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Reaction of D_2 with palladium fulleride $C_{60}Pd_{4.9}$

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Fullerene deuteride was obtained by the reaction of deuterium with solid palladium fulleride $C_{60}Pd_{4.9}$ under fairly mild conditions. The compound was identified by FD-MS, UV-Vis and IR spectroscopies, and TLC.

Key words: fullerene, fullerene deuteride, palladium fulleride; mass spectrometry; UV-Vis and IR spectroscopies.

Hydrogenation of fullerenes is an important problem from both scientific and practical viewpoints.[1] The direct solid-phase noncatalytic hydrogenation of fullerenes occurs at high hydrogen pressures (500—850 bar) and temperatures (573—623 K).[2]

The preliminary results of the study of the reaction of D_2 with palladium fulleride, resulting in the formation of fullerene deuteride $C_{60}D_x$, are presented in this work.

Palladium fulleride $C_{60}Pd_{4.9}$ was prepared by the reaction of C_{60} with $Pd_2(dba)_3 \cdot CHCl_3$ (dba is dibenzylidene acetone) in toluene by the known procedure.[3] The synthesis of $C_{60}Pd_{4.9}$ is characterized by a specific feature: the molar fraction of Pd in the initial solution is 10-fold higher than that of C_{60}. The precipitate formed was multiply washed with toluene to remove unreacted initial reagents and the dba formed. The precipitate was characterized by chemical analysis and XPS, and its composition corresponds to the formula $C_{60}Pd_{4.9}$. Palladium is homogeneously distributed in the sample, *i.e.*, no clusterization of metal atoms typical of Pd/C catalysts occurs.

The reaction of D_2 with $C_{60}Pd_{4.9}$ in the solid phase was carried out for 2 h at 473—673 K and 20 atm of deuterium pressure. The reaction mixture was cooled to room temperature, then toluene was added, and the brown solution formed was separated from the precipitate by filtration. The filtrate was evaporated to dryness, and a brown residue obtained was dried for several hours *in vacuo* at 373 K.

The reaction product was analyzed by mass spectrometry (field desorption, the current of heating of the emitter was 30 mA) on a MAT-731 mass spectrometer. Unlike the electron impact mode, the mass spectrum of fullerene hydrides in the field desorption mode consists mainly of monocharged molecular ions.[4] The mass spectrum obtained (see Fig. 1) exhibits the peaks corresponding to the products of addition of different numbers of deuterium atoms to a fullerene molecule. The most intense peaks correspond to the addition of 2, 4, 18, and 26 deuterium atoms. In addition, the peaks corresponding to the compounds containing 1, 3, 8, 11, 16, and 33 deuterium atoms are observed. Products with different

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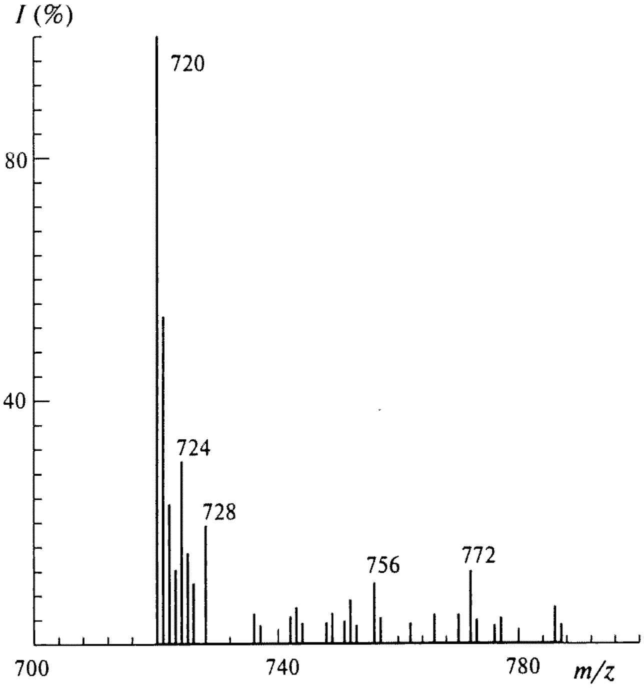

Fig. 1. Mass spectrum of the products of the reaction of D_2 with $C_{60}Pd_{4.9}$.

contents of hydrogen atoms are also observed upon liquid-phase catalytic hydrogenation of fullerenes in the presence of Pd/C (see Ref. 5).

The IR spectrum of the reaction product obtained at 473 K contains a broad absorption band with a center at 2150 cm^{-1} (ν(C—D)), which is absent in the spectrum of the initial palladium fulleride. At 673 K, the intensity of this band increases, and two shoulders at 2190 and 2100 cm^{-1} appear in the spectrum.

The position of the XPS peak of $Pd3d_{5/2}$ for the reaction product is shifted by 0.2 eV at 473 K and by 0.9 eV at 673 K to lower bond energies relative to that of the initial fulleride (336.4 eV) and approaches the position typical of palladium metal (335.3 eV). The ratio of integral intensities C1s/Pd3d for the reaction product at 673 K is 3.3-fold lower than that for the initial fulleride, which testifies to the clusterization of palladium atoms.

The solution of the product obtained in toluene becomes brown that is typical of fullerene hydrides.[1] The peaks at 407 (C_{60}), 435, and 715 nm in the visible spectral range of the spectrum of the solution are also present in the spectrum of hydride.[6] Two spots are observed on the TLC plate: the position of the first spot corresponds to free C_{60}, while the position of the second spot with a center at $R_f = 0.13$ (Silufol-254, CH_2Cl_2 : *n*-hexane = 3 : 4) can be assigned to fullerene deuteride.[4]

Thus, fullerene hydride was obtained for the first time under fairly mild conditions by the reaction of gaseous deuterium with solid palladium fulleride.

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