# Synthesis and properties of crystalline fullerene hydrides

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The interaction of crystalline fullerene $C_{60}$ with highly pure hydrogen, which was evolved from hydrides of intermetallic compounds of rear-earth metals and nickel, was studied. Crystalline fullerene hydrides containing from 10 to 30 hydrogen atoms per fullerene molecule were synthesized (1.0—2.5 MPa and 300—673 K). Crystalline hydrides release hydrogen at 800 K with retention of the structure of the fullerene molecule.

**Key words:** fullerene, hydrogen, hydride, intermetallide, synthesis.

The properties of fullerene hydrides have not been adequately studied although the possibility of their use for accumulation and storage of hydrogen has been reported in the literature.[1—3] Several procedures for the preparation of fullerene hydrides are known.[3] Previously,[4] it has been demonstrated that direct noncatalytic hydrogenation of fullerene $C_{60}$ proceeded efficiently only at very high pressure (50—85 MPa).

We have studied the possibility of hydrogenation of solid fullerenes with gaseous hydrogen under relatively mild conditions (1.0—2.5 MPa and 573—673 K) in the presence of hydride-forming metals or intermetallic compounds.[5—6] The presence of metallic components favors activation of molecular hydrogen and its spillover at the double bonds of fullerenes. However, hydrogenation of these compositions is of little use for the preparative synthesis of fullerene hydrides because it is very difficult to isolate the target compounds from mixtures with hydrides of metals or intermetallic compounds. Besides, studies of chemical conversions in fullerite—metal phase—hydrogen systems demonstrated that a slight increase in the temperature of evolution of hydrogen can induce the formation of carbide.[7]

In this work, we report the results of studies of hydrogenation of crystalline fullerene $C_{60}$ with hydrogen evolved from hydrides of intermetallic compounds, which do not come in direct contact with fullerenes. Unlike commercial $H_2$, hydrogen obtained by the above procedure does not contain oxygen-containing impurities, which often retard processes with the participation of molecular hydrogen, in particular, hydrogenation of metals and alloys.

## Experimental

We used crystalline fullerene $C_{60}$ (purity 99.8 wt.%), which was characterized by IR and UV spectroscopy and X-ray diffraction analysis. Laboratory accumulators based on hydrides of intermetallic compounds $LaNi_5$, $La_{0.75}Ce_{0.25}Ni_5$, $La_{0.75}RE_{0.25}Ni_5$, and $La_{0.67}RE_{0.33}Ni_5$ (RE is a commercial mixture of rare-earth metals) were used as the source of hydrogen.[8]

Hydrogenation of fullerene was carried out at 1.0—2.5 MPa and 300—673 K using a standard high-pressure apparatus. The temperature was controlled with an accuracy of ±10 °C. The pressure was maintained with an accuracy of ±0.02 MPa. Samples were degassed at 500 K *in vacuo* (~1 Pa). Hydrogen was accumulated in a reaction autoclave at 573—673 K by heating a metallohydride accumulator to 373 K. To enhance the efficiency, hydrogenation was carried out in the cyclic thermal mode. The sample was heated to 673 K under a hydrogen pressure and kept at this temperature for 1 h. Then the reaction mixture was cooled to room temperature, and the cycle was repeated. After three cycles, hydrogen was renewed by replacing it with a fresh portion from the metallohydride accumulator. This mode of hydrogenation was repeated no less than five times due to which the process proceeded more completely and samples with a homogeneous distribution of hydrogen throughout the volume were obtained.

The samples were unloaded under an inert atmosphere after cooling of the autoclave to 300 K. The IR absorption spectra were recorded on Specord 75 IR and Perkin—Elmer 1600 spectrometers. The samples for IR studies were prepared as KBr pellets (2 mg of the sample under study per 300 mg of KBr). The magnetic characteristics of the initial and final samples were determined using a M 4500 (EG&G PARC) vibration magnetometer. The thermogravimetric analysis of the samples was performed on Q-1000 and C-1500 derivatographs under an atmosphere of argon with heating at a rate of 10

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K $min^{-1}$. The temperature of the endothermic effects was detected from the position of the minimum on the DTA curve. The X-ray diffraction patterns were obtained on an ADP-1 diffractometer (Cu-Kα radiation). The hydrogen content was determined by combustion of samples under a stream of oxygen using an apparatus for semimicroanalysis of organic compounds.

## Results and Discussion

Hydrogenation of crystalline fullerene afforded crystalline fullerene hydrides containing from 10 to 30 hydrogen atoms per fullerene molecule. The hydrogen content increased as the number of "heating to 673 K — cooling to 300 K" cycles and the rate of replacement of hydrogen in the reactor were increased. Apparently, this is associated with the removal of trace amounts of impurities, in particular, of oxygen and a water vapor, which were evolved from fullerene in the process under consideration.

The typical IR spectra of hydrogenated and deuterated fullerenes are shown in Fig. 1. In the spectrum of fullerene hydrides, absorption bands typical of the initial fullerene $C_{60}$ (527, 577, 1182, and 1428 $cm^{-1}$) are absent. The spectra of the samples of hydrides under study have rather intense absorption bands in the region of 2800—3000 $cm^{-1}$, which correspond to stretching vibrations of C—H bonds. In the case of deuterides, a broad band appears in the region of 2050—2200 $cm^{-1}$. This band is assigned to C—D stretching vibrations. Broad absorption bands at ~1620 $cm^{-1}$ are associated with vibrations of water molecules adsorbed by a KBr powder upon its grinding. The IR spectrum in the region of C—H stretching vibrations (2927, 2895, and 2848 $cm^{-1}$) (Fig. 2) differs from the spectrum of hydride $C_{60}H_{36}$, which contains three absorption bands with approximately equal intensities at 2910, 2850, and 2830 $cm^{-1}$.[10—12]

X-ray diffraction analysis demonstrated that hydrides and deuterides of fullerene were homogeneous systems with the structures of the initial fullerene (Fig. 3). The parameter of the face-centered cubic lattice increases monotonically as the amount of hydrogen in fullerene hydride increases (1.418, 1.430, and 1.455 nm for the initial $C_{60}$ and for the $C_{60}H_{10}$ and $C_{60}H_{26}$ compositions, respectively).

The character of the IR spectra and the X-ray diffraction patterns of the hydrogenated samples and the absence of the typical red-brown color of fullerenes in a toluene solution suggest that fullerene reacted virtually completely with hydrogen.

When the synthesized fullerene hydrides were heated, a pronounced endothermic effect and gas evolution were observed at 800 K. The weight was gradually decreased at $T > 900$ K. The amount of the gas removed at 800 K (2.7—3.8 wt.%) virtually coincided with the amount of hydrogen in the initial hydride. This effect corresponds to decomposition of fullerene hydride accompanied by evolution of gaseous hydrogen, which agrees with the result obtained by us for hydrogenated fullerene—metal compositions[5,7] and with the published data on decomposition of fullerene hydrides.[1,3] A gradual decrease in the weight at a temperature higher than 900 K is associated with sublimation of fullerene. The shape of this region is similar to the portion of the thermogravimetric curve of the initial fullerene.

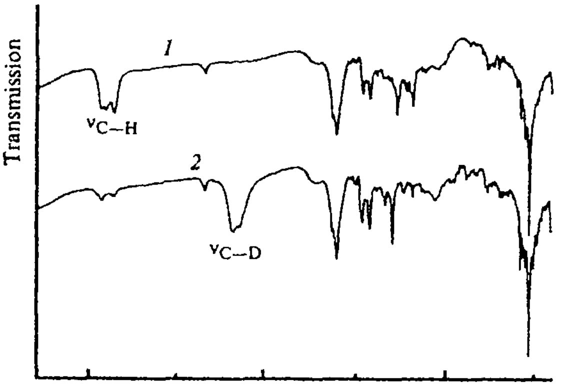

**Fig. 1.** IR spectra of fullerene hydride (*1*) and fullerene deuteride (*2*).

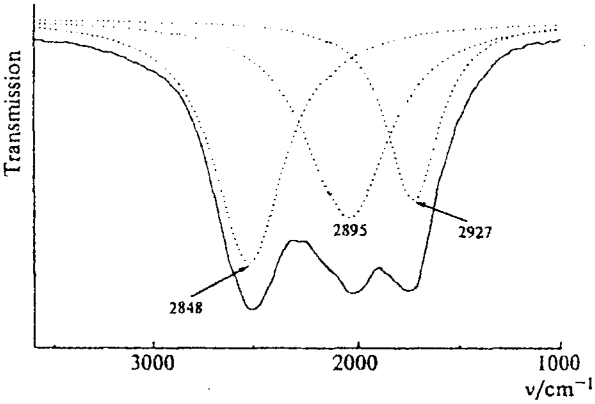

**Fig. 2.** Fragment of the IR spectrum of fullerene hydride in the region of stretching C—H vibrations. The Gaussian functions, the sum of which describes best the profile of absorption band, are indicated by dashed lines.

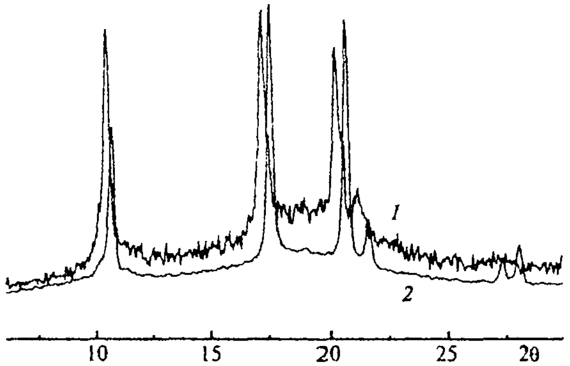

**Fig. 3.** X-ray diffraction powder patterns of fullerene deuteride $C_{60}D_x$ (*1*) and the initial fullerene $C_{60}$ (*2*).

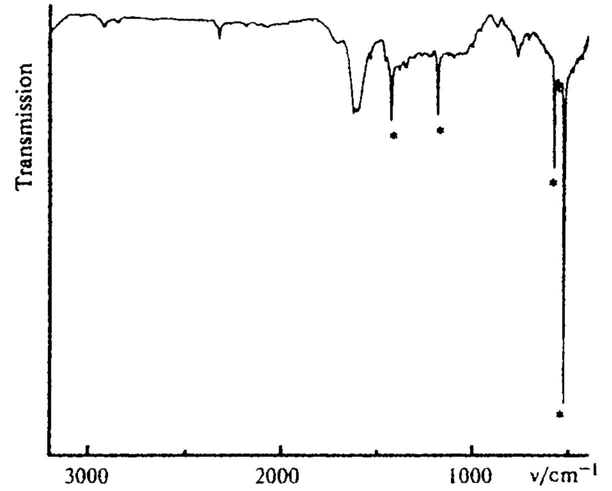

**Fig. 4.** IR spectrum of the product of decomposition of fullerene hydride at 800 K. Absorption bands corresponding to vibrations of atoms of the $C_{60}$ molecule are marked with asterisks.

In the IR spectrum of the product of decomposition of fullerene hydride at 800 K (Fig. 4), absorption bands at 527.0, 576.8, 1182.4, and 1428.4 $cm^{-1}$ are clearly seen. The positions of these bands virtually coincide with those of absorption bands observed in the spectrum of solid fullerene $C_{60}$. In addition, the spectrum has absorption bands at 552.6, 562.2, 712.2, 766.4, 796.8, 879.8, 1352.5, 1384.5, and 1539.8 $cm^{-1}$. Some of these bands are similar to absorption bands observed in the spectrum of photopolymerized $C_{60}$ containing four-membered carbon rings between fullerene molecules.[13] The X-ray diffraction pattern of the dehydrogenation product is similar to that of the initial fullerene. These samples are soluble in toluene. The samples dehydrogenated at 800 K were repeatedly hydrogenated with hydrogen from a metallohydride accumulator to form fullerene hydrides. Therefore, it can be assumed that the reaction is reversible

$$C_{60} + xH_2 \rightleftarrows C_{60}H_{2x}.$$

Studies of the magnetic properties of hydrogenated samples of fullerene demonstrated that they contained a ferromagnetic phase. The presence of this phase can be explained by the fact that the stream of hydrogen evolved from the metallohydride accumulator can carry away microimpurities of metal or metallohydride particles. For hydrides of intermetallic compounds $LaNi_5$, $La_{0.75}Ce_{0.25}Ni_5$, $La_{0.75}RE_{0.25}Ni_5$, and $La_{0.67}RE_{0.33}Ni_5$, metallic nickel (according to magnetic measurements, its amount in the hydride was ~0.2 wt.%) may occur as such ferromagnetic phase. However, the fact that fullerene hydride and other derivatives of fullerene can exhibit ferromagnetic properties must not be ruled out (see, for example, Ref. 14).

The metallohydride procedure for the preparation of highly pure hydrogen[8,9] is based on the ability of a number of intermetallic compounds to reversibly and selectively absorb substantial amounts of hydrogen according to the reaction:

$$RT_n + xH_2 \underset{p_{des},\ T_{des}}{\overset{p_{abs},\ T_{abs}}{\rightleftarrows}} RT_nH_{2x} + Q,$$

where R is a rare-earth metal, Ti, or Mg; T is a 3d metal; $n = 1-5$; and $Q$ is the heat effect. The equilibrium of this reaction can be readily shifted by a slight change in the pressure ($p_{abs} > p_{des}$) or in the temperature ($T_{abs} < T_{des}$) of the system. Hydrogen evolved from hydride phases contained no more than 0.0001% of gaseous impurities. Processes with the participation of hydrogen released by hydride phases often proceed more efficiently than processes with the participation of hydrogen from alternative sources. For example, when type A hydrogen (according to the certificate $H_2 > 99.99\%$, $O_2 < 0.01\%$, and water vapor $<0.2$ g $m^{-3}$) or type B high-quality hydrogen (according to the certificate $H_2 > 99.95\%$, total amount of accompanying gases ($O_2$, $N_2$, $CH_4$, CO, $CO_2$, *etc.*) $< 0.05\%$, and water vapor $< 0.2$ g $m^{-3}$) was used, hydrogenation of fullerene did not occur under the above-mentioned conditions. Oxygen-containing impurities, which inhibit processes of hydrogenation with molecular hydrogen, are absent in hydrogen released by hydrides of intermetallides. Moreover, when intermetallides are used as the source of hydrogen, the gaseous phase contains catalytically active particles. This can explain the efficiency of hydrogen supplied by intermetallic compounds. The presence of these microimpurities agrees with the fact that samples of hydrogenated fullerenes exhibit ferromagnetic properties. The absence of oxygen-containing impurities and the presence of microimpurities of catalysts can substantially decrease the activation energy of the process, increase both the reaction rate and the degree of conversion of the substrate, and decrease the initial temperature of the reaction. Solid fullerenes generally contain substantial amounts of oxygen. In the case of hydrogenation of solid fullerenes, oxygen chemisorbed by fullerenes can be more readily removed (apparently, as water vapor and/or as metal oxides) by hydrogen containing microimpurities of catalytically active metal compounds.

Therefore, upon interaction of solid fullerene with hydrogen from a metallohydride accumulator based on hydrides of intermetallic compounds of rare-earth metals and nickel, hydrogenation of C=C double bonds of fullerene molecules occurs under substantially milder conditions. The nature of this phenomenon remains unclear and calls for further investigation. The persistence of the structure of fullerene molecules upon thermal decomposition of hydrides accompanied by release of hydrogen and the ability of fullerenes to repeatedly interact with hydrogen show promise for realization of the multicyclic hydrogenation—dehydrogenation procedure.

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## References

1. A. Hirsch, *Chemistry of Fullerenes*, Thiele, Stuttgart, 1994, 117.
2. R. M. Baum, *Chem. Eng. News*, 1993, **22**, 8.
3. N. F. Gol'dshleger and A. P. Moravskii, *Usp. Khim.*, 1997, **66**, 353 [*Russ. Chem. Rev.*, 1977, **66** (Engl. Transl.)].
4. C. Jin, R. Hettich, R. Compton, D. Compton, D. Jouce, J. Blencoe, and T. Burch, *J. Phys. Chem.*, 1994, **98**, 4215.
5. B. P. Tarasov, V. N. Fokin, A. P. Moravskii, and Yu. M. Shul'ga, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 679 [*Russ. Chem. Bull.*, 1997, **46**, 649 (Engl. Transl.)].
6. B. P. Tarasov, V. N. Fokin, A. P. Moravsky, Yu. M. Shul'ga, and V. A. Yartys', *J. Alloys and Comp.*, 1997, **250**, 25.
7. B. P. Tarasov, V. N. Fokin, A. P. Moravskii, and Yu. M. Shul'ga, *Zh. Neorg. Khim.*, 1997, **42**, 920 [*Russ. J. Inorg. Chem.*, 1997, **42** (Engl. Transl.)].
8. B. P. Tarasov and S. P. Shilkin, *Zh. Prikl. Khim.*, 1995, **68**, 21 [*Russ. J. Appl. Chem.*, 1995, **68** (Engl. Tranl.)].
9. V. N. Fokin, E. E. Fokina, and S. P. Shilkin, *Zh. Obshch. Khim.*, 1996, **66**, 1249 [*J. Gen. Chem. USSR*, 1996, **66** (Engl. Transl.)].
10. Yu. M. Shul'ga, V. I. Rubtsov, A. S. Lobach, and N. F. Gol'dshleger, *Pis'ma Zh. Tekh. Fiz.* [*J. Tech. Phys. Lett.*], 1995, **21**, 75 (in Russian).
11. M. I. Attalla, A. M. Vassallo, B. H. Tattam, and J. V. Hanna, *J. Phys. Chem.*, 1993, **97**, 6329.
13. A. M. Rao, P. Zhou, K. A. Wang, G. N. Hager, J. M. Holden, Y. Wang, W. T. Lee, X. X. Bi, P. C. Eklund, D. S. Cornett, M. A. Dunkan, and I. J. Amster, *Science*, 1993, **259**, 955.
14. Yu. M. Shul'ga, A. S. Lobach, Yu. G. Morozov, V. N. Spektor, and A. A. Ovchinnikov, *Zh. Fiz. Khim*, 1998, **72**, 125 [*Russ. J. Phys. Chem.*, 1998, **72** (Engl. Transl.)].

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# The role of hydrogen atoms in CIDNP effects in the reaction of diisobutylaluminum hydride with $CCl_4$

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Integral polarization of chloroform, methylene dichloride, and pentachloroethane was observed in the $^1$H NMR spectra during the exothermal reaction of a 1 *M* solution of $\mathrm{Bu^i{}_2AlH}$ in 1,4-dioxane with $CCl_4$. CIDNP was shown to appear in the diffusion radical pair of the hydrogen atom and trichloromethyl radical.

**Key words:** CIDNP, hydrogen atom, trichloromethyl radical, radical reaction, diisobutylaluminum hydride, carbon tetrachloride.

We have shown previously[1] that during the reactions of trialkylalkanes with $CCl_4$, chemically induced dynamic nuclear polarization (CIDNP) appears in the radical pair (RP) of alkyl and trichloromethyl radicals. When $R_3Al$ is replaced by $R_2AlH$, the formation of RP consisting of the H atom and $^{\cdot}CCl_3$ should be expected, because the Al—H bond is the most active. Examples of CIDNP involving H atoms are known in radiation chemistry.[2]

## Results and Discussion

During the fast exothermal reaction of an 1 *M* solution of $\mathrm{Bu^i{}_2AlH}$ in dioxane-$d_8$ with an equivalent or higher quantity of $CCl_4$, the detector of an $^1$H NMR spectrometer shows negatively polarized signals of chloroform and methylene dichloride with chemical shifts at 7.53 and 5.3 ppm, respectively, in the spectrum of the reaction mixture (Fig. 1). In addition, a positively po-

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