ON THE ATOMIC STRUCTURE OF THE POLYYNE FORM OF CARBON

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Abstract

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The structure of open forms of carbon is presumably based on macromolecules of linearly polymerized carbon of the polyyne type ($—C \equiv C—C \equiv C—$) and cumulene type ($= C = C = C =$), with various degrees of "cross-linking," in contrast to diamond and graphite, whose macromolecules are spatially and planarly polymerized forms of carbon.

In the present study we examined the X-ray diffraction pattern and infrared spectra of carbonaceous products of acetylene condensation, obtained by the interaction of acetylene with aqueous solutions of salts of divalent copper and by subsequent oxidation of the polymeric copper acetylenides with red prussiate of potash* ($^{1-3}$). The proposed mechanism for the formation of the polyyne structure of carbon may be described by the scheme

$$4HC \equiv CH + 2Cu^{2+} = HC \equiv C—C \equiv CH + 2HC \equiv CCu + 4H^+;$$

$$4HC \equiv C—C \equiv CH + 2Cu^{2+} = HC \equiv C—C \equiv C—C \equiv C—C \equiv CH + HC \equiv C—C \equiv CCu + 4H^+$$

and so on.

X-ray photographs and infrared spectra were taken from samples washed with hydrochloric acid solution. In Fig. 2 an X-ray photograph is presented, obtained with filtered iron radiation in a cylindrical camera of radius 71.62 mm. On the X-ray photograph two relatively sharp interference bands are clearly reproduced, one of which corresponds to the Bragg period 3.90 Å and the other to 2.62 Å. The first band should be assigned to intermolecular interference in a bundle of densely packed parallel rectilinear polyyne carbon chains. The magnitude of the period of the second band, which should be assigned to intramolecular interference in the carbon chain, is somewhat greater than the sum of the lengths of the triple ($d_{C\equiv C} = 1.19$ Å) and single ($d_{C—C} = 1.36$ Å) interatomic bonds in the diacetylene molecule. It is necessary to note the presence on the X-ray photographs of a considerable background of incoherent scattering and a broad interference halo, which indicates a poorly ordered part of the molecular carbon chains with an average intermolecular spacing of ~ 4.0 Å.

Fig. 1

Figure 1: Fig. 1

Fig. 1

In Fig. 1 are shown IR spectra taken from samples pressed into pellets with potassium bromide on a double-beam IKS-14 spectrophotometer in the region 640–3900 cm^{-1} (NaCl and LiF prisms). It is interesting that the spectra include absorption bands characteristic both of the polyyne ($\text{—C} \equiv \text{C—C} \equiv \text{C—C} \equiv \text{C—}$) and of the cumulene ($= \mathrm{C} = \mathrm{C} = \mathrm{C} =$) struc-

[*] The synthesis of the products was carried out by A. M. Sladkov and Yu. P. Kudryavtsev at the Institute of Organoelement Compounds, Academy of Sciences of the USSR.

To the article by V. I. Kasatochkin, O. I. Egorov, and Yu. G. Aseev, p. 125.

Fig. 2

To the article by N. N. Karlov, p. 168.

Fig. 1. Clayey formations in white quartz sands of the Sivash Formation near Dnepropetrovsk; 1-5 —fragments of tubes-burrows of *Orphiomorpha nodosa* Lundgren; 6, 7 —tubes of Annelidae (?); 8 —coprolite (?) natural size.

structures of carbon atomic chains. The polyyne structure is reflected by the bands of valence vibrations of triple bonds of monosubstituted $RC \equiv CH$ at 2100 cm^{-1} (very strong) and disubstituted $R_1C \equiv CR_2$ at 2200 cm^{-1}. The spectrum also contains bands characteristic of triple bonds, corresponding to vibrations of $\equiv CH$ groups at the ends of the carbon chain: valence vibrations at 3300 cm^{-1} and 3250 cm^{-1}, and deformation vibrations at 1250 cm^{-1} (overtone).

The cumulene structure of the carbon chains is reflected by absorption bands at 1950 cm^{-1} (very strong) and 1060 cm^{-1} (weak), corresponding to vibrations of cumulated double bonds, the assignment of which was examined in detail in the study of allene spectra ([4,5]). In addition to the indicated bands, the spectrum also contains a broad absorption band with a maximum near 1640 cm^{-1}, characteristic of the aggregate of complex valence vibrations of conjugated double bonds in the polyene structure of carbon chains. The appearance of these bands, in our opinion, may be attributed to the "cross-linking" of part of the polyyne carbon chains with rupture of triple bonds, leading to a spatially "cross-linked" structure of polyene nature.

The polymeric carbonaceous products of acetylene condensation studied, according to the infrared spectra and X-ray diffraction data presented, are open forms of carbon in which rectilinear macromolecules of polyyne and partially cumulene structure are assembled into molecular bundles of parallel carbon chains. Part of the macromolecules is "cross-linked" into a spatially disordered conjugated polyene structure.

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