Influence of the structure of carbyne on the preparation of diamond

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The influence of the structure of carbyne on the preparation of diamond was considered. Carbyne obtained by the dehydrohalogenation of polyvinylidene halides is a precursor of diamond and α-carbyne.

Key words: carbon, carbyne, diamond, allotropic modifications.

At the present time, the most accessible methods for obtaining carbyne are the oxidative dehydropolycondensation of acetylene[1] and the low-temperature dehydrohalogenation of polyvinylidene halides by a solution of alkali in alcohol in the presence of THF or acetone.[2] The latter method makes it possible to obtain carbyne in the form of films, fibers, and coatings, which have found application in medicine, in particular, in surgery.[3]

Carbynes synthesized by different methods have some differences. For example, carbyne obtained by the dehydropolycondensation of acetylene does not form diamond under the conditions of its synthesis from graphite (9 GPa, 1800 °C, Fe or Ni as the catalyst),[4] while carbyne synthesized by the dehydrohalogenation of polyvinylidene halides forms diamond at lower pressures and temperatures (5—6 GPa, 1000 °C).[5] In this case, the addition of ultradispersed diamond to carbyne makes it possible to obtain diamond at normal pressures and at 360 °C.

The reasons for the different behavior of carbynes obtained by different methods have been studied in this work.

Experimental

Polyvinylidene fluoride (PVF) films in DMF were used as the subject of the investigation. The films were dehydrofluorinated in the fixed state (the film was preliminarily extended along one axis) by two methods: under the action of $NaNH_2$ in liquid ammonia[6] followed by treatment with a solution of alkali in alcohol or by treatment with a solution of KOH in alcohol in the presence of acetone[2] at −20 °C. IR spectra of the films were recorded on a double-beam UR-20 spectrophotometer according to the standard procedure. The preparation of diamond from β-carbyne in the presence of ultradispersed diamond (UDD) has been described previously.[7] In the absence of UDD, β-carbyne was heated in a metallic crucible for 400 h at 360 °C.

Results and Discussion

The IR spectroscopy data and the quantitative yield of oxalic acid in the ozonolysis of the product[8] confirm that the polyyne form of carbyne (α-carbyne) is primarily formed during the oxidative dehydropolycondensation of acetylene. α-Carbyne with an even number of carbon atoms is formed by the stepwise mechanism of the oxidative dehydropolycondensation of acetylene (Scheme 1).

Scheme 1

$$4\,HC{\equiv}CH \xrightarrow{Cu^{2+}} HC{\equiv}C{-}C{\equiv}CH + 2\,HC{\equiv}C{-}Cu + 4\,H^+,$$

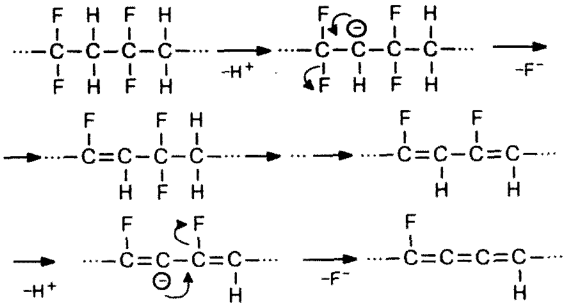
$$4\,HC{\equiv}C{-}C{\equiv}CH \xrightarrow{Cu^{2+}} HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}CH +$$

$$+\ 2\,HC{\equiv}C{-}C{\equiv}C{-}Cu + 4\,H^+\ \textit{etc.}$$

Carbyne obtained by this method does not transform into diamond under the conditions of its synthesis from graphite.[4]

The cumulene form of carbyne $-(C{=}C{=}C{=}C)_n-$ (β-carbyne) is mainly formed as a result of the exhaustive dehydrofluorination of PVF by an alkali in alcohol in the presence of acetone (Scheme 2).[2]

Scheme 2



β-Carbyne is easily transformed into diamond at lower pressures and even at normal pressures when ultradispersed diamond is added.[7]

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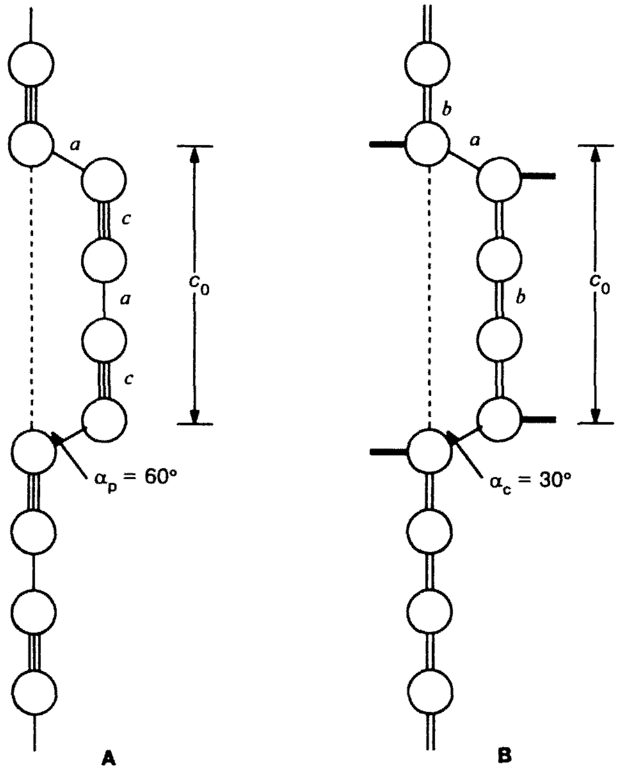

Fig. 1. Models of α-carbyne (**A**) and β-carbyne (**B**) according to Heimann[9] (a = 0.1379 nm, b = 0.1282 nm, and c = 0.1207 nm).

A zigzag-like model of the structure of the carbon chains, in which linear regions alternate with regular breaks (Fig. 1), has been suggested previously.[9] No cleavage of the bonds occurs at the points of the breaks of the polyyne chain, but in the β-carbyne structure unsaturated bonds are formed and alkali metals are intercalated at the points of the breaks, and cross-links are easily formed. The UDD added reacts smoothly at the points of the breaks, and heating results in the opening of the cumulated bonds to release heat, which favors the epitaxial synthesis of new UDD.[10]

It is of interest that after heating in an argon flow at 150 °C, the PVF film, which was dehydrofluorinated completely by the alkali in alcohol in the presence of acetone, already contains C atoms in the sp^3-hybridization state.* The addition of UDD catalyzes the formation of diamond in this film, *i.e.*, the existence of C atoms with sp^3-hybridization of the atomic orbitals favors this process.

We attempted to obtain carbyne from this precursor. It has been previously shown that the treatment of PVF film with sodium amide in liquid NH_3 results in the formation of α-carbyne.[6] However, the structure of the initial polymer is retained even after 400 h of treatment. To accelerate the process we combined two methods: dehydrofluorination under the action of $NaNH_2$ in liquid NH_3 and dehydrofluorination by a solution of KOH in alcohol in the presence of acetone. During the treatment the film was oriented along one axis and fixed. As a result, we obtained for the first time the spectrum of α-carbyne, which contains no "dip" in the region of 1100—1700 cm^{-1} typical of the zigzag-like chain of carbyne (Fig. 2). Evidently, this carbyne film will not transform easily into diamond, because its structure is identical to that of the powder obtained by the oxidative condensation of acetylene.

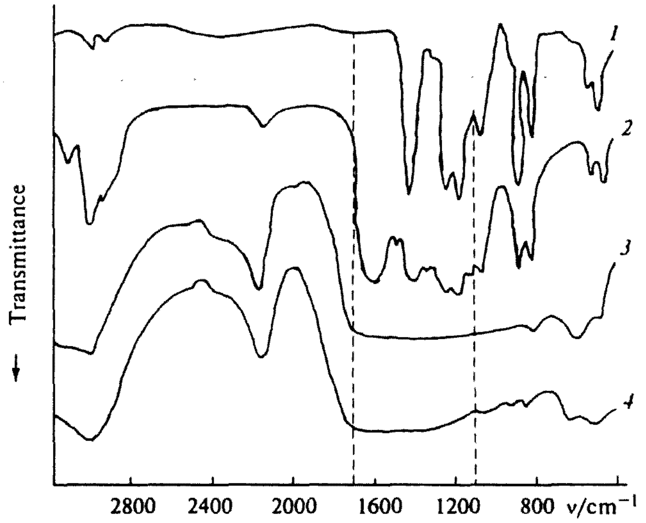

Fig. 2. IR spectra of the initial PVF film (*1*); film treated with alkali in alcohol in the presence of THF for 20 h (*2*); film treated with $NaNH_2$ in liquid NH_3 for 100 h (*3*), and then with alkali in alcohol in the presence of acetone for 1 h (*4*).

Thus, the product of the dehydrohalogenation of polyvinylidene halides is a precursor of diamond and α-carbyne. The existence of the zigzag in the structure of the initial β-carbyne is the reason for its easy transition to diamond (with the addition of UDD) or into diamond-like carbon (in the absence of UDD).

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Mechanoactivation of solid-phase iodochlorination of olefins with potassium dichloroiodate(I)

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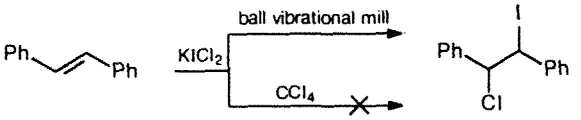
Mechanoactivation of iodochlorination of olefins with a new reagent, potassium dichloroiodate(I), was studied.

Key words: potassium dichloroiodate(I), iodochlorination; reactivity, mechanoactivation.

Solid-phase methods are promising in the development of techniques of organic synthesis[1] and chemical technology.[2] Much attention is being given to the study of the mechanisms of mechanoactivated chemical reactions.[2] The mechanical properties of reagents are likely to significantly influence the results of these processes, and hence solid-phase procedures are quite promising for the study of the action of solid reagents on solid organic substrates. We have found that stilbene (**1**), which almost does not react with potassium dichloroiodate(I), $KICl_2$, on stirring in CCl_4, undergoes preparative iodochlorination under the action of this reagent in a ball vibrational mill. This process is probably mechanoactivated by the energy that is released locally during the mechanical destruction of the hard and brittle stilbene crystals in the vibrational mill.



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(85%)

In contrast, methyl cinnamate (**2**), which easily undergoes iodochlorination under the same conditions in solution, remains unchanged when treated with $KICl_2$ in the ball vibrational mill. This can be explained by the fact that during mechanical treatment of the soft and low-melting crystals of ester **2** mechanical energy is consumed to melt it, and there is no mechanoactivation of iodochlorination. Thus, the data obtained by us suggest that solid-phase iodochlorination of olefins with potassium dichloroiodate(I) is decisively influenced by the mechanical properties of the olefin.

Experimental

The solid-phase syntheses were carried out in a plastic chamber 20 cm^3 in volume (working agents were steel balls: 44 with a diameter of 4 mm and 27 with a diameter of 2 mm) rotating at a frequency of 5—7 Hz and with a vibrational amplitude of 2 cm along the vertical axis and 2 cm along the horizontal axis. The ^{1}H NMR spectrum was recorded on a Bruker FT-80 instrument (80 MHz) in CCl_4 with HMDS as the internal standard. Chromatographic analysis was performed using Silufol UV-254 plates.

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