

Fullerenes and quasi-fullerenes as products of fullerenization of molecules of aliphatic and aromatic hydrocarbons

A.I. Kharlamov¹, M.E. Bondarenko^{1,*}, G.A. Kharlamova², V.V. Fomenko³

¹ *Frantsevich Institute for Problems of Materials Science of NASU, Krzhizhanovsky St. 3, 03680 Kiev, Ukraine*

² *Taras Shevchenko National University of Kiev, Volodymyrs'ka St. 64, 01601 Kiev, Ukraine*

³ *National University of Food Technologies, 68 Volodymyrska str., 03001 Kiev, Ukraine*

(Received 14 April 2015; published online 22 August 2015)

Fullerenization as process of thermal (750-1000°C) of transformation of aliphatic and aromatic hydrocarbons molecules in molecules of quasi-fullerenes ($C_nH_{n-6}-C_nH_{n-2}$ ($n=20-54$)) and fullerenes (in particular, the equiatomic composition $C_{60}H_{60}$) was performed for the first time. Main feature of fullerenization process is, that its products are formed in all volume of reactionary space, but are located (are deposited and are condensed) in it a low-temperature zone. Extracted from pyrolytic soot the products of benzene and n-hexane fullerenization contain the condensed molecules containing up to 4.8 and 5.1 % of hydrogen accordingly, which allocation at thermolysis is began with 50°C and proceeds up to 750°C. Products of benzene and n-hexane fullerenization can be perspective for hydrogen storage.

Keywords: Fullerenes, Quasi-fullerenes, Fullerenes, Fullerenization, Pyrolysis, Dehydrogenation, Hydrocarbons, Hydrogen Storage.

PACS numbers: 81.05.Tp, 81.16.Be

1. INTRODUCTION

As against already known superhigh-temperature (1800-3500°C) of methods of carbon sublimation (laser ablation and arc discharge) and burning of benzene in a smoky flame by us was developed [1-4] essentially more low-temperature (< 1000°C) process (fullerenization [3] of organic molecules) obtaining of carbon molecules. The process of fullerenization includes reactions of thermal transformation of organic molecules, in particular, aromatic hydrocarbons and pyridine in fullerenes and quasi-fullerenes a well as in them hydrogenated forms. (We shall remind that process of aromatization is reactions of transformation of paraffin and olefin hydrocarbons in aromatic hydrocarbons, in particular benzene, and also pentadiene.) The main distinctive feature of fullerenization process (how method of pyrolysis of the authors [1-4]) molecules of aromatic hydrocarbons and C_5H_5N is what alongside with fullerene C_{60} as products are formed quasi-fullerenes (in particular, C_{48} , C_{42} , C_{40}) and them hydrogenated molecule (fullerenes $C_{60}H_4-C_{60}H_{60}$, $C_{70}H_x$ and quasi-fullerenes ($C_nH_{n-6}-C_nH_{n-2}$ ($n=20-54$)). Moreover, in mass spectra of some powdery products of fullerenization of organic molecules, also distinctly, as well as in mass spectra of carbon plasma are detected small carbon clusters (C_3-C_{18}) [1-3].

Thus we believe that the mechanism of growth of the closed carbon molecules from thermoactivated molecules of aromatic hydrocarbons (or pyridine) is essentially other, distinct from most frequently of discussed mechanisms. Basic elements («by building blocks») of fullerenization process (or growth of carbon molecules) are the molecules of precursor and fragments of them destruction, in particular, cyclopentadien: fullerene and quasi-fullerenes are formed as a result of reaction of their polycondensation, whereas fullerenes and quasi-

fullerenes at the expense of reaction of their polymerization. The reactions of polymerization in the thermodynamic relation are more preferable (the break only 3 π -bonds $C=C$ for formation of new 6 bonds $C-C$ is required) in comparison with reactions of polycondensation (the break 6 bonds $C-H$ is required). Therefore in conditions of fullerenization of aromatic hydrocarbons molecules are observed (according to experimental results [1-4]) preferable formation fullerenes and quasi-fullerenes, instead of carbon molecules. Undoubtedly, in parallel with reactions of polymerization and polycondensation the reactions of destruction of precursor molecules are realized. However to the destruction of C_6H_6 molecules can precede complete their dehydrogenation with formation of ring molecules C_6 (pseudonew or cumulenic structure), which also easily break up on clusters of the smaller sizes (C_3-C_5). Fullerenization of heteroatomic molecules C_5H_5N in homoatomic molecules C_{60} and C_{48} and the detection in products also clusters C_3-C_{18} [1, 2] only confirms a hypothesis about the important role of a stage of dehydrogenated destruction of precursor molecules in process of fullerenization.

According to the discussed mechanism of fullerenization it is possible to assume, that the reaction of polymerization with formation of hydrogenated carbon molecules will be appreciable to be accelerated in conditions of the greater allocation of hydrogen at a previous stage of dehydrogenation of precursor molecules. Therefore it is possible to expect, that in reactionary conditions of fullerenization process the reactions of aromatization n-hexane will promote preferable (in comparison with carbon molecules) formation of fullerenes and quasi-fullerenes with the large contents of hydrogen. This conclusion conforms the supposition of Kroto as discoverer of fullerenes, what molecules C_n (where $20 < n < 60$), which contain adjacent pentagons,

* mebondarenko@ukr.net

can be formed mainly as their hydrogenated forms [5].

Here it is important to note, that now, despite of huge interest of the numerous researchers to obtaining of hydrides of fullerenes C_{60} and C_{70} , samples with high (more than 60 %) contents of hydrogen, and furthermore equiatomic composition fullerene $C_{60}H_{60}$ is not still prepared. All techniques, developed for today [5, 6], of fullerenes preparation are based on the only approach: on the hydrogenation of previously synthesized fullerene (fullerite or palladium fulleride) by various sources of hydrogen. In heterogeneous hydrogenation processes or fullerene at the presence of the catalyst, or fullerite with use of super-high pressure and increased temperatures resulting more saturated by hydrogen fullerenes ($C_{60}H_{48}$ - $C_{60}H_{52}$) or contain in addition or catalyst (5 % Ru/C), or polyaromatic hydrocarbons fragments as fragments of destruction of closed fullerene structure. We believe, that only in conditions of homogeneous reactions, which, undoubtedly, are realized in fullerenization process of benzene (or n-hexane) molecules, as the reactions of polymerization of precursors vapours and products its destruction, can be synthesized molecules of fullerenes and quasi-fullerenes with the increased contents of hydrogen.

In this work, to our knowledge, the opportunity of realization of process of fullerenization of aromatic (benzene) and aliphatic (n-hexane) hydrocarbons molecules is investigated with the purpose of synthesis of maximum saturated by hydrogen fullerenes and quasi-fullerenes as potential sources of hydrogen.

2. EXPERIMENTAL

The new method of pyrolysis (NMP) as process of fullerenization of organic compounds vapours described by us earlier [1-4], essentially differs from two known CVD methods (continuous flow and flash pyrolysis). In conditions of NMP the composition of resultant products depends not only on reactionary conditions (temperature, reagent concentration and time of its stay in the most high-temperature zone reactor), but also place of localization of these products in reactionary space. At realization of NMP a part of condensed substances and pyrolytic soot are taken out in a reactionary flow from high-temperature ($< 1000^{\circ}C$) zone and are located in more low-temperature ($< 300^{\circ}C$) zone.

The experiments on fullerenization of benzene and n-hexane molecules were carried out in absence of the catalyst and at temperatures 950 (regime 1), or at $900^{\circ}C$ (regime 2). The quantity and composition of products of fullerenization of n-hexane (H1 и H2) or benzene (B1 and B2), obtained accordingly at 950 and $900^{\circ}C$ and condensed in low-temperature zone, differs rather appreciably. Then condensed substances extracted by benzene from the resulting products. Benzene solutions concentrated and by method of salting out by ethanol were deposited the condensed in low-temperature zone molecules. A deposit carefully dried for more complete removal of the used solvents, and then certified and investigated by methods chemical and X-ray analyses, NMR and IR spectroscopy, temperature-programmed desorption mass spectrometry (TPDMS) and also by a method of matrix-assisted laser (nitrogen, 337 nm) desorption/ionization (MALDI) (Bruker Daltonics flexAnalysis). The analysis of thin

structure of peaks of the majority detected in mass spectra of clusters (cations and anions) was carried out on a technique in detail described earlier [1-4], that has allowed more correctly to present composition of molecules synthesized at n-hexane and benzene fullerenization.

3. RESULTS AND DISCUSSION

In accordance with the chemical analysis deposited from extracts the products of benzene (B1, B2) and n-hexane (H1, H2) fullerenization contain carbon, hydrogen and no more than 1.7 mass% of oxygen. The oxygen, probably, is in adsorbed state on nanosized particles of a product. In products B2 and H2 are contained not less than 2.8 and 4.0 mass% of hydrogen respectively. Products B1 and H1, obtained at higher temperature, contain ~ 4.8 and 5.1 mass% of hydrogen respectively. It is possible to believe, that condensed in a low-temperature zone of molecules as the products of benzene and n-hexane fullerenization consist basically of carbon and hydrogen. The most complete information on quantity and state of hydrogen in these molecules, their molecular formula can be received from thermodesorption and mass spectrometric researches as well as from features of structure of them NMR and IR spectra.

From thermodesorption curves follow that the appreciable allocation of hydrogen at thermolysis of products B1, B2 and H1, H2 (Fig. 1a) is fixed practically in all investigated temperature interval (25 - $750^{\circ}C$) and is begun already with $\sim 50^{\circ}C$. Comparison of desorption thermograms of hydrogen (Fig. 1a) and mass spectra of volatile products of thermal decomposition of identical mass (3 mg) samples, for example, H1 and H2 shows that the quantity of hydrogen in these samples appreciably is differed that is coordinated to the data of the chemical analysis. First increased (peak-like) the allocation of hydrogen is observed at temperature $\sim 50^{\circ}C$. The most intensive allocation of hydrogen is begun with $350^{\circ}C$. (At fullerenes thermolysis synthesized at hydrogenation of fullerenes the allocation of hydrogen is observed only at temperatures above 400 - $500^{\circ}C$ [7].)

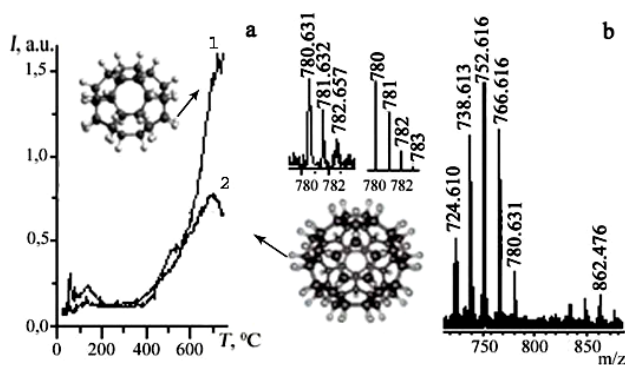


Fig. 1 – Thermograms dehydrogenation of samples: 1 – H1, 2 – H2 with the model of $C_{32}H_{30}$ molecule in the inset (a); anions mass spectrum of the sample H2 with expansion around m/z 780 peak and the calculated isotope mass ratio for $C_{60}H_{60}$ molecule and their model in the insets (b)

Mass spectrometric study of a gas phase of thermolysis of both products B1 and H1 of n-hexane and benzene fullerenization, obtained at more high-temperature regime 1, has shown, that allocation of saturated hydro-

carbons (in particular, methane, ethane and propane) as destruction indicators of a fullerene cage is begun at lower temperatures, than this process is observed at fullerenes dehydrogenation.

It is important to note, that thermal destruction of polyaromatic hydrocarbons (PAHs), for example anthracene or pyrene, is begun at much higher temperatures (above 600°C) and agrees of mass spectra (database NIST (National Institute of Standards and Technology USA)) hydrogen at destruction PAHs molecules practically is not allocated.

For the condensed molecules formed at benzene (or n-hexane) fullerenization are written down also MALDI mass spectra of negative and positive ions. Mass spectra of anions and cations all products contain intensive (especially in a spectrum of anions) peak with m/z 2.43 appropriate to hydrogen.

By a mass spectrometric method MALDI was shown that the products B2 and H2 (Fig. 1b), obtained at low-temperature regime 2, mainly consist from fullerenes $C_{60}H_x$ (including fullerene of equiatomic composition, $C_{60}H_{60}$) and $C_{70}H_x$ of a various degree of hydrogenation.

At a spectrum of the product of more high-temperature fullerenization benzene B1 (Fig. 2) there is a group of intensive peaks, in which the values m/z 254, 276, 302, 326, 350, 376, 400, 424, 450, 476, 500, 524, 550 and 574, change strictly on 24 or 26 units.

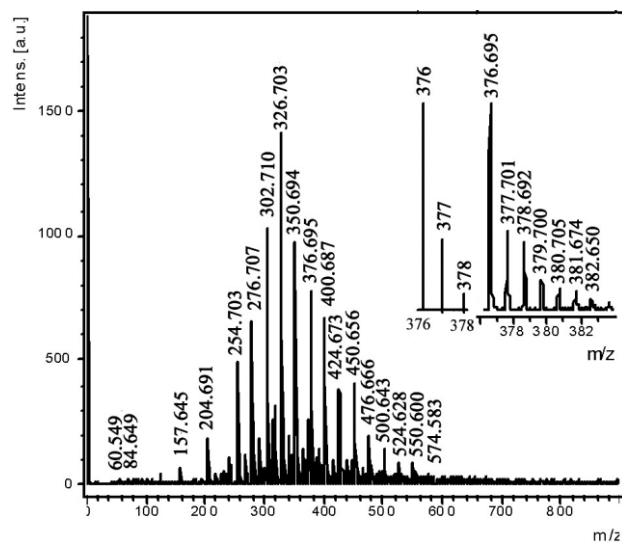


Fig. 2 – Cations mass spectrum of the product B1 with the expansion around m/z 376 and the calculated isotope mass ratio for $C_{30}H_{16}$ molecule in the inset

From the spectra of the high resolution of each of these peaks follows, that the ratio of intensities in them of lines $^{12}C_n$ and $^{12}C_{n-1}^{13}C$ corresponds to natural isotope distribution of carbon for such molecules as: $C_{20}H_{14}$, $C_{22}H_{12}$, $C_{24}H_{14}$, $C_{26}H_{14}$, $C_{28}H_{14}$, $C_{30}H_{16}$ (Fig. 2, inset), $C_{32}H_{16}$, $C_{34}H_{16}$, $C_{36}H_{18}$, $C_{38}H_{20}$, $C_{40}H_{20}$, $C_{42}H_{20}$, $C_{44}H_{22}$ и $C_{46}H_{22}$. It is possible, that the carbon molecules C_{20} – C_{46} , which do not answer isolated pentagons rule (IPR), are more stably (as assumes Kroto [5]) as partially hydrogenated molecules, in particular of molecules of quasi-fullerenes of compositions $C_{20}H_{14}$ – $C_{46}H_{22}$. However from thin spectra of all group of detected cations also precisely it is visible, that the lines $^{12}C_{n-2}^{13}C_2$ considerably exceed accounted values of isotope distribution of carbon, char-

acteristic for all above quasi-fullerenes. Therefore it is possible to consider, that in mass spectra are detected also more hydrogenated molecules quasi-fullerenes such as $C_{20}H_{16}$ – $C_{46}H_{24}$. Really, from thin spectra (Fig. 2, inset) it is possible distinctly to see, that each of the basic peaks represents a few peaks, which can be characteristic for more hydrogenated molecules of quasi-fullerenes.

At a spectrum of the product of high-temperature (regime 1) fullerenization n-hexane H1 this group of peaks is wider and begun with m/z 276 and proceeds up to 722 (Fig. 3).

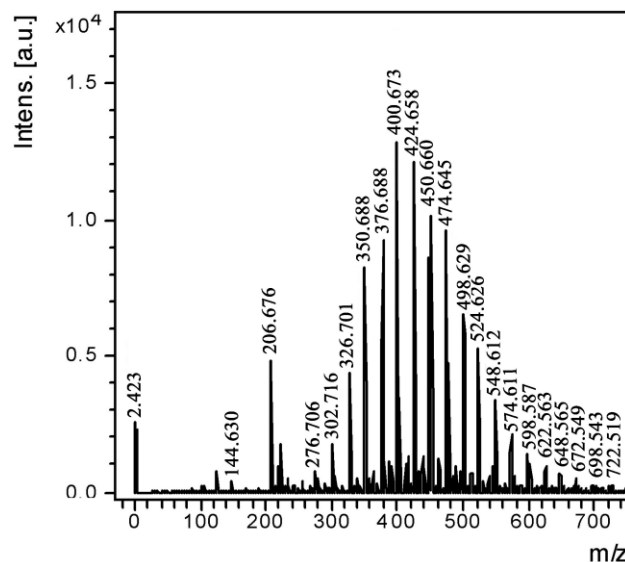


Fig. 3 – Cations mass spectrum of the product H1

At the examinations of mass spectra of condensed molecules obtained at fullerenization of benzene and n-hexane could be seen, that to the given values of m/z can correspond to fullerenes or quasi-fullerenes of different compositions. Therefore for the determination of the correct formula of carbon molecules hydrides are necessary also their IR spectroscopic research.

The structures of IR spectra of products of n-hexane (H1, H2) and benzene (B1, B2) fullerenization in many aspects remind structure of IR spectra of fullerenes, obtained by different methods [5-7]. So, values of the basic absorption bands in IR spectrum of a sample H2 (2919 and 2855 cm^{-1} (C–H stretching), 1383 cm^{-1} (C–H bending); 1601, 1464, 1174, 869, 748, 700 and 430 cm^{-1} ($C_{60}H_x$ cage)) are rather close to values of fullerene $C_{60}H_{36}$ synthesized from C_{60} by a method Birch-Huckel. Moreover, these values also are close to theoretical values counted for hypothetical fullerene $C_{60}H_{60}$ [8]. It is known, that the molecules of partially hydrogenated fullerenes (for example, $C_{60}H_{36}$) have smaller symmetry, than fullerene C_{60} (has only four modes with symmetry F_{1u}) and fullerene $C_{60}H_{60}$, for which 9 active modes (1-9 F_{1u}) are accounted. (Three modes (2912 and 2907 cm^{-1} (sp^3 C–H stretching); 1299 cm^{-1} (sp^3 C–H bending)) are concerned to vibrations of C–H bonds and six modes (1612, 1450, 1163, 885, 487 and 435 cm^{-1} ($C_{60}H_x$ cage)) are concerned to vibrations of fullerene cage. Therefore IR spectra of a sample H2, as well as fullerene $C_{60}H_{36}$, have the a little bit greater number of bands, than at C_{60} and $C_{60}H_{60}$.

Considering of the data of the TPD MS and MALDI

mass-spectrometric analysis it is possible to believe, that at n-hexane (or benzene) fullerenization are formed mainly fullerenes and quasi-fullerenes. More saturated with hydrogen product H1 (as well as B1) contains, probably, and more saturated by hydrogen quasi-fullerenes, in which C=C bonds should be very little. Therefore it is important to study these samples by NMR method.

In solid state ^{13}C NMR spectrum of, for example, sample H1 (Fig. 4a) two groups of signals in the field of 20-50 ppm and 120-150 ppm, characteristic, agrees [5-7], for fullerenes hydrides, distinctly are visible. Groups of signals in the field of 120-150 ppm and in the field of 20-50 ppm can belong accordingly to aromatic sp^2 and sp^3 atoms of carbon bonded with atoms of hydrogen in partially hydrogenated carbon molecules.

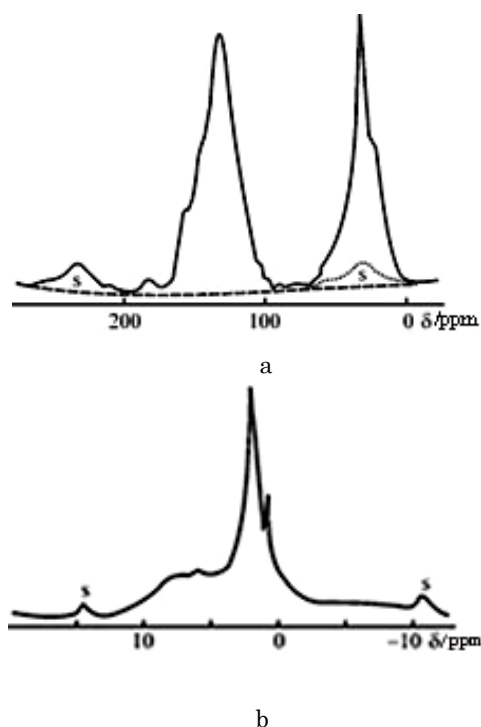


Fig. 4 – Solid state NMR ^{13}C (a) and ^1H (b) spectra of the product H1

REFERENCES

1. A.I. Kharlamov, G.A. Kharlamova, M.E. Bondarenko, *Russ. J. Appl. Chem.* **86**, 167 (2013).
2. *Advanced Sensors for Safety and Security*, NATO Science for Peace and Security Series B: Physics and Biophysics (Eds. A. Vaseashta, S. Khudaverdyan) (Dordrecht: Springer Netherlands: 2013).
3. A.I. Kharlamov, G.A. Kharlamova, M.E. Bondarenko, *Russ. J. Appl. Chem.* **86**, 1174 (2013).
4. A.I. Kharlamov, M.E. Bondarenko, N.V. Kirillova, *Russ. J. Appl. Chem.* **85**, 233 (2012).
5. Cataldo, S. Iglesias-Groth, *Fullerenes: The Hydrogenated Fullerenes* (Dordrecht: Springer: 2010).
6. N.F. Goldshleger, A.P. Moravsky, *Usp. Khim.* **66** (1997).
7. A.A. Peera, *Fullerene hydrides and studies toward the synthesis of fulvalenes*. Ph.D.Thesis. (Houston: Texas: 2004).
8. R. Stoldt, R. Maboudian, C. Carraro, *Astrophys. J.* **548** (2001).

In ^1H NMR spectrum of a sample H1 (Fig. 4b) presents only signal in the field of 2-3 ppm, which, as a rule [5-7], belongs to fullerenes hydrides. (2 peaks of small intensity in this spectrum are satellites from rotation.) Observable signals at δ 2.1-2.5 ppm usually [7] connect to hydrogen in fullerene with higher, than in fullerene $\text{C}_{60}\text{H}_{36}$, contents of hydrogen. Is remarkable, what in the spectra of ^1H NMR of the samples H1 (as well as B1) there are no signal in the field of δ 7-8 ppm. This fact convincingly confirms that in the samples H1 and B1 are absent atoms of hydrogen, which could be connected with sp^2 atoms of carbon located on external perimeter of plane polycyclic aromatic molecules. Hence, the molecules of a product H1 (as well as B1) with m/z 254-698 (Fig. 2, 3) have fullerene-like structure and, hence, are not polycyclic aromatic hydrocarbons. Besides in the mass spectra of PAHs are absent ions of hydrogen H^+ or $[\text{H}_2]\text{H}^+$ (according to the database NIST), whereas in the mass spectra of the products of n-hexane (or benzene) fullerenization the hydrogen ions $[\text{H}_2]\text{H}^+$ start to register with 50°C .

4. CONCLUSIONS

The study of benzene and n-hexane pyrolysis has resulted in opening its new reaction, reaction of fullerenization, at which molecules of aromatic and aliphatic hydrocarbons at temperatures higher 950°C are transferred to the closed molecules mainly quasi-fullerenes (C_nH_{n-6} C_nH_{n-2} ($n=20-54$)). Quasi-fullerenes with high hydrogen content (4.8-5.1%) have a wide temperature range of dehydrogenation from 50°C to over 750°C unlike fullerenes C_{60}H_x which dehydrogenation begin at temperatures above 400°C only. Quasi-fullerenes can be perspective for hydrogen storage.