Thermal decomposition of deuterofullerite

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The volatile products of thermal decomposition of deuterofullerite $C_{60}D_{19}$ were studied by mass spectrometry. It was found that D_2, CD_4, and C_6D_6 molecules are present in the gas phase above deuterofullerite heated to 773 K. Deuterocarbons appear in the gas phase already at 673 K.

Key words: deuterofullerite, thermal decomposition, mass spectrometry.

The decomposition of hydrofullerenes $C_{60}H_x$ is of interest from the viewpoint of using fullerene-based materials as a medium for hydrogen accumulation. It was established by thermogravimetric analysis (TGA)[1—3] that the weight of the $C_{60}H_x$ begins to decrease noticeably at 723 K on heating in an inert medium. H_2 and fullerene were found in the products of thermal decomposition of hydrofullerenes. The complete reversibility of formation of $C_{60}H_2$ was established for the anodic oxidation of the C_{60} films supported on the graphite electrode.[4] The authors of the work[5] concluded that hydrogenation process is reversible. At the same time, it is known[6] that the products of $C_{60}D_{24}$ thermal decomposition at 823 K contain, along with fullerene molecules, an admixture identified by IR spectroscopy as a fullerene polymer. In addition, methane was found[3] in the gas-phase products of $C_{60}H_{18.7}$ decomposition at temperatures above 823 K.

The purpose of this work is to study the products of thermal decomposition of deuterofullerite, *viz.*, solid deuterofullerene, by mass spectroscopy. Deuterofullerite was chosen to distinguish the products of thermal decomposition from hydrocarbon admixtures, which can appear in the system due to desorption from cool walls and/or vacuum lubricants.

Experimental

IR absorption spectra were recorded on a Specord-75 IR spectrometer in KBr pellets prepared from 2 mg of the substance and 300 mg of KBr. X-ray diffraction patterns were recorded using a DRON ADP-1 diffractometer with monochromatic Cu-Kα radiation. Mass spectra of gases accompanying deuterofullerite were detected in the temperature range from room to 773 K on an MI 1201V mass spectrometer in the *m/z* interval from 4 to 90 (EI, 70 eV).

Fullerene C_{60} synthesized by us contained 99.8 wt.% of the main substance. Before deuteration fullerene was purified by vacuum sublimation to remove the solvent (toluene). A laboratory deuterium accumulator based on $La_{0.75}Mm_{0.25}Ni_5$ (Mm is a technical blend of rare-earth metals).[7]

Fullerene was deuterated at $P = 2.5$ MPa and $T = 723$ K in a standard high-pressure installation. The temperature was monitored with an accuracy of ±10°, and the accuracy of pressure monitoring was ±0.02 MPa. Samples were preliminarily degassed by heating to 500 K *in vacuo* (~1 Pa). Deuterium was supplied to a reactor-autoclave directly from the accumulator heated to 373 K. In order to enhance efficiency, deuteration was conducted in the cyclic thermal mode, *i.e.*, the sample under the D_2 pressure was heated to 723 K, stored at this temperature for 1 h, the reaction mixture was cooled to ~20 °C, and the cycle was repeated. After three cycles, the gas phase was removed, and a fresh portion of D_2 was supplied from the accumulator. This deuteration mode was repeated five times. Found (%): C, 95.05; D, 5.01. $C_{60}D_{19}$. Calculated (%): C, 94.99; D, 5.01.

In experiments on thermal decomposition a deuterofullerite sample (16—40 mg) was placed in a quartz cell of a pyrolyzer connected through a fine adjustment valve with the supply system of the mass spectrometer. After the sample was annealed (373 K, 1 h), and ampule and supply system were evacuated to $\sim 2 \cdot 10^{-5}$ Pa. Gas sampling to a pre-evacuated ampule was started from 373 K. Only the temperature at which the gas collection was stopped and mass spectrometric analysis was began is presented in the mass spectra (Table 1).

Results and Discussion

The diffraction patterns of the sample under study and initial fullerite with the face-centered crystalline lattice can be compared in Fig. 1. As expected,[8] the type of lattice did not change upon deuteration. However, the diffraction peaks were broadened and shifted toward smaller angles. The lattice constant a_0 of deuterofullerite calculated from peak (111) was 14.71 Å (for the initial fullerite, a_0 = 14.18 Å). The studied deuterofullerite is close in a_0 value to hydrofullerite $C_{60}H_{18.7}$ studied in Ref. 3. The value of 14.71 Å substantially exceeds that obtained for $C_{60}D_{24}$ (14.55 Å),[8] perhaps, due to a lower temperature of synthesis of $C_{60}D_{24}$.

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Table 1. Mass spectra of the gas phase above deuterofullerite heated to 673 and 773 K

m/z	*I*/rel. units		Assignment*
	673	773	
4	—	300	$[D_2]^+$
12	2	95	
13	—	5	
14	11	357	
15	3	33	
16	24	910	
17	10	460	
18	139	9100	$[CD_3]^+$, (CD_4)
19	22	1170	
20	280	13500	$[CD_4]^+$, (CD_4)
21	—	142	
22	—	7	
24	—	25	
25	—	3	
26	10	187	$[C_2D]^+$, $(C_2D_2$, C_2D_4, $C_2D_6)$
27	5	59	
28	72	3826	$[C_2D_2]^+$, $(C_2D_2$, C_2D_4, C_2D_6, $C_6D_6)$
29	8	141	
30	84	3800	$[C_2D_3]^+$, $(C_2D_4$, $C_2D_6)$
31	20	580	
32	323	8700	$[C_2D_4]^+$, $(C_2D_4$, $C_2D_6)$
33	13	357	
34	67	1850	$[C_2D_5]^+$, (C_2D_6)
35	18	267	
36	75	3667	$[C_2D_6]^+$, (C_2D_6)
37	—	43	
38	—	23	
39	2	3	
40	3	40	
41	4	10	
42	7	153	
43	5	13	
44	15	718	
45	—	17	
46	—	143	
47	—	10	
48	—	77	
49	—	17	
50	—	150	
51	—	33	
52	—	250	$[C_3D_8]^+$, (C_3D_8); $[C_4D_2]^+$, (C_6D_6)
53	—	7	
54	—	27	$[C_4D_3]^+$, (C_6D_6)
80	—	6	
81	—	3	
82	—	18	
83	—	17	
84	5	138	$[C_6D_6]^+$, (C_6D_6)
85	—	9	

* Ions are presented in brackets, and initial molecules are in parentheses.

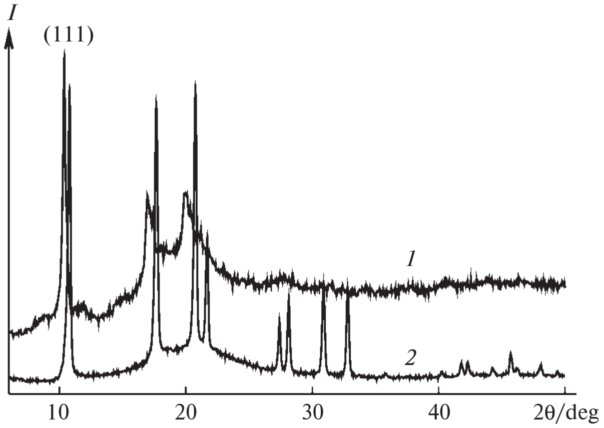

Fig. 1. Diffraction patterns of powered deuterofullerene $C_{60}D_{19}$ (*1*) and initial C_{60} (*2*).

The absorption band at 2150 cm^{-1} attributed to stretching vibrations of the C—D bonds is the most intense in the IR spectrum of the studied sample.[7]

The mass spectrum of the gas-phase decomposition products of deuterofullerite heated to 773 K is presented in Table 1. This is below the temperature, which corresponds, according to TGA data, to the maximum rate of gas evolution (803 K). The residual pressure in the quartz vessel after preliminary annealing of the sample for 15—20 min at 373 K was at most $7 \cdot 10^{-3}$ Pa. After the end of the preliminary annealing, the quartz vessel was disconnected from the vacuum system and heated to a high temperature, which was accompanied by the pressure increase to $(1—3) \cdot 10^2$ Pa. After storage at a required temperature for several minutes, the quartz vessel was connected through a needle valve with the ionization chamber of the mass spectrometer.

As can be seen in Table 1, the spectrum contains a rather intense peak of the CD_4^+ ion with *m/z* 20 along with the peak of D_2^+ (*m/z* 4). Peaks with *m/z* 4 and 20 were not found in residual gases of the mass spectrometer and quartz vessel. These peaks are also absent from the spectra of the products of preliminary degassing of the deuterofullerite samples. However, if the sample pre-degassed at 373 K was heated to 673 K rather than to 773 K, a peak with *m/z* 20 appears in the spectrum and that with *m/z* 4 disappeared. The total amount of the gas evolved from the sample at 673 K (~1 Pa) is much smaller than that evolved at 773 K (300—700 Pa). These values agree with the intensities of peaks in the mass spectra.

The gas phase above $C_{60}D_{19}$ at 773 K contains C_6D_6 along with CD_4. This is indicated by the peak with *m/z* 84, being the most intense in the $60 \le m/z \le 100$ interval. For the decomposition of hydrofullerite $C_{60}H_x$, the peak of $C_6H_6^+$ with *m/z* 78 is the most intense in this mass spectral region.

Heating to 773 K does not change the diffraction pattern of the sample. The IR spectrum of $C_{60}D_{19}$, obtained under these conditions, exhibits a slight decrease in the peak intensity at 2150 cm^{-1}. Chemical analysis showed that the composition of the sample under such a treatment changed insignificantly and corresponded to the molecular formula $C_{60}D_{17,18}$.

Thus, our data confirm the conclusions**[3]** about methane evolution on heating hydrofullerene to 773 K. The obtained results also demonstrate the possibility of formation of benzene C_6D_6 upon heating deuterofullerite to 773 K.

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