbon in detected clusters: C_4 , C_5 , C_6 , C_7 , C_8 , C_9 , C_{10} and C_{11} . The spectrum of cations contains some peaks of small intensity with m/z : 429 and 219.

Mass spectra of cations and anions of a sample B_2 contain two general peaks with m/z 72 (cluster C_6) and m/z 144 (cluster C_{12}). In mass spectrum of anions (Figure 2) the periodicity already marked for B_4 is observed among the most intensive peaks: 8 clusters with consecutive (in 12 units) increasing of number of carbon atoms from C_3 up to C_{14} (Figure 2, inset). Also peaks with m/z 219 and 429 are contained in a spectrum of cations, those were found out in a spectrum of a product B_4 . Therefore it is possible to assume that in ethanol and water the substance (or substances) is dissolved which is exposed to destruction with formation of small carbon clusters from C_3 up to C_{12} under action of a laser beam. Though, probably that separate small carbon molecules are stabilized in ethanol and in water as well. Earlier a similar range of carbon clusters was detected only in carbon plasma [2], in gases of benzene combustion [9] and at a

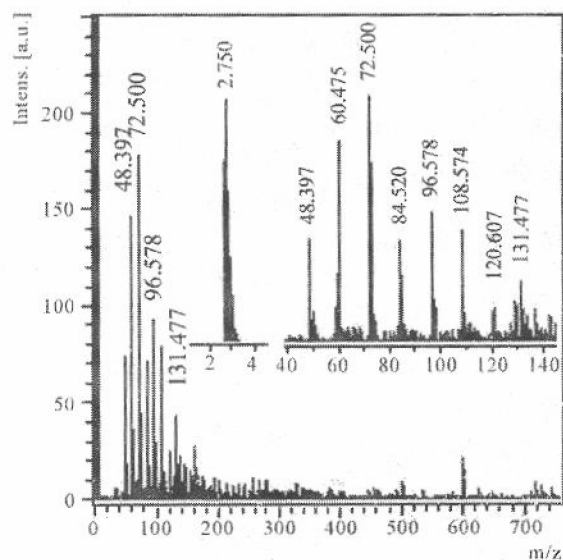


Figure 1. Anions mass spectrum of a water solution of the product B_4 with m/z 40 - 150 and 2 - 4 regions in the insets.

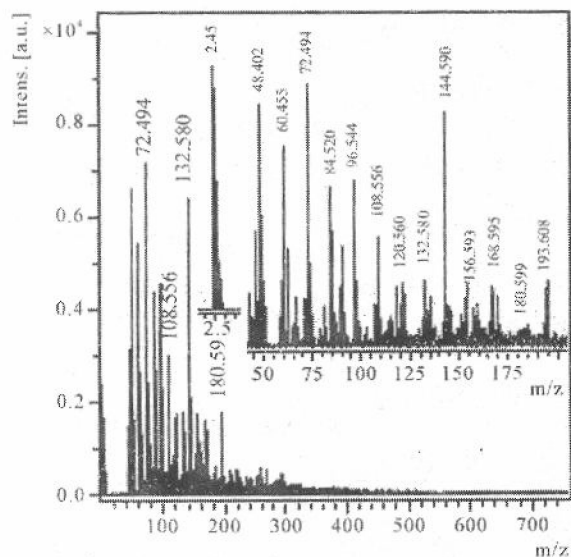


Figure 2. Anions mass spectrum of the ethanol solution of the product B_2 with m/z 45 - 200 and 2 - 4 regions in the insets.

laser irradiation of fullerene soot [35]. Probably, in fullerene soot formed at oligomerization of carbon clusters not only soluble in toluene C_{60} and C_{70} can be condensed as products by their increased clusterization. Precursors of C_{60} and C_{70} also can be condensed in this soot with formation of fixed (or otherwise deactivated) radicals (molecules), mainly soluble in alcohol and water.

In mass spectra of anions and cations of an extract B_1 there are groups of peaks with m/z 720, 696, 672, 648 and 624 (Figure 3(a)), which, as it is accepted to consider, are characteristic for fullerene C_{60} and clusters C_{58} ,

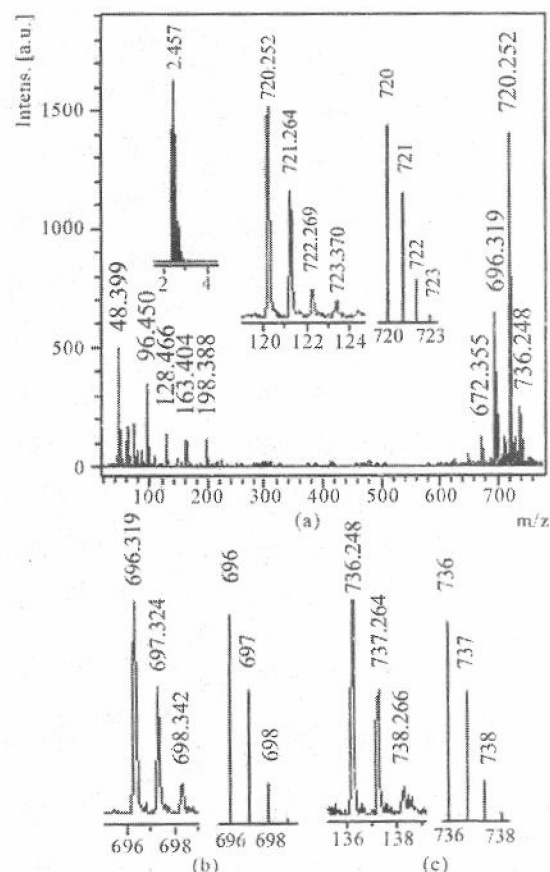


Figure 3. Anions mass spectrum of the toluene solution of the product B_1 (a) with the expansions of the experimental and theoretical isotope distributions for C_{60} in the inset, the expansions around the (b) m/z 696, (c) m/z 736 peaks and the calculated isotope mass ratios for C_{58} , $C_{60}H_{16}$ molecules respectively.

C_{56} , C_{54} and C_{52} . Really, from thin structure of peaks C_{60} (Figure 3(a), inset), and C_{58} (Figure 3(b)) follows that the isotope distribution in these peaks completely corresponds to natural distribution of isotopes of carbon in molecules C_{60} and C_{58} . In a spectrum of anions distinctly (against to a spectrum of cations) the periodicity in a range of peaks with m/z from 48 up to 120 also is visible which was observed in mass spectra of negative ions of products soluble in water and ethanol. It is accepted to consider that clusters group closest on the size to C_{60} and group of smallest clusters are formed at destruction C_{60} or its derivatives ($La@C_{60}$, $C_{60}O$ [36]) only at powerful laser irradiation. It is possible that substances soluble in water and ethanol are dissolved as well in toluene. Hydrogenated fullerenes $C_{60}H_6$, $C_{60}H_{16}$ and $C_{60}H_{20}$ which peaks distinctly are visible in spectra of both anions and cations are dissolved as well in toluene. According to thin structure of peak with m/z 736 (Figure 3(c)) the isotope distribution in it completely corresponds to cal-

culated ratio of isotopes for a molecule $C_{60}H_{16}$.

2.2. Products of Zone C

Product C contains mainly transparent light particles. According to the data of the X-ray microanalysis (X-ray microanalyzer Camebax SX-50) the product consists only of carbon. The product C is practically completely dissolved in ethanol. Mass spectrum of anions (Figure 4) of an ethanol solution C_1 contains a group of the most intensive peaks with m/z 36, 48, 60, 72, 84, 96, 108, 120, 132, 144 and 156, which can correspond to anions of small carbon molecules from C_3 up to C_{13} (Figure 4, inset). Peaks with m/z 169 and 181, it is possible, correspond to hydrogenated molecules. According to thin structure of peak with m/z 576 isotope distributions in it correspond to a molecule C_{48} .

Mass spectrum of cations (Figure 5) contains a group of peaks which the values m/z (85, 97, 109, 133 and 193) can correspond to protonated molecules C_7 , C_8 , C_9 , C_{11} and C_{16} (Figure 5(b)). Three distinct peaks with m/z 72, 180 and 396 can correspond to molecules C_6 , C_{15} and C_{33} . Though, from thin structure of peak with m/z 396 (Figure 5(a), inset) follows that a part of molecules C_{33} are partially hydrogenated. Hence, the molecules C_7 , C_8 and C_9 are detected either as anions, or as protonated clusters. Only molecule C_6 is detected in both spectra.

2.3. Products of Zone D

Soluble in toluene substances from a product D were extracted and deposited by ethanol. Deposited red-brown powder D_1 was dissolved in acetone. Mass spectra of anions (Figure 6) and cations (Figure 7) of an acetone extract D_1 essentially differ. First of all, in a spectrum of anions a peak with m/z 576 is distinctly seen which, as is marked earlier, presents in mass spectrum of a product C_1 dissolved in ethanol. In a spectrum the peak with m/z 576 is distinctly seen as well, the isotope distribution in which ((Figure 6(a), inset) differs from natural isotope distribution of carbon in a molecule C_{48} . It is probably, molecule C_{48} is partially hydrogenated (up to $C_{48}H_2$). Hence, quasi-fullerene C_{48} is located in different zones of reactionary space and is easily dissolved both in ethanol and in acetone.

In a spectrum of anions (Figure 6(b)) there is a large group of very intensive peaks with relatively small values m/z : 36, 48, 60, 72, 84, 96, 108, 120, 132, 144, 156, 168 and 180. Periodicity of occurrence of these peaks is 12 units that can demonstrate the belonging of these peaks to clusters from C_3 up to C_{15} . The similar structure of mass spectrum of anions was found out and for a product C_1 (Figure 4, inset), dissolved in ethanol. The very intensive peak with m/z 255 can correspond to hydrogenated molecule $C_{21}H_3$ (or $C_{20}H_{15}$). Just the peak with m/z 255

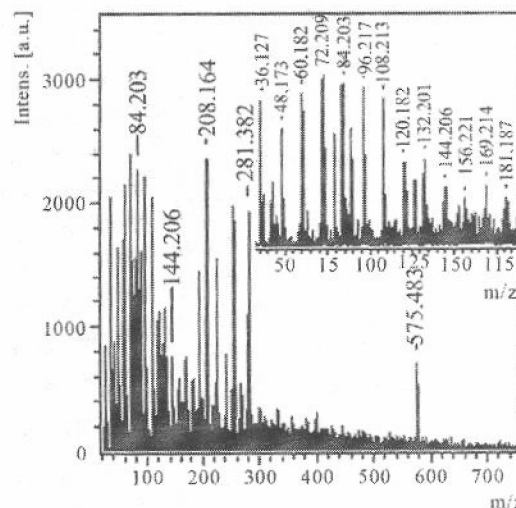


Figure 4. Anions mass spectrum of the ethanol solution of the product C_1 with m/z 45 - 185 region in the inset.

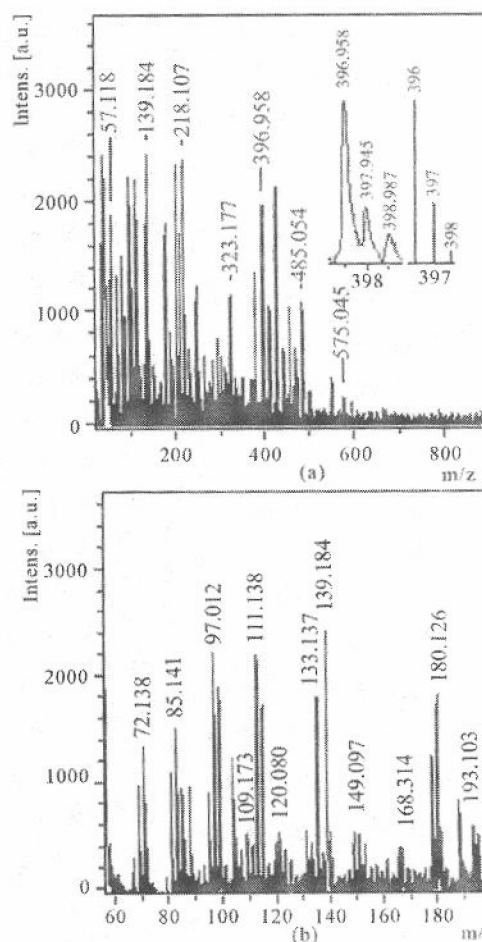


Figure 5. Cations mass spectrum of the ethanol solution of the product C_1 with the expansions of the experimental and theoretical isotope distributions for C_{33} in the inset (a), m/z 55 - 200 region (b).

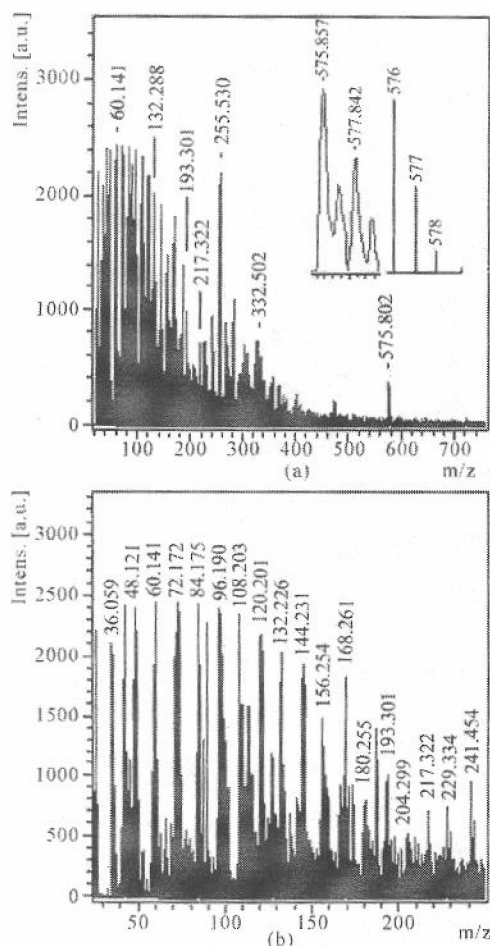


Figure 6. Anions mass spectrum of the acetone solution of the product **D**₁ with the expansions of the experimental and theoretical isotope distributions for C_{48} in the inset (a), m/z 45 - 250 region (b).

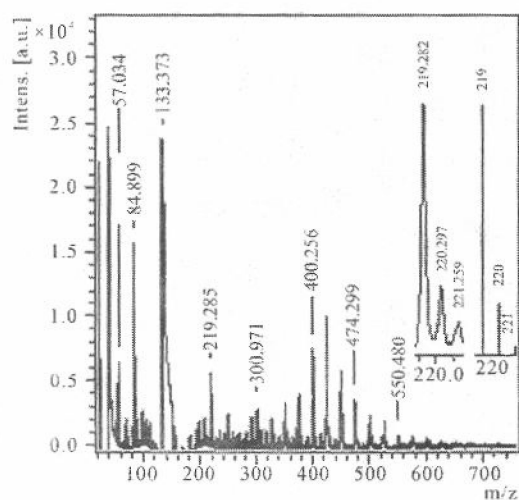


Figure 7. Cations mass spectrum of the acetone solution of the product **D**₁ with the expansion around the m/z 219.

allows to see some difference in mass spectra of anions of products **C**₁ (transparent light particles) and **D**₁ (red - brown powder). However, mass spectra of cations testify to essential distinctions of these products (Figure 5, Figure 7). In mass spectrum **D**₁ most intensive peak with m/z 133 as well as rather intensive peaks with m/z 85 and 219 is contained. It is possible to believe, that peaks with m/z 85 and 133 correspond to minimally hydrogenated molecules. The peak with m/z 219 can correspond also to protonated molecule $C_{18}H_3$ (Figure 7, inset). It is possible, that the product **D**₁ contains stabilized by other products of benzene pyrolysis molecules **C**₇ and **C**₁₁, which are decomposed on clusters mainly of smaller size C_3 - C_5 under laser beam.

Thus, clusters C_3 - C_{15} as well as C_{60} or C_{48} are detected as anions in all three products of benzene pyrolysis. In a spectrum of cations the molecules C_6 - C_9 and C_{11} as well as C_{15} and C_{33} are detected only.

2.4. Products 1B of Zone B

It is necessary to note that the composition of products of benzene pyrolysis, in particular, located in a zone **B** essentially depends on a regime of synthesis. From a product **1B** obtained at lower temperature of pyrolysis were extracted by toluene the condensed substances and some of them deposited at addition of ethanol. The obtained deposit **2B** as red (wax-similar) film was again dissolved in toluene and its mass spectra are submitted in Figure 8. Mass spectrum of anions (Figure 8(a)) contains the most intensive peak with m/z 168 as well as less intensive peaks with m/z 96, 132 and 216. From thin structure of peaks with m/z 96 and 168 follows, that the distribution of isotopes of carbon in them corresponds to molecules C_8 and C_{14} . At the same time, from the extended spectrum it is possible to see that some of small carbon molecules, for example C_{13} , are hydrogenated essentially. The spectrum of cations (Figure 8(b)) testifies a high degree of hydrogenation of a product **2B**. The most intensive peak with m/z 139 according to its thin structure corresponds to a hydrogenated molecule $C_{11}H_7$. The peaks with the large values m/z also correspond to hydrogenated molecules of carbon or thermostable polyaromatic hydrocarbons (PAHs) which can be intermediate at the formation C_{60} and its hydrides.

According to the chemical analysis a red product **2B** consists of carbon, hydrogen (up to 4.2% mass.) and oxygen (up to 3.1% mass.). The composition of volatile products of thermal decomposition **2B** 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) [37]. A sample **2B** at the bottom of molibdenium-quartz ampoule was evacuated at room temperature up to

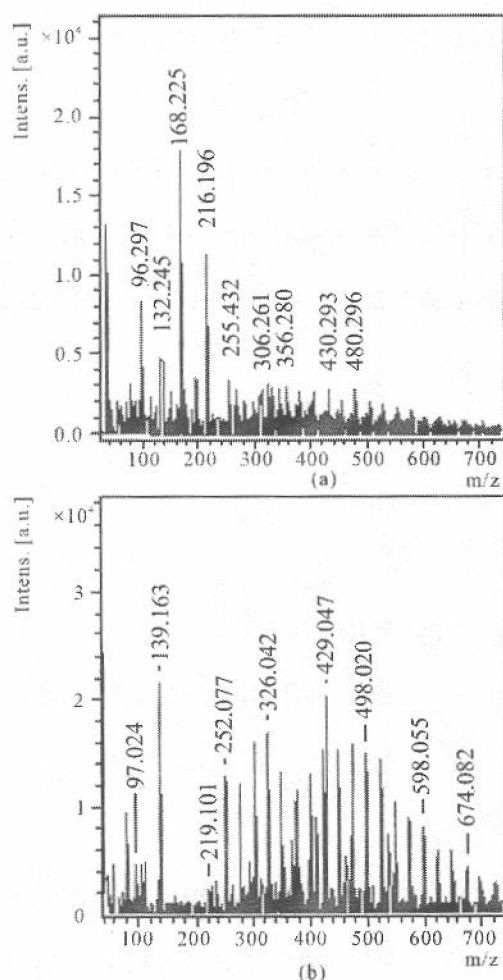


Figure 8. Anions (a) and cations (b) mass spectra of the toluene solution of the product 2B.

5×10^{-5} Pa. The linear heating of a sample up to 650°C was carried out with speed $0.15 \text{ K}\cdot\text{s}^{-1}$ [37]. The volatile thermolysis products passed through a high-vacuum valve (5.4 mm 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 - 210 amu. The hydrogen as can see from a curve of thermodesorption (Figure 9(a)) begins allocation from a sample 2B already at room temperature (in vacuum) and in enough large amount. It is improbable that PAHs in a similar way can be decomposed. It should be noted that the intensive peaks of hydrogen is also observed in the MALDI mass spectra of water, ethanol and toluene solutions of the product **B₄** (Figure 1, inset), **B₂** (Figure 2, inset) and **B₁** (Figure 3(a), inset) respectively. Mass spectrum EI at 200°C on Figure 9(b) is presented. Intensive peaks with 18, 28 and 44 amu correspond to molecular ions desorbed water, nitrogen and carbon dioxide, respectively. Ions with 31

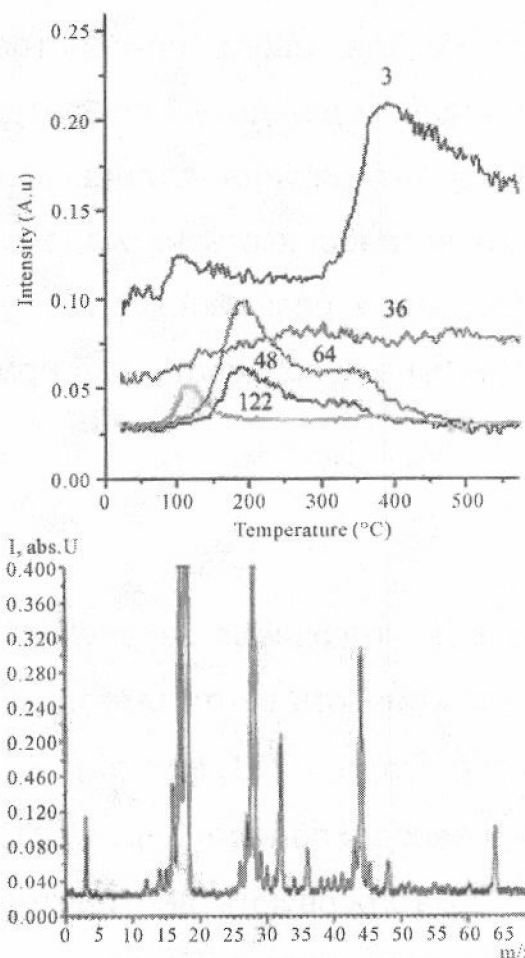


Figure 9. Experimental thermogram for selected m/z 3, 36, 48, 64 and 122 peaks (a) and representative mass spectrum at 200°C (b) for the product 2B.

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 C_3 , C_4 and C_5H_2 with molecular mass 36, 48 and 64 accordingly. It is possible that detected on MALDI mass spectra carbeneous (C_8 and C_{14}) and hydrogenated molecule (C_{11}H_7) are thermo unstable already at low temperatures.

Thus, firstly clusters, distinctive for carbon plasma, are generated at destruction of substances obtained at hydro-carbon pyrolysis. Pyrolysis is carried out at temperatures excluding evaporation of carbon therefore small carbon clusters (C_3 - C_5) can be formed only due to dehydrogenation and destruction of benzene molecules. The destruction of a molecule C_6H_6 can be proceeded its complete dehydrogenation with formation of a linear or ring molecules C_6 of polyynic or cumulenic structure. Clusters C_7 - C_{11} and C_{15} can be products of clusterization C_3 - C_6 . The formation of molecules C_{60} , C_{48} and C_{33} can be

realized owing to polycondensation of molecules C_6H_6 , while hydrides ($C_{60}H_6$, $C_{60}H_{16}$, $C_{60}H_{20}$) are formed because of reactions of polymerization of molecules C_6H_6 or hydrogenation of the formed molecules C_{60} . It is possible, that the radicals, for example C_6H_5 , are formed at partial dehydrogenation of molecules C_6H_6 which further, as well as C_6 , can be precursors of carbon molecules and clusters. However absence of biphenyl ($C_6H_5-C_6H_5$) in products of benzene pyrolysis as product of the first stage of reaction of polycondensation C_6H_6 , but presence of clusters C_{12} (m/z 144) and C_{18} (m/z 216) as dimer and trimer C_6 accordingly, can testify to preferable formation C_{60} and C_{48} from carbon clusters, instead of from hydrocarbons radicals.

Very important question connected to the detailed mechanism of the formation C_{60} and C_{48} , remains, open: whether clusters C_6 of an initial molecule C_6H_6 accept participation in formation of molecules C_{60} and C_{48} ? Or these large carbon molecules are formed only due to increase of clusterization of fragments (C_3-C_5) of disintegration C_6 ?

Pyridine (C_5NH_5) is heterocyclic analogue of benzene (C_6H_6) therefore from precursors C_5N or C_3-C_5 should be formed accordingly heteroatomic or monoatomic fullerenes and quasi-fullerenes. Our preliminary researches [29,30] have shown that at pyridine pyrolysis large nitrogen-carbon containing molecules are formed which further study represents not only scientific but also practical interest.

3. Conclusion

New method of organics pyrolysis for generation of carbon clusters as an alternative powerful laser (or arc-discharge) evaporation of graphite is developed. Condensation products obtained at new method of pyrolysis of benzene vapours by mass spectrometric method are studied. In products of all kinds of carbon molecules and some hydrides are detected. Obtained experimental results firstly demonstrate that the small carbon molecules can be generated in reactionary conditions excluding evaporation of carbon. The first stage of the transformation of benzene molecules to carbon molecules is their dehydrogenation and destruction. Firstly fullerene C_{60} and quasifullerenes C_{48} and C_{33} as well as small carbon molecules and some hydrides molecules in different substances are detected simultaneously.

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