UNIVERSITAS SCIENTIARUM
Revista de la Facultad de Ciencias
PONTIFICIA UNIVERSIDAD JAVERIANA
Vol. 9, No. 2, 59-64

INITIAL STAGES OF CARBON GENESIS IN THE UNIVERSE

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ABSTRACT

The formation possibility of the most widespread carbon compounds had been showed on the base of detonation nanodiamonds thermodynamic data. These reactions may play a key role in the life origin and in the atmosphere formation of the Solar system giant planets

Key words: detonation, diamonds, properties, reactivity, origin of life.

RESUMEN

La posibilidad de formación de los compuestos de carbón más comunes se habían mostrado sobre la base datos termodinámicos de detonación nanodiamantes. Estas reacciones pueden jugar un papel clave en el origen de vida y en la formación de la atmósfera de los planetas gigantes del sistema solar.

Palabras clave: detonación, diamantes, propiedades, reactividad, origen de vida.

INTRODUCTION

Greiner (Greiner, 1988) marked the similarity of the detonation nanodiamonds (DND) with the diamonds of the meteoric origin. Now they believe, the diamonds in space are formed at space explosions of the super new stars (Henbest, 1980), in peripheral area of red giant stars (Cleggett-Haleim *et al.,* 2001) and at shock collision carboncontained meteorites (Fisenko *et al.,* 1987). Alamandola and his colleagues (Alamandola *et al.,* 1992, 1993) consider, that carbon of interstellar clouds contains up to 20% nanodiamonds. However some of the researchers reject the existence of the nanodiamonds in the interstellar space. Their opinion is based on the data of ultraviolet spectroscopy of carbon compounds in interstellar dust clouds. An extraordinary wide strip in the field of a spectrum near to 217 nanometers was detected and it was supposed, that it was connected with to presence of graphite, polycyclic molecules such as naphthalene or fine fullerenes, for example C_{60}. However any of them did not answer completely the character of absorption. In 1997 Henrard has assumed (Henrad *et al.,* 1997), big fullerenes (C_{60}, C_{240}, C_{540}, etc.), covered with ice should show that adequate character of absorption of light. In these fullerenes at not too big sizes (less than 20 nanometers) weak bonded electrons have the oscillatory levels adequate to transitions UF-in the field of a spectrum. Therefore dust clouds of such carbon products could be characterized by absorption in a ultraviolet part of a spectrum. He assumed that molecular crystals of carbon were born in atmospheres of stars and in the beginning they had the structure of a diamond, which then were hydrated by molecules of water. However Beegle (Beegle *et al.,* 1997) believes that actually on unusual absorption is caused by congestions of large molecules of naphthalene like substances. The results of the program of researches with an infra-red space telescope (ISO) also did not allow to come to a certain opinion on this problem: Presence of fullerenes (Garcia-Lario *et al.,* 1999), nanodiamonds (Jones *et al.,* 2000), mixes allotropic forms of carbon (Kwok *et al.,* 1999) was supposed. The first researches of structure of the interstellar dust, carried out by a space vehicle «Stardust» with five particles of dust, showed presence of polymeric heteroaromatic bonds (Kruger *et al.,* 2000).

The detonation nanodiamonds are differing from other types of diamonds. It is connected with an unusual mechanism of their formation through liquid phase of carbon. Therefore they have narrow average size of particles 4-6 nm and contain hollow spheres in (Vereshchagin *et al.,* 2000) and resemble solid diamond foam. They have tetragonal crystal structure (Vereshchagin *et al.,* 2004) Owing the high surface the enthalpy formation (estimation) of DND is +3.425 MJ/kg (diamond in a standard condition of +0.158 MJ/kg). On the same reason DND have unusual reactivity to carbon dioxide (adsorption up to 753 K) and to mixture of hydrogen and nitrogen - they evolved HCN at 573 K (Vereshchagin *et al.,* 1996).

On the base of these data, it is possible to assume the following model of transformations of carbon in interstellar space (Vereshchagin, 2002).

Reactions of the detonation nanodiamonds with hydrogen (proton)

Under explosion of the stars rich with carbon, the nanodiamonds should be formed through a liquid phase in the hydrogen and helium medium. The liquid carbon will be crystallized in the form of solution with hydrogen and helium. The process of crystallization of the diamond drops of will run from a surface of DND. Owing to a difference between of density of liquid and crystal diamonds (3.22 g/sm^3 against 3.515 g/sm^3 at crystal) at such character of process of free space crystallization inside particles can be formed. This free space will be filled with hydrogen and helium. It is established, that diamonds in a space have the critical size 2.9…3 nm (Anisichkin *et al.,* 1988 and Badziag *et al.,* 1990). In that case internal diameter of a cavity will be not less than 1.54 nanometers, and wall thickness - will make not less than 0.78 nm (or approximately 5 lengths of bond C-C) (assuming, that the density of star diamond will be equal to density of the DND – 3.05 g/sm^3) not less. It is abnormal great values of curvature of a surface DND cause their high reactionary ability. Hydrogen which is inside at raised pressure (by our estimations for the DND up to 20 MPa) can leave on a surface of particles and desorbed itself as molecules of methane. It will reduce the thickness of walls of diamond particles. Interaction of the atomic and molecular hydrogen which is not taking place inside particles of the DND (allocated proceeds during activity of stars), with a surface diamond nanoparticles runs the same way therefore the further reduction of a wall thickness can begin. A limiting case of this transformation is the formation of the one-dimensional closed structure (fullerenes type) and transition of carbon from sp^3 in sp^2 under condition with the subsequent hydrogenation high-energy molecules of hydrogen or protons and transformation to flat polycyclic fragments such as molecules of naphthalene. The thermodynamic probability of such reaction is great enough, as standard enthalpy formations of fullerenes C_{60} equals to +2346 ± 12 kJ/mol (Diky *et al.,* 2000) or +3.258 MJ/kg. At the same time by our calculations limiting value enthalpy formations of nanodiamonds makes + 41.1 kJ/mol or +3.425 MJ/kg (enthalpy formations of diamond in a standard condition of +0.158 MJ/kg). To estimate such transformation we shall make the following assumptions. Star origin nanodiamonds will consist only of carbon and hydrogen on their surface. Taking into consideration, that for particles of this size the share of surface atoms makes approximately 25% and that not compensated bonds of atoms of carbon will be connected to atoms of hydrogen, we shall receive the gross formula of detonation nanodiamonds $CH_{0.25}$. Then the equation of prospective reaction of fullerenes formation C_{60} will the following:

$$64CH_{0.25(s)} \rightarrow C_{60(s)} + 4CH_{4(g)}.$$

In view of these assumptions, we received the value minus 3692.8 kJ/mol C_{60} for energy of Gibbs under standard conditions. Therefore, in principle nanodiamonds can form fullerenes.

From the thermodynamic point of view it is possible the formation of naphthalene structures from DND, and fullerenes. However the velocity of such processes can very insignificantly due to low temperatures of interstellar space, but high kinetic energy of colliding particles can compensate low temperature of near surrounding space:

$$10CH_{0.25(s)} + 2.75H_{2\,(g)} \rightarrow C_{10}H_{8(g)}\ \Delta G_{298}^{0} = -267.6\ \text{kJ/mol}$$

$$C_{60}(s) + 24H_2(g) \rightarrow 6C_{10}H_{8\,(s)}\ \Delta G_{298}^{0} = -541.6\ \text{kJ/mol}\ C_{10}H_8.$$

From the thermodynamic point of view the subsequent hydrogenation of aromatic cyclic structures up to methane is possible, but, more probably, with participation of atomic hydrogen it possible also:

$$C_{10}H_{8(s)} + 36H_{2(g)} \rightarrow 10CH_{4(g)}\ \Delta G_{298}^{0} = -1.624\ \text{kJ/mol}\ CH_4.$$

Heating the particles of DND to the temperature higher than 1473 K under influence of high-energy space particles should lead to graphitization of DND.

Detonation nanodiamonds reactions with nitrogen and hydrogen (proton)

As DND are capable to react with N_2 and H_2 under soft conditions (Vereshchagin *et al.,* 1996*)* in products of reaction can be found out molecules of hydrocyanic acid:

$$CH_{0.25(s)} + H_{2(g)} + N_{2(g)} \rightarrow HCN_{(l)} + 3H_{2(g)} \rightarrow NH_{3(g)} + CH_{4(g)}.$$

Thus it should be noted, that the mechanism of hydrocyanic acid formation should include some more stages. From the thermodynamics point of view HCN in process

$$CH_{0.25(s)} + 0.4875H_{2(g)} + 0.5N_{2(g)} \rightarrow HCN_{(l)}$$

was impossible due to thermodynamic reasons as Gibbs potential is positive - + 70 kJ/mol HCN. From the thermodynamics point of view the hydrocyanic acid formation from nitryls – cyanogens, dicyanogen or dicyanoacetylene is more favorable. Accepting the data received of hydrocyanic acid formation should from the DND in laboratory conditions, it is possible to assume, that N_2 chemosorbed with dissociation on the surface of DND with nitryl groups formation, which are hydrogenated by H_2 (also by atomic hydrogen) with evolution of hydrocyanic acid.

Nanosize of detonation diamonds also assumes very high curvature of the surface that will promote, apparently, dissociation of the adsorbed diatomic molecules on atoms.

The observed hydrocyanic acid formation in soft conditions can give the additional data for consideration of initial stages of carbon genesis in the Universe. So, according to the classic theory of origin of a life on the Earth on data (Miller, 1953), formation HCN occurs in the electric discharge:

$$2CH_4 + N_2 ===> 2HCN + 3H_2$$

$$CO + NH_3 ===> HCN + H_2O$$

In view of our data a hydrocyanic acid is formed and in more mild conditions that can add the theory to the new approach.

Further, the atmosphere composition of Solar system planets-giants can include ammonia and methane in a molar ratio approximately 1:1 (table 1) (if taking into account the aerosols composion).

TABLE 1

Structure of a gas atmosphere of planets-giants of Solar system

Planet	Composition the atmosphere [http://nssdc.gsfc.nasa.gov/planetary]
Jupiter	H_2 - 89.8%; He - 10.2%
	impurities (ppm): **CH_4 - 3000; NH_3 - 260;**
	HD - 28; C_2H_6 - 5.8; H_2O - ~4
	Aerosoles: solid **NH_3, H_2O, NH_4HS**
Saturn	H_2 - 96.3%; He - 3.25%
	impurities (ppm): **CH_4 - 4500; NH_3 - 125;**
	HD - 110; C_2H_6 - 7
	Aerosoles: solid **NH_3, H_2O, NH_4HS**
Neptune	H_2 - 80.0%; He - 19.0%; CH_4 1.5%
	impurities (ppm): HD - ~192; C_2H_6 - ~1.5
	Aerosoles: solids **NH_3, H_2O, NH_4HS, CH_4**(?)
Uranium	H_2 - 82.5%; He - 15.2%, **CH_4- ~2.3%**
	impurities (ppm): HD - ~148
	Aerosoles: solids **NH_3, H_2O, NH_4HS, CH_4**(?)

Precisely the same parity between these gases is observed at restoration of hydrocyanic acid by hydrogen $HCN + 3H_2 = CH_4 + NH_3$. In view of these data it is possible to assume, that at the first stage of formation of the Solar system planets-giants hydrocyanic acid was originally formed from ultradisperse carbon, hydrogen and nitrogen then was reduced up to ammonia and methane (Vereshchagin, 2003).

CONCLUSIONS

Therefore, in products of carbon stars explosion can be a plenty of the various carbon substances formed in the reactions of a primary carbon, – hollow diamond nanoparticles and products of their hydrogenation can be submitted: fullerenes, polycyclic structures, hydrocyanic acid, ammonia, methane. Besides it, the DND under heating are capable to graphitize. In such case, it is quite probably to admit, that detonation nanodiamonds is a primary state of carbon in the Universe.

REFERENCES

ALLAMANDOLA, L.J.; SANDFORD, S.A.; TIELENS, A.G.G.M. and HERBST, T. *Spectroscopy of Dense Clouds in the C-H Stretch Region: Methanol and "Diamonds"*. Astrophys. J. 1992; V. 399, 134-146.

ALLAMANDOLA, L.J.; SANDFORD, S.A.; TIELENS, A.G.G.M. AND HERBST, T. *"Diamonds" in Dense Molecular Clouds: A Challenge to the Standard Interstellar Medium Paradigm. Science*. 1993; V. 260; 64-66.

ANISICHKIN, V.F.; TITOV, V.M. *Thermodynamic stability of diamond phase. Combustion explosion and shock waves*. 1988; V. 34, N° 3, 135-137.

BADZIAG, P.; VERWOERD, W.S.; ELLIS, W.P.; GREINER, N.R. Nanometre-sized diamonds are more stable than graphite. *Nature*. 1990; V. 343, 244-245.

BEEGLE, L.W.; WDOWIAK, T.J.; ROBINSON, M.S.; CRONIN, J.R.; MCGEHEE, M.D.; CLEMETT, S.J.; GILLETTE S. Experimental Indication of a Naphthalene-Base Molecular Aggregate for the Carrier of the 2175 A Interstellar Extinction Feature. *The Astrophysical Journal*. 1997; V. 487, N° 2, Pt.1. 976.

CLEGGETT-HALEIM, P.; FARRAR, D. *Diamonds in the sky challenge galaxy evolution theories?* http://titan02.ksc.nasa.gov/shuttle/missions/status/ r93-58.

DIKY, V.V.; KABO, G.J. Thermodynamic properties of C_{60} and C_{70} fullerenes. Russian Chemical Reviews. 2000; V. 69, N° 2, 95-104.

FISENKO, À.Â.; ÒÀTSIY, V.F.; SEMENOVA, L.F.; KASHKAROV, L.L. *Interstellar diamond in Allende CV3: comparative analysis on kinetics of oxidation. Àstronom. Vestnik (in Russian)*. 1997; 31, N° 1, 82-90.

GARCÍA-LARIO, P.; MANCHADO, A.; MANTEIGA, M. Infrared Space Observatory Observations of IRAS 16594-4656: a New Proto-Planetary Nebula with strong 21 micron Dust Feature. *Astrophysical Journal*. 1999; V. 513, N° 2, 1: 941-946.

GREINER, N.R.; PHILLIPS, D.S.; JOHNSON, F.J.D. Diamonds in detonation soot. *Nature*. 1988; V. 333, N° 6172, 440-442.

HENBEST N. Astronomers catch the diamonds in stardust. *New scientist*. 1987; n° 1580, 34-35.

JONES, A.P.; d'HENDECOURT, L. Interstellar nanodiamonds: the carriers of midinfared emission bands? *Astronomy and Astrophysics*. 2000; V. 355, N° 3, 1191-1194.

KRUGER, F.R.; KISSEL, J. *First direct chemical analysis of interstellar dust*. Sterne und Weltraum. 2000; V. 39, N° 5, 326-329.

KWOK, S.; VOLK, K.M.; HRVINAK, A. High resolution ISO spectroscopy of 21 mum Feature. *Astrophysical Journal Letters*. 1999; V. 516, 99. 12.

MILLER S. Origin of life. *Science*. 1953; V. 117, 528-529.

VERESHCHAGIN, A.L.; PETROVA, L.A. *Interaction atmospheric nitrogen with diamond-like phase of carbon.* Ultradispersive powders, materials and nanostructures: Materials of conference (17-19 dec. 1996), Krasnoyarsk 1996: KGTU. 42-43 (in Russian).

VERESHCHAGIN, A.L.; SAKOVICH, G.V. Diamond fullerenes are formed during a detonation. *Journal of Science Education*. 2000; V. 1, N° 2, 126-127.

VERESHCHAGIN A.L. *Detonation nanodiamonds*. Barnaul, 2001; 178 p. (in Russian).

VERESHCHAGIN A.L. *Transformations of detonation nanodiamonds in interstellar space*. Physics and chemistry of ultradispersive systems: Materials of VI Allrussia conference (Tomsk 24-27 Aug. 2002). M.: 2002; 38-39.

VERESHCHAGIN A.L. Detonation nanodiamonds - primary state of carbon in the Universe. Science session of MePHI. 2003; V. 8, 285-286 (in Russian).

VERESHCHAGIN, A.L.; YUR'EV, G.S. Structure of Detonation Diamond Nanoparticles. *Inorganic Materials*. 2003; V. 39, N° 3, 247-253.

Recibido: 08-02-2004
Aceptado: 18-08-2004