Interaction of platinum fulleride $C_{60}Pt$ with deuterium

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X-ray photoelectron spectra and catalytic properties of platinum fulleride $C_{60}Pt$ were studied. The value of the bond energy of $Pt4f_{7/2}$ (72.4 eV) found for platinum in the starting $C_{60}Pt$ suggests a partial charge transfer from Pt to C_{60}. The interaction of solid platinum fulleride with gaseous deuterium leads to the formation of fullerene deuterides $C_{60}D_x$ and Pt clusters.

Key words: platinum fulleride, reduction, fullerene deuterides, X-ray photoelectron spectra.

Catalytic hydrogenation of fullerenes usually occurs by the action of Pd or Ru/C catalysts.[1,2] The behavior of mechanical mixtures of fullerene and palladium in the presence of molecular deuterium was studied.[3] The catalytic activities of fullerides $C_{60}Pd_x$ ($x > 3$) and $C_{60}Pt_x$ ($x \approx 1$) and those of C_{60}-supported palladium and the $C_{60}Pd(PPh_3)_2$ complex in hydrogenation of unsaturated compounds are known.[4—7] In the case of platinum,[5] unlike palladium, the $C_{60}Pt$ compounds are also active. In this connection, it is of interest to study the behavior of individual metal fullerides during their interaction with hydrogen.

In this work, we report the results of studying the reaction of gaseous D_2 with solid platinum fulleride $C_{60}Pt$.

Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer, and X-ray photoelectron spectra were recorded on a Varian-IEE-15 spectrometer with a magnesium anode ($h\nu$ = 1253.6 eV). Samples for the IR spectroscopic study were prepared in pellets with KBr in a dry argon atmosphere.

Mass spectra were recorded on a MAT-731 mass spectrometer with ionization of a sample in the field desorption regime (the current of heating of the emitter was 30 mA). For the preparation of the sample, toluene was added to the reaction mixture, and the brown solution was separated from the precipitate by centrifuging, concentrated, and deposited on the emitter followed by evaporation of a solvent excess. The analysis was performed by successive sweeps of the mass spectrum with a gradual increase in the current of heating of the emitter.

Thermal analysis of the samples was carried out on a Q-1000 derivatograph in an argon atmosphere.

A sample of fullerene C_{60} isolated by column chromatography from the toluene extract of electric-arc fullerene soot and evacuated at room temperature was used (the content of crystallization toluene did not exceed 4%). IR, ν/cm^{-1}: 527, 576, 1183, 1429.

Complex $Pt(dba)_2$ (dba is dibenzylideneacetone) was obtained by the previously described procedure[8]; the data of elemental analysis and IR spectrum of the $Pt(dba)_2$ synthesized agree with the published data.

Platinum fulleride $C_{60}Pt$ was obtained by the reaction of C_{60} with $Pt(dba)_2$ in toluene according to the known procedure.[5] The precipitate that formed was repeatedly washed with toluene and ether to remove the unreacted starting reagents and dba that formed and evacuated at 323 K (6 h). Found (%): C, 78.96; Pt, 20.4. $C_{60}Pt$. Calculated (%): C, 78.68; Pt, 21.3.* IR, ν/cm^{-1}: 486, 525, 578, 666, 697, 726, 736, 755, 1183, 1425, 1460. The treatment of the sample with ether results in the appearance of free C_{60} (TLC, Silufol-254, benzene—hexane, 1 : 10).

Deuteration of $C_{60}Pt$ in the solid phase was carried out for 2 h at 1—2 MPa and temperatures of 373, 473, 548, 623, 673, and 723 K on the setup described previously.[10] The temperature was controlled with an accuracy of ±10 °C, and the pressure was maintained within ±0.02 MPa. Samples were predegassed by heating to 373 K in a vacuum (~1 Pa). High-purity deuterium was introduced at 293 K into a reactor-autoclave from a multiple-action metal-hydride battery based on $LaNi_5$ intermetallide. At low temperatures (373—548 K), to

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* Perhaps, specific features characteristic of elemental analysis of fullerene compounds are manifested in the analysis (see, *e.g.*, Ref. 9).

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increase the efficiency of deuteration, the "heating to a specified temperature—cooling to 298 K" cycle was repeated 5 times. Unloading of samples was carried out in an inert atmosphere after cooling of the autoclave to 298 K.

Results and Discussion

Parameters of $C_{60}Pt$: IR and XP spectra. The IR spectrum of the starting $C_{60}Pt$, as that of $C_{60}Pd_x$ ($x \approx 1$),[4] contains absorption bands (AB) at 525 (s), 578 (w), 666 (w), 697 (s), 726 (w), 736 (w), 755 (m), 1183 (m), 1425 (m), and 1460 cm^{-1} (w). The IR spectrum observed for platinum fulleride is close to that of the $C_{60}Pt$ sample prepared from C_{60} and $Pt(cod)_2$ (cod is cyclooctadiene).[11] Note that free C_{60} appeared in the sample only if dibenzylideneacetone formed in the formation of $C_{60}Pt$ by the reaction

$$C_{60} + Pt(dba)_2 \longrightarrow C_{60}Pt_1 + 2\ dba$$

was washed out with a polar solvent, for example, ether, which is capable of solvating fullerene in $C_{60}Pt$; in other cases, free C_{60} was observed neither spectrally, nor chromatographically.

The X-ray photoelectron spectrum of $C_{60}Pt$ is a doublet with sufficiently narrow components. The half-width (Δ) of the $Pt4f_{7/2}$ line in the spectrum of $C_{60}Pt$ is larger than that of $Pt4f_{7/2}$ of metallic platinum or K_2PtCl_4. Comparison of the bond energy (E_b) of $Pt4f_{7/2}$ (72.4 eV) for platinum fulleride (Table 1) with a similar value for metallic platinum (71.3 eV) indicates a partial charge transfer from the Pt atom to C_{60}. The half-width of the C1s line of $C_{60}Pt$ is larger than that of the C1s line of the starting C_{60}. The atomic ratio $[Pt/C_{60}]$ calculated from the integral intensities of the Pt4f and C1s lines using photoionization cross sections[12] is equal to 0.70, which is lower than the platinum content in the sample according to the chemical analysis data. This deviation of the $[Pt/C_{60}]$ value obtained from the XP spectrum ($[Pt/C_{60}]^{XPS}$) can be due, for example, to screening of Pt atoms by surrounding fullerene molecules or clusterization of platinum. The last assumption is less probable, because the formation of platinum fulleride from C_{60} and $Pt(dba)_2$ occurs under mild conditions.

Table 1. Parameters of XP spectra of platinum compounds

Compound	Conditions of treatment	$[Pt/C_{60}]$	E_b of $Pt4f_{7/2}$ /eV	ΔC1s	ΔPt4f
$C_{60}Pt$	—	0.70	72.4	2.05	5.30
$C_{60}Pt$	D_2, 373 K	0.49	72.2	2.00	5.20
$C_{60}Pt$	D_2, 473 K	0.44	72.4	2.00	5.15
$C_{60}Pt$	D_2, 548 K	0.55	72.4	2.00	5.20
$C_{60}Pt$	H_2, 623 K	0.49	72.4	2.15	5.35
$C_{60}Pt$	D_2, 623 K	0.58	72.1	2.15	5.45
$C_{60}Pt$	D_2, 673 K	0.55	72.4	2.10	5.35
$C_{60}Pt$	D_2, 723 K	0.54	72.2	2.15	5.50
$C_{60}Pt$	523 K	0.49	72.2	2.20	5.25
$C_{60}Pt$	D_2, 723 K; Ar, 873 K	0.25	71.7	2.05	5.65
C_{60}	—	—	—	1.90	—
$C_{60}D_{24}$	—	—	—	2.40	—
$Pt(PPh_3)_4$	—	—	71.7	—	5.35
K_2PtCl_4	—	—	73.3	—	5.15

Deuteration of $C_{60}Pt$. It is known that the IR spectra[2,13] of fullerene C_{60} deuterides contain a sufficiently intense absorption band in the 2100—2190 cm^{-1} region due to stretching vibrations of the C—D bonds, and this spectral region is free of absorption of the crystallization solvent (toluene) and aliphatic hydrocarbons, whose molecules can adsorb on the surface of KBr pellets from the atmosphere. Therefore, we used IR spectroscopy as a method of detecting the appearance of C_{60} deuterides in the $C_{60}Pt$—deuterium system. The IR spectra of the starting compound $C_{60}Pt$ and free C_{60}, which is probably present in the sample, also contain no AB in this region

IR spectra of reduced $C_{60}Pt$. No AB in the 2100—2190 cm^{-1} region are observed in the IR spectra of the samples obtained in the $C_{60}Pt$—D_2 system at room temperature and 1—2 MPa. The absorption in this region, indicating the beginning of fullerene reduction, appears when the temperature of treatment of the $C_{60}Pt$ samples with gaseous deuterium increases to 373 K (Fig. 1). Further increase in the temperature of interaction results in an increase in the intensity of absorption in the 2100—2190 cm^{-1} region, and the spectrum of the $C_{60}Pt$ sample treated with deuterium at 723 K contains sufficiently intense overlapping bands at 2130 and 2170 cm^{-1} (Fig. 1).

The IR spectra of the $C_{60}Pt$ samples treated with deuterium at high temperatures exhibit other characteristic features. For example, AB of $C_{60}Pt$ related to vibrational modes of C_{60} (525, 578, 1183, and 1425 cm^{-1}) undergo substantial changes upon increase in the temperature of treatment of platinum fulleride with deuterium: the relative intensity of AB at 525 and 1183 cm^{-1} decreases noticeably, AB at 578 and 1425 cm^{-1} are broadened, and the intensity of AB at 697 cm^{-1}, being high for $C_{60}Pt$ (see Fig. 1), decreases due to an increase in the degree of reduction of coordinated fullerene.

Note that the activity of the reduced samples with respect to oxygen increases as the temperature of reduction of $C_{60}Pt$ with gaseous deuterium decreases. For example, unlike the samples reduced at 623—723 K, the samples treated with deuterium at 373—548 K burned in air even after evacuation. Only the bands of C_{60} remained in the IR spectrum of the "combustion" product.

Thermogravigrams of deuterated $C_{60}Pt$ samples. The platinum fulleride samples deuterated at 373—548 K begin to evolve deuterium at ~700 K, whereas the samples deuterated at 623—723 K evolve deuterium at 783—803 K, *i.e.*, as standard fullerene deuterides $C_{60}D_x$.[14] In all cases, the platinum clusters (as indicated by the

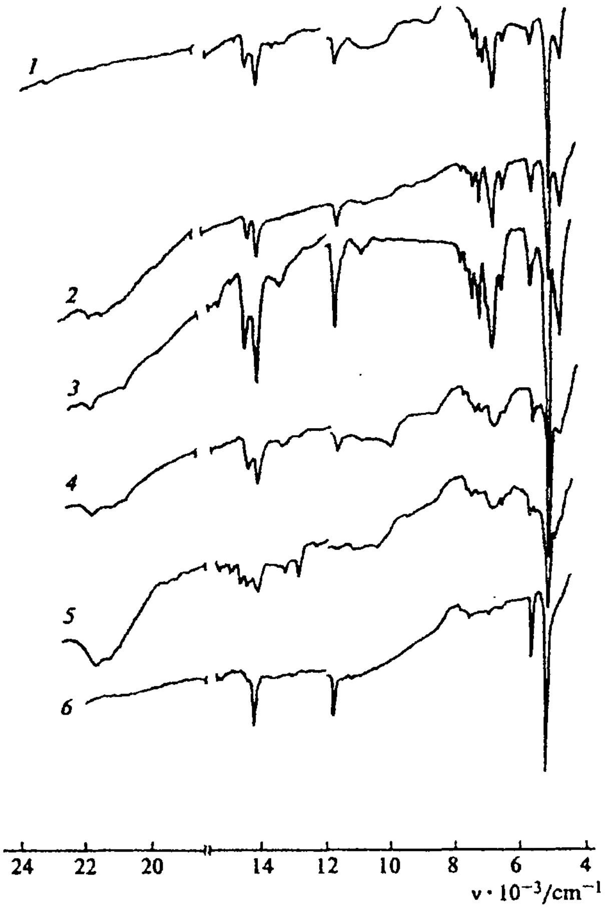

Fig. 1. IR spectra of platinum fulleride $C_{60}Pt$ (*1*) and $C_{60}Pt$ samples deuterated at 373 K (*2*), 548 K (*3*), 623 K (*4*), and 723 K (*5*). IR spectrum of $C_{60}Pt$ sample reduced at 723 K after its dehydrogenation at 873 K (*6*).

X-ray diffraction patterns of the samples) and fullerene C_{60} are products of the high-temperature (873 K) treatment of the reduced samples of platinum fulleride. The IR spectrum of the product obtained after heating at 873 K of the $C_{60}Pt$ sample treated with deuterium at 723 K exhibits only bands characteristic of vibrational modes of C_{60} (see Fig. 1), and this product is stable in air. However, after this treatment, the major part of fullerene is present, most likely, in the chemically bound state (perhaps, in the form of polymer), because, as shown spectrophotometrically, only ~25% of C_{60} present in the thermolysis products goes into the solution.

Electronic absorption spectra. A toluene solution of the product obtained by the reaction of $C_{60}Pt$ with deuterium becomes brown, which is characteristic of lower hydrofullerenes.[2] Absorption bands at 407 (C_{60}), 432, and 710 nm are observed in the visible spectral region of the solution. Chromatographic analysis (TLC, Silufol-254, CH_2Cl_2—hexane, 3 : 4) also confirmed the presence of fullerene and its hydrides in the solution.

Mass spectra. The product formed after deuteration of platinum fulleride at 623 K was analyzed by mass spectrometry. The mass spectrum obtained exhibits the peaks corresponding to the products of addition of different numbers of deuterium atoms to the fullerene molecule. The most intense peaks correspond to the addition of 2, 4, and 6 D atoms. In addition, peaks with m/z 726, 730, and 738 corresponding to the products with odd number of D atoms (3, 5, and 9) and peaks that can indicate the presence of $C_{60}D_{26}$ and $C_{60}D_{34}$ deuterides are observed. The spectrum also contains the peak of the starting fullerene with m/z 720, which can be formed due to both thermal decomposition of fullerene hydrides during mass spectrometric analysis (lower hydrides are less stable[2]) and degradation of hydrides during prolonged storage. This was observed[15] in the mass spectrometric study of the hydride $C_{60}H_{36}$.

XP spectra of reduced $C_{60}Pt$ samples. The deuterated (or hydrogenated) samples are characterized by a decrease in $[Pt/C_{60}]^{XPS}$ as compared to the starting $C_{60}Pt$. Similarly, this value decreases after heating platinum fulleride in a vacuum at 523 K (see Table 1). Perhaps, the temperature treatment favors the formation of fine platinum particles. The beginning of platinum clusterization is also evidenced by an increase in the half-width of the Pt5d peak in the valent band, whereas the half-width of the $Pt4f_{7/2}$ peak even somewhat decreases. This effect has been described previously.[16] After heating at 873 K (thermogravimetry) of the $C_{60}Pt$ sample treated with deuterium at 723 K, the $[Pt/C_{60}]^{XPS}$ value decreases noticeably and amounts to 0.25. The E_b of $Pt4f_{7/2}$ for this sample also decreases and approaches E_b of $Pt4f_{7/2}$ for metallic platinum (see Table 1). This indicates a considerable degree of clusterization of platinum atoms at a high temperature and agrees with the appearance of metallic platinum in the sample, according to the XP data.

The E_b value of $Pt4f_{7/2}$ for all samples (except for those subjected to the high-temperature treatment) remains almost unchanged or somewhat decreases (see Table 1), as a rule, by at most 0.3 eV. We failed to observe regularities in the change in the E_b value of $Pt4f_{7/2}$ under different reduction conditions. At the same time, such parameters as half-widths of the Pt4f and C1s lines make it possible to classify the reduced samples into two groups: "low-temperature" ($T \le 548$ K) and "high-temperature" (623 K < T < 723 K). For the first group, the half-widths of the Pt4f and C1s lines are narrower than those for the starting sample, and the opposite situation is typical of the second group.

Based on the results of analysis of the IR and XP spectra, thermogravigrams, and chemical activity of the deuteration products, we can assume that deuterides with the $C_{60}PtD_x$ empirical formula are formed in the interaction of $C_{60}Pt$ with D_2 at 373—548 K and 1—2 MPa, whereas fullerene deuterides $C_{60}D_x$ and Pt clusters are formed when the interaction occurs at 623—723 K. When the deuterated samples are heated to temperatures >873 K, deuterium is formed, and platinum clusters and partially polymerized C_{60} are the thermolysis products.

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