The influence of temperature and pressure on α- and β-carbynes

Yu. P. Kudryavtsev and N. A. Bystrova*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

Different behaviors of α- and β-carbynes under conditions of high temperatures and pressures were studied.

Key words: carbon, diamond, carbyne, diamond-like carbon, skeleton diamond.

Oxidative dehydropolycondensation of acetylene (**1**) and low-temperature carbonization of polyvinylidene halides (**2**) are the main chemical methods for preparing carbynes. Polymers with a system of conjugated triple bonds (α-carbyne) are synthesized by the first method, and the second method is used for synthesis of polymers with a system of cumulated double bonds (β-carbyne). The latter is also used for preparing films and fibers.

Based on the data of quantum-chemical calculations for an infinite homoatomic linear system of C atoms, the behavior of α- and β-carbynes under high temperatures and pressures is not expected to differ substantially.[1] However, this is not the case.

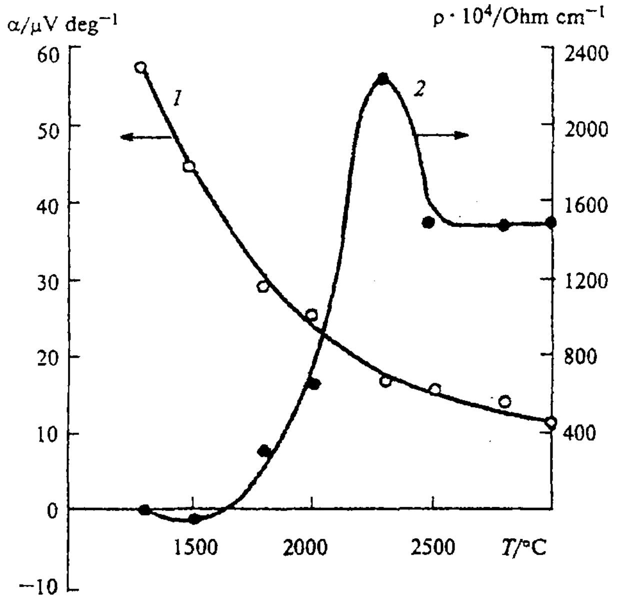


Fig. 1. Temperature dependences of the specific electric resistance ρ (*1*) and thermal emf α (*2*) for the carbyne sample obtained by the oxidative dehydropolycondensation of acetylene.

α-Carbyne is stable toward high temperatures, and its transformation into graphite begins only at 2300 °C (Fig. 1).[2,3]

β-Carbyne films synthesized by dehydrofluorination of oriented polyvinylidene fluoride (PVDF) films under mild conditions are less stable, and their heating at 300 °C results in the appearance of a Raman absorption band in the region of 1345 cm^{-1} (Fig. 2), which is characteristic of the diamond film obtained by the electric-arc method from methane.[4]

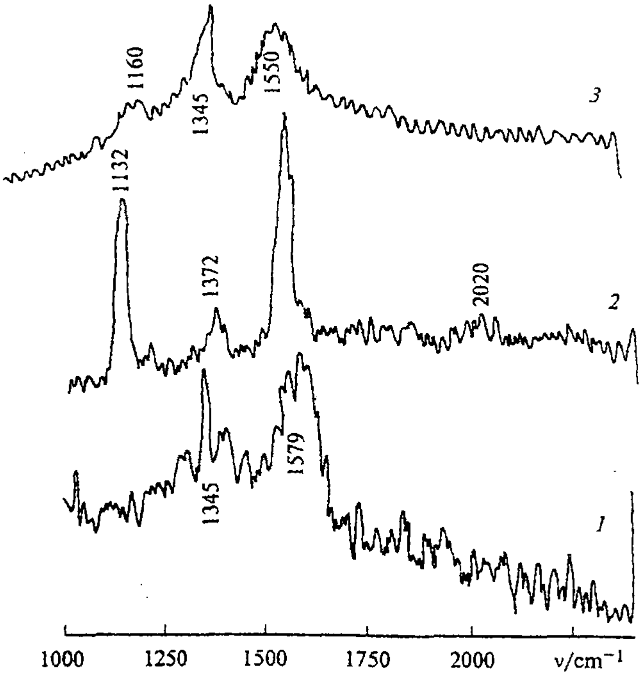


Fig. 2. Raman spectra of β-carbyne samples synthesized by the low-temperature dehydrofluorination of PVDF: *1*, heated at 300 °C; *2*, starting β-carbyne; and *3*, diamond film obtained by the electric-arc method from methane.[4]

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 589—591, April, 1998.

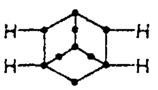
1066-5285/98/4704-0566 $20.00 © 1998 Plenum Publishing Corporation

The ^{13}C NMR spectra of solid samples of β-carbyne synthesized by the low-temperature carbonization of polyvinylidene halides and heated at 130 °C exhibit[5] signals with chemical shifts at 93 (sp), 125 (sp^2), and 48 ppm (sp^3), which indicate that these samples contain "cross-linked" structures.

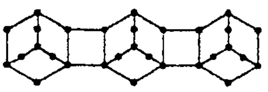
This conclusion agrees with the IR spectroscopy data. The band in the region of 2100 cm^{-1} (Fig. 3, curve *1*), which is characteristic of the β-carbyne film, disappears after heating at 150 °C (Fig. 3, curve *2*).

The results of differential thermal analysis (DTA) indicate the phase transition in the 360—400 °C region (Fig. 4).

The amorphous β-carbyne powder, being heated to 360 °C in the presence of a catalytic amount of ultradispersed diamond (UDD), is transformed[6] into a new UDD. In the absence of UDD, heating of the amorphous β-carbyne powder to 360—400 °C results in the formation of a new crystalline cubic form of carbon.[7] The mass spectra of the products of β-carbyne pyrolysis at 250 and 300 °C exhibit peaks with *m/z* 124 and 360, respectively. Probably, in the 150—330 °C temperature range, carbyne chains undergo "cross-linking" with simultaneous opening of the double bonds and formation of adamantane structures.



(*m/z* 124)



(*m/z* 360)

Unlike α-carbyne, β-carbyne is sensitive to the action of an electron beam and ion radiation.[8] Ion bombardment leads to the rearrangement of the electronic structure of β-carbyne due to "cross-linking" of adjacent carbon chains. The maximum on the curve in the X-ray photoelectron spectrum of the β-carbyne sample after 15-min ion bombardment is shifted to that of natural diamond (Fig. 5, curve *6*).

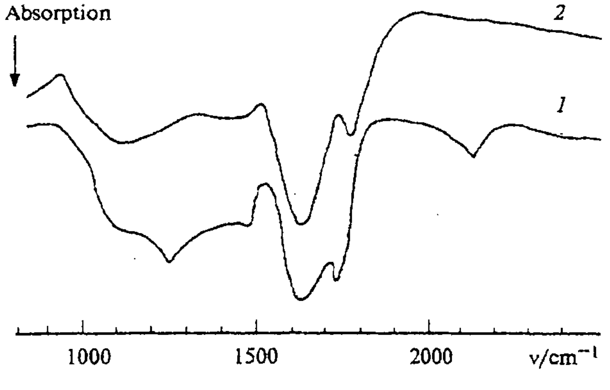


Fig. 3. IR spectra of the β-carbyne sample: starting (*1*) and heated at 150 °C (*2*).

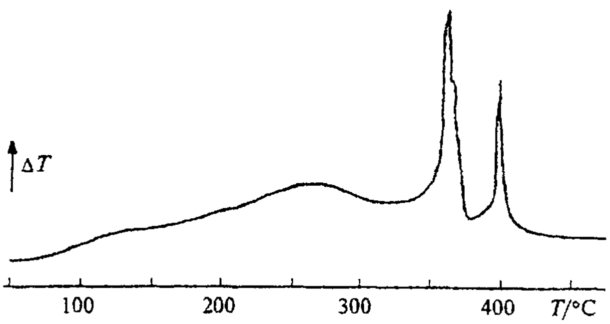


Fig. 4. DTA curve of the β-carbyne sample.

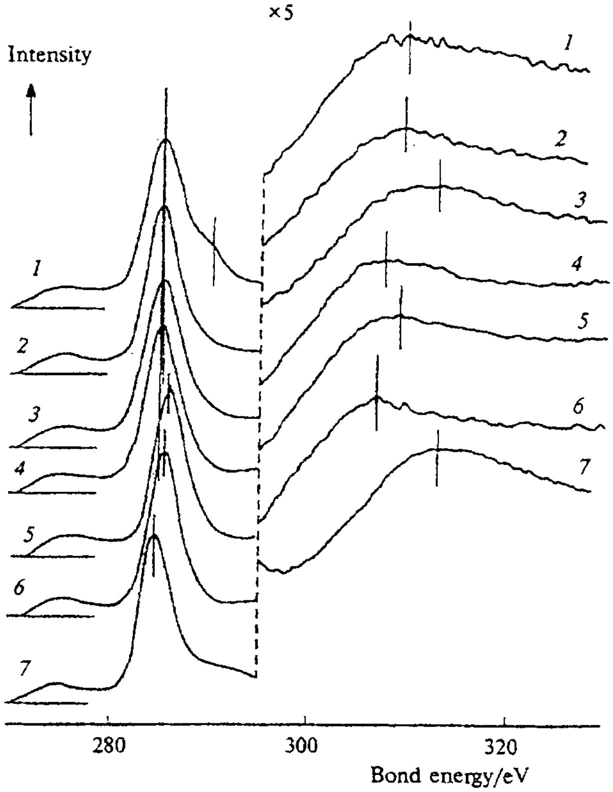


Fig. 5. X-ray photoelectron spectra of β-carbyne samples: *1*, starting sample; *2—5*, after ion bombardment; *6*, natural diamond; and *7*, natural graphite.

Samples of α- and β-carbynes differ substantially when they are affected by high pressures and temperatures. For example, α-carbyne obtained from acetylene is not transformed into diamond under conditions of its synthesis from graphite (9 GPa, 1800 °C with or without a catalyst).[9]

Unlike α-carbyne, β-carbyne samples always contain admixtures of metal, oxygen, or halogen atoms.[10] The quantitative formation of diamond from β-carbyne occurs[11] at 7.7 GPa and 1400 °C. β-Carbyne can also be transformed into diamond-like carbon under atmospheric pressure even at 360 °C. Heating of the β-carbyne sample in air at 250—300 °C results in the formation of the crystalline cubic phase.[12]

Different carbyne samples differ in color (for example, chaoite crystals are white[13]) and hardness (>9 according to the Mohs scale[14]). Amorphous α-carbyne samples obtained from acetylene have a graphite hardness and can be recommended as antifriction materials, whereas β-carbyne behaves as an abrasive. These differences in behavior of α- and β-carbynes can be explained by the fact that they are not straight chains, but have regular breaks in the structure.[15] The carbyne structure is stabilized by the interchain interaction in break points. Unlike α-carbyne, the double bonds in β-carbyne are cleaved in the break points, which determines its instability and possibility to form "linkages." Quantum-chemical calculations show that a forbidden band is absent in β-carbyne,[16] which is evidence for its instability and an easy transformation of β-carbyne into diamond-like carbon.

The carbon obtained by heating of β-carbyne exhibited a close similarity to the natural skeleton diamond in both crystal morphology and X-ray diffraction data.[17]

Thus, unlike α-carbyne, β-carbyne possesses a lower thermal stability and even at 250—400 °C is capable of transforming into diamond-like or cubic forms of carbon.

Experimental

β-Carbyne samples were synthesized by dehydrofluorination of PVDF: a 0.05% solution of PVDF in DMF was supported onto a KBr crystal surface and exposed at 150 °C for 1 h. The polycrystalline PVDF film obtained was dehydrofluorinated at 0 °C for 30 min by a solution of potassium alcoholate in dehydrated EtOH. The film was washed in aqueous EtOH and exposed at 300 °C for 1 h.

X-ray patterns were obtained on a DRON-3 diffractometer. Raman spectra were recorded on a Ramanor U-1000 spectrometer with excitation of an Ar^+—Kr^+ laser.

References

1. N. A. Popov and E. M. Shustorovich, *Zh. Strukt. Khim.*, 1965, **6**, 596 [*J. Struct. Chem.*, 1965, **6** (Engl. Transl.)].
2. V. V. Korshak, V. I. Kasatochkin, Yu. P. Kudryavtsev, and K. Usenbaev, *Dokl. Akad. Nauk SSSR*, 1961, **136**, 1342 [*Dokl. Chem.*, 1961, **136** (Engl. Transl.)].
3. I. B. Rabinovich, B. V. Lebedev, V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, and L. Ya. Martynenko, *Dokl. Akad. Nauk SSSR*, 1966, **168**, 599 [*Dokl. Chem.*, 1966, **168** (Engl. Transl.)].
4. I. I. Aksenov, V. V. Vasil'ev, V. E. Strel'nitskii, E. D. Obraztsova, and V. G. Ral'chenko, *Proc. VI Int. Symp. "Tonkie plenki v mikroelektronike"* [*Thin Films in Microelectronics*], Moscow—Kiev—Kherson, 1995, 33 (in Russian).
5. Yu. P. Kudrjavtsev, R. B. Heimann, and S. E. Evsyukov, *J. Mater. Sci.*, 1997, 5565.
6. Yu. P. Kudriavtsev and S. E. Evsyukov, *Diamond and Related Compounds*, 1997, **6**, 1743.
7. T. D. Varfolomeeva, S. V. Popova, A. G. Lyapin, V. V. Brazhkin, Yu. P. Kudryavtsev, and S. E. Evsyukov, *Pis'ma v ZhETF*, 1997, **66**, 237 [*JETP Lett.*, 1997, **66** (Engl. Transl.)].
8. L. A. Pesin, V. L. Kuznetsov, Yu. P. Kudryavtsev, and S. E. Evsyukov, *Khim. Vys. Energ.*, 1996, **3**, 234 [*High Energy Chem.*, 1996, **3** (Engl. Transl.)].
9. V. I. Kasatochkin, V. V. Korshak, Yu. P. Kudrjavtsev, A. M. Sladkov, and L. E. Sterenberg, *Carbon*, 1975, **11**, 70.
10. Yu. P. Kydryavtsev, S. E. Evsyukov, M. B. Guseva, V. G. Babaev, V. V. Khvostov, and L. V. Krechko, *Carbon*, 1992, **30**, 213.
11. V. V. Korshak, Yu. V. Korshak, Yu. P. Kudryavtsev, S. E. Evsyukov, M. B. Guseva, V. G. Babaev, V. V. Khvostov, and T. D. Varfolomeeva, Russ. Fed. Pat. 1.533.221, 1993 (*Chem. Abstrs.*, 1994, **120**, 110831a).
12. Yu. P. Kudryavtsev and N. A. Bystrova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2805 [*Russ. Chem. Bull.*, 1996, **45**, 2663 (Engl. Transl.)].
13. A. El. Goresy and G. Donney, *Science*, 1969, **161**, 363.
14. V. I. Whittaker, US Pat. 4.248.909, 1981, *Chem. Abstrs.*, 1981, **94**, 161416w.
15. R. B. Heimann, J. Kleiman, and N. M. Salansky, *Carbon*, 1984, **22**, 147.
16. R. E. Peierls, *Quantum Theory of Solids*, Clarendon Press, Oxford, 1956, 108 pp.
17. T. G. Shumilova, *Mineralogiya skeletnykh almazov iz metamorficheskikh porod* [*Mineralogy of Skeleton Diamonds from Metamorphous Rocks*], Geoprint, Syktyvkar, 1996, 40 pp. (in Russian).

Received April 1, 1997;
in revised form November 26, 1997