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GEOCHEMISTRY

Hydrogenation during Adiabatic Cavitation in a Hydrocarbon Medium

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It was shown theoretically [1, 2] that diamond can be synthesized in nature during adiabatic cavitation, which takes place, for instance, in a rapidly ascending kimberlite melt. Solid particles containing diamond nanocrystals were obtained in experiments on cavitation in a benzol medium [3]. The adiabatic collapse of cavitation bubbles was provided by the pressure drop at the front of a shock wave generated in the collapse zone. All solid particles had almost spherical shape, and their size varied from 10 to 17 μm. This particle size distribution was responsible for the minimal diameter of bubbles after the termination of their adiabatic compression. The shape of particles indicates that the collapse of bubbles was a symmetric process; i.e., bubbles underwent an instantaneous confining compression up to final size without change of their spherical shape.

The presence of diamond nanocrystals in the particles indicates that the collapse provided favorable thermodynamic conditions for the stability of diamond matter within bubbles. Hence, the pressures developed in the bubbles were ~10*n* kbar [4]. Increase of pressure up to these values corresponds to contraction of the bubble by 10^5–10^6 times during its collapse. Hence, the initial size of the bubbles was ~1 mm. Bubbles of this size were generated by a profiled jet pipe, whose minimum and maximum sizes in the experimental device were 3 and 10 mm, respectively. At a bubble size of 1 mm, the propagation time of the shock wave was 10^{-6} s, which is three orders of magnitude lower than the time of asymmetric collapse, during which the maximum pressure reached *n* kbar at a temperature less than 1000°C [5].

The thermodynamic conditions in the bubbles during their adiabatic compression were such that the kinetic energy of any particle in a volume of the cavitating bubble was significantly higher than the atom-bonding energy in the molecule of the working organic liquid (benzol). Hydrogen atoms released during the formation of diamonds and the high-carbon phase should trigger the hydrogenation of the working liquid. High temperatures at sites of bubble collapse should also provoke variations in the initial composition of the working liquid.

This work presents the results of study of products of organic synthesis that accompany the adiabatic cavitation synthesis of diamonds.

The experiment with the cavitation synthesis of diamonds was performed using benzol of analytical grade. The chromatogram of the initial benzol is shown in Fig. 1. Samples of the precipitate in the benzol used as the working liquid in the cavitation experiments were processed in the following way. Aliquots (30–50 ml) were taken from a total volume of 0.5 l of benzol treated in the cavitation experiment, emptied in pure Petri dishes, and evaporated in a weak air flow in the draught cupboard. A distinctly visible film of polymer material with diamond- and graphite-type inclusions described in [3] remained on the glass.

The precipitate was studied by IR Fourier spectrometry on a Bruker 113v (United States) spectrometer. For measurements, the precipitate was diluted with KBr (approximate weight proportions 1 : 40) and pressed in pellets. The sample represented a film of reaction products on glass after centrifugation and complete evaporation of benzol. It contains at least two fractions: a soft polymer in the form of fine (~1 mm) chips and a non-evaporating or slowly evaporating oily liquid. The spectral dependence of optical density on the frequency of transmitted radiation $D = \lg\frac{1}{T}$ for two samples is shown in Fig. 2.

The products of benzol hydrogenation in the cavitation experiment were also analyzed by gas–liquid chro-

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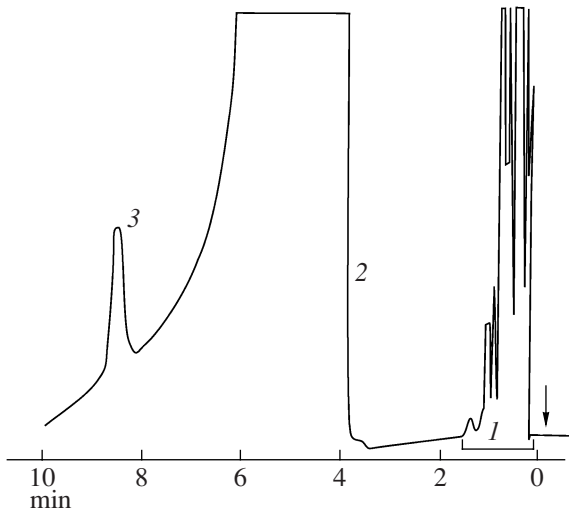

Fig. 1. Chromatogram of initial benzol. Sample volume 15 μl. Signals of products of benzol hydrogenation are absent. (*1*) Light admixtures in the initial benzol (aliphatic and, possibly, unsaturated acyclic hydrocarbons); (*2*) benzol; (*3*) admixture heavier than benzol (unidentified).

matography. We used an LKhM-8MD gas chromatograph with a stainless steel column (3 m long and 4 mm across) filled with ChromaTone N sorbent containing 10% tricyanoetoxypropane. The rate of He carrier gas flow was 20 ml/min. The column temperature was 50°C. The volume of aliquots was varied from 0.5 to 15 μl to determine the subordinate hydrogenation products of benzol. Gas-chromatographic studies were performed according to two procedures: (i) without any additional operations after cavitation; (ii) after concentration of the cavitation-treated benzol in the course of its slow freezing in the chamber at –5°C up to solidification of ~0.9 total volume of the analyzed sample. This procedure provided an approximately ten times higher concentration of subordinate hydrogenation products in the remaining liquid portion of the sample.

To identify the products formed during the cavitation compression of benzol, the retention time of admixtures recorded by chromatographs was compared with the parameters of the retention of known products of benzol hydrogenation. We identified cyclohexane, cyclohexene, cyclohexadiene-1.3, and cyclohexadiene-1.4 (Fig. 3). This figure shows an example of the chromatogram obtained in the gas-chromatographic analysis of benzol subjected to cavitation after concentration.

The spectrum shown in Fig. 2 demonstrates an increase in the optical density in the high-frequency region, which suggests an increase in the scattering on sample particles. It reflects the composition of the organic "coat" of the synthesized diamond-bearing solid phase.

Two lines (ν = 2171 and 2076 cm^{-1}) visible in the spectrum can be interpreted as two closely spaced lines of diamonds: 2030 cm^{-1} (TO + TA) and 1980 cm^{-1} (LO + TA(X)), where LO and TO are longitudinal and transverse optical vibrations of the crystal lattice; LA and TA are longitudinal and transverse acoustic vibrations; and L and X are critical points.

Organic carbon in the organic portion is confined to the methylene groups, which are reliably identified based on stretching asymmetric and symmetric vibrations $\nu_{as}(>CH_2)$ = 2921 cm^{-1} and $\nu_s(>CH_2)$ = 2851 cm^{-1}, as well as on scissorlike deformation and pendulum vibrations $\delta_s(>CH_2)$ = 1468 cm^{-1} and $\delta(>CH_2)$ = 721 cm^{-1}. The number of methyl groups is approximately an order of magnitude lower than that of methylene ($\nu_{as}(-CH_3)$ = 2955 cm^{-1}).

Chromatograms in Fig. 3 indicate that hydrogenation of benzol in the experiment produced subordinate

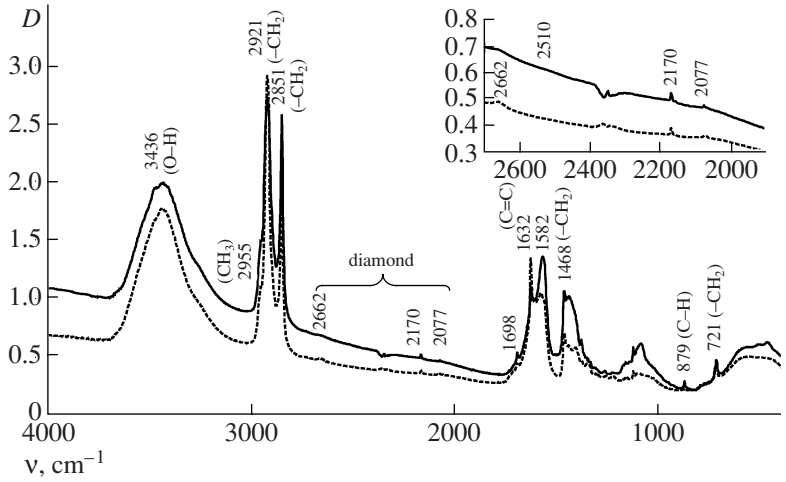

Fig. 2. Spectral dependence of optical density of solid products of the cavitation treatment of benzol on the frequency of transmitted radiation.

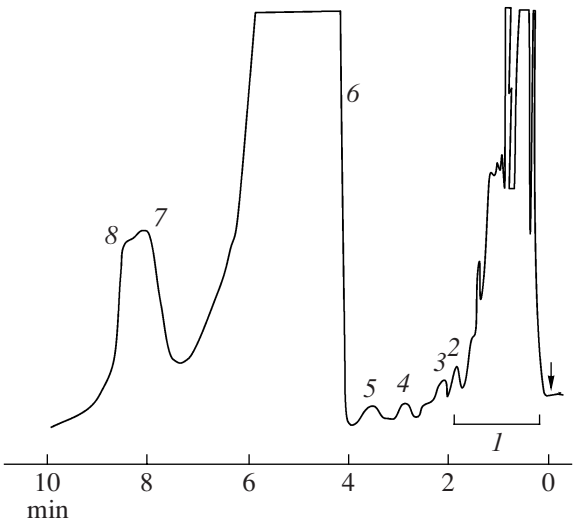

Fig. 3. Chromatograms of benzol after cavitation treatment and concentration by freezing. Sample volume 15 μl. Peaks: (*1*) light admixtures present in the initial benzol, possibly, together with the newly formed acyclic components; (*2*) cyclohexane; (*3*) cyclohexene; (*4*) cyclohexadien-1.4; (*5*) cyclohexadien-1.3; (*6*) benzol; (*7*) unidentified heavier admixture present in the initial benzol; (*8*) newly formed unidentified admixture heavier than benzol.

amounts (~0.0*n*%) of cyclohexadiene-1.3, cyclohexene, and cyclohexane [6].

Thus, our study showed that the cavitation-mediated adiabatic collapse of vapor bubbles in hydrocarbon liquid (benzol) leads to both the hydrogenation and the formation of high-molecular polymer products.

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