Reaction of Platinum Fulleride C₆₀Pt with Dihydroanthracene

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Abstract—9,10-Dihydroanthracene ($C_{14}H_{12}$) reacts with platinum fulleride C_{60} Pt at 513–623 K under anaerobic conditions to form anthracene and hydrofullerenes identified by IR and mass spectroscopy. The Pt $4f_{7/2}$ binding energy of platinum in the initial fulleride (72.4 eV) indicates partial charge transfer form Pt to C_{60} , which agrees with the results of X-ray fluorescence spectroscopic study of C_{60} Pt.

Intensive study of activation of saturated hydrocarbons with metal complexes revealed parameters affecting the reactivity of C–H bonds in alkanes, the main features of the mechanism of alkane activation with transition metal complexes, and new reactions of saturated hydrocarbons including methane [1]. The activation of the C–H bond with platinum complexes is intensively studied [1, 2].

Fullerenes are promising catalysts of hydrocarbon reactions [3] since their compositions and temperatures of their operation can be varied in a wide range. For example, hydrogenation of fullerene C_{60} by hydrogen transfer from 9,10-dihydroanthracene to the fullerene at 623 K yields, depending on the reaction conditions, $C_{60}H_{18}$ or $C_{60}H_{36}$ with a high selectivity [4]. Platinum fulleride $C_{60}Pt$ reacts with molecular deuterium (373–723 K, 1–2 MPa D₂) to form $C_{60}D_x$ (x = 2-26) and platinum clusters [5].

In this work the behavior of platinum fulleride as a component of systems activating the C–H bonds was studied with the reaction of C_{60} Pt with 9,10-dihydroanthracene as example. It is known [6] that hydrogen transfer from 9,10-dihydroanthracene to an acceptor at moderate temperatures is considerably accelerated in the presence of Pd/C catalyst.

Properties of C₆₀**Pt: IR and X-ray photoelectron spectra.** Platinum fulleride is slowly precipitated after mixing toluene solutions of C₆₀ and Pt(dba)₂ (dba is dibenzylideneacetone) [7]:

$$C_{60} + Pt(dba)_2 \rightarrow C_{60}Pt_{\sim 1} + 2dba.$$

This is a black-brown amorphous compound stable in air. The known physicochemical properties of platinum metal fullerides suggest their polymeric structure [8, 9]. Platinum fulleride C_{60} Pt, similar to C_{60} Pd_n (n = 1-7), is insoluble in the majority of common solvents. The IR spectrum of C_{60} Pt contains the following bands, cm⁻¹: 525 s, 578 w, 666 m, 697 s, 726 w, 736 w, 755 m, 1183 m, 1425 m, and 1460 w. In addition, a number of weak bands typical for polymeric fullerene are present in the 600–700 cm⁻¹ range [10].

The X-ray photoelectron spectrum (XPS) of C_{60} Pt is a doublet of relatively narrow lines typical for the individual substances. The halfwidth (Δ) of the Pt $4f_{7/2}$ line in the spectrum of C₆₀Pt is greater than that of the Pt $4f_{7/2}$ line in the spectrum of metallic platinum or K_2 PtCl₄. The Pt $4f_{7/2}$ binding energy (BE) in platinum fulleride (72.4 eV, see table) is higher than that in metallic platinum (71.3 eV) and lower than that in K_2 PtCl₄ (73.3 eV). This indicates partial electron transfer form platinum to C_{60} [5]. This assumption agrees with the results of X-ray fluorescence spectroscopic study of palladium fulleride. The similarity of the X-ray fluorescence spectra of $C_{60}Pt$ and $C_{60}Pd_{1.1}$ (see figure) suggests similar nature of the chemical bond in these compounds. Okotrub et al., based on the X-ray fluorescence spectroscopic data and model quantum-chemical calculations of $C_{60}Pd_{1,1}$, concluded that palladium atoms in $C_{60}Pd_n$ are bound to C_{60} molecules by donor-acceptor bond [11].

The $[Pt/C_{60}]$ molar ratio calculated form the integral intensities of the Pt 4*f* and C 1*s* lines with the use of photoionization cross section is 0.70 [5] and is lower than that determined from the results of elemental analysis. This underestimation of $[Pt/C_{60}]_{XPS}$ can be due, for example, to shielding of the platinum atoms

Sample no.	Compound	<i>T</i> , K	Reaction time, h	Anthracene, %	[Pt/C ₆₀] _{XPS}	BE Pt 4 <i>f</i> _{7/2}	ΔC 1 <i>s</i>	$\Delta Pt 4f$
1 2 3 4 5 6 7 8 9 10 11 12	$\begin{array}{c} C_{60} Pt \\ C_{60} Pt^{b} \\ C_{60} C_{60} D_{24} \\ C_{60} H_{36} \\ Pt, metal \\ K_{2} Pt Cl_{4} \end{array}$	513 513 513 623 513 523	0.4 1.0 1.8 0.4 1.8 2.0	1.4 3.1 9.5 80.0 6.4	0.70 0.60 0.55 0.53 0.5	72.4 72.3 72.3 72.15 72.10 72.2 71.3 73.3	2.05 2.15 2.1 2.2 2.15 2.25 2.20 1.9 2.4 3.1	5.30 5.35 5.40 5.45 5.50 5.25

Dehydrogenation of 9,10-dihydroanthracene with C_{60} Pt (9,10-dihydroanthracene/ C_{60} Pt ~100)

 a 9,10-Dihydroanthracene/C_{60} ~100. b Heating of C_{60}Pt in a vacuum.

by fullerene molecules or to formation of platinum clusters. The latter assumption is less probable since the platinum fulleride is formed from C_{60} and $Pt(dba)_2$ under mild conditions. As noted in [5], the $[Pt/C_{60}]_{XPS}$ ratio in the initial $C_{60}Pt$ decreases form 0.7 to 0.5 after heating this compound at 523 K in a vacuum (these conditions are close to those of reaction of platinum fulleride with 9,10-dihydroanthracene).

Reduction of C_{60} Pt with dihydroanthracene. Heating of the platinum fulleride with 9,10-dihydroanthracene at 513 K yields anthracene $(C_{14}H_{10})$ which is accumulated with time. The yield of hydrogenated derivatives of C₆₀ increases simultaneously. The sublimation residue of the reaction mixtures formed after short contact of C₆₀Pt with 9,10-dihydroanthracene contains free fullerene, which indicates that platinum fulleride is unstable at the reaction temperature. It should be noted that anthracene traces (detected by absorption at $\lambda = 354$ nm) are sometimes present in the final product even after sublimation of volatile products at 443 K (see Experimental). As the reaction temperature is increased to 623 K (these conditions are similar to those of reduction of fullerene to $C_{60}H_{36}$ by noncatalytic hydrogen transfer from 9,10-dihydroanthracene to C₆₀ [4]), the C₁₄H₁₀ yield sharply increases (see table) and hydrogen appears in the gas phase. The solubility in toluene of the product of C_{60} Pt reduction increases with increasing reaction time (at 513 K) or temperature. The UV-visible absorption spectra of toluene solutions of C_{60} Pt reduced with 9,10-dihydroanthracene at 513 K change with the reaction time. The changes in the spectrum of the product formed by 1.8-h reduction are the most pronounced. The spectra of C_{60} Pt reduced with 9,10dihydroanthracene at 513 and 623 K (see table, sample nos. 4 and 5, respectively) contain a strong band at 345 nm, with the band of sample no. 5 being more intense. This band is assigned to $C_{60}H_{18}$ [12]. In combination with the results of TLC (system B, R_f 0.1 [4]) these data indicate the presence of hydrofullerene $C_{60}H_{18}$ in the reduction products. TLC analysis showed also the presence of $C_{60}H_{36}$ in sample no. 5 (system B, R_f 0.35 [4]).

IR spectra of reduced C_{60} **Pt.** In the 3000–2800 cm⁻¹ range the IR spectra of the residue formed after completion of reduction of C_{60} Pt with 9,10-di-hydroanthracene and sublimation of unchanged 9,10-di-hydroanthracene, anthracene, and other products of



X-ray fluorescence spectra of (1) PtC_{60} and (2) $Pd_{1,1}C_{60}$.

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9,10-dihydroanthracene conversion contain stretching vibrations of aliphatic C-H bonds. The intensity of these bands increases with increasing reaction time or temperature. This indicates reduction of the fullerene to hydrofullerenes. In addition, appearance of a number of weak bands in the region of C-C stretching vibrations and bending and skeleton vibrations of C-C-C bonds indicates that the symmetry of the reduced fullerene differs from that of the initial C_{60} Pt. The absence of stretching vibration bands of C-H bonds of aromatic hydrocarbons indicates (within the sensitivity limits) that cycloaddition of the fullerene to C₁₄H₁₀ formed by dehydrogenation of 9,10-dihydroanthracene does not occur. Cycloaddition of C₆₀ to anthracene to form 1:1 adduct is known [13] to occur on heating a C_{60} - $C_{14}H_{10}$ mixture in a naphthalene melt.

The products of reaction of C₆₀Pt with 9,10-dihydroanthracene showed also some other features of the IR spectra, similar to those observed in our previous work [5]. As the reaction time (at 513 K) or temperature increases, the intensity of the absorption bands assigned to the C_{60} fragment in C_{60} Pt (527, 576, 1183, 1429 cm⁻¹) decreases and the halfwidth of these bands increases. The intensity of the strong band of C_{60} Pt at 697 cm⁻¹ appreciably decreases with time of reduction of platinum fulleride with 9,10-dihydroanthracene at 513 K. These changes are the most pronounced in the case of reduction of C_{60} Pt with 9,10dihydroanthracene at 623 K. In the IR spectra of this reaction mixture a number of weak bands in the range $500-540 \text{ cm}^{-1}$ is present, the band at 697 cm⁻¹ virtually disappears, etc.

The residue formed after separation of the soluble fraction to be analyzed by mass spectroscopy was washed with toluene and repeatedly with hexane (until the bands at 330 and 433 nm assigned to C_{60} and its reduction products disappeared from the UV spectrum) and evacuated at 343 K for 4 h. The IR spectrum of this residue contains, along with the bands of adsorbed solvent molecules, a number of weak broad bands present in the spectrum of the reduced platinum fulleride. Since hydrogenated fullerenes are low-soluble compounds, they are incompletely extracted with toluene from the reduced platinum fulleride. In addition, the broadening of the absorption bands can be due to the presence of polymeric fullerenes.

Reaction of [60]fullerene with 9,10-dihydroanthracene. We found that reaction of C_{60} with 9,10-dihydroanthracene at 513 K yields a red-brown difficultly soluble substance (see table, sample no. 6). The UV spectrum of a toluene extract of this substance contains the band at 330 nm. The TLC analysis confirms the presence of free C_{60} . The IR spectrum of sample no. 6 is similar to that of polyfullerene [10]: the bands of the C_{60} fragment (526, 576, 1182, and 1430 cm⁻¹), a number of bands in the 700–800 cm⁻¹ range, and the band at 1456 cm⁻¹ are present in the spectrum. It should be noted that the yield of anthracene in reaction of C_{60} Pt with 9,10-dihydroanthracene at 513 K is about 1.5 times higher than in reaction of C_{60} with 9,10-dihydroanthracene (see table, sample nos. 4 and 6, respectively).

Noncatalytic hydrogen transfer from 9,10-dihydroanthracene to C_{60} at 623 K is known [4] to yield $C_{60}H_{18}$ or $C_{60}H_{36}$, depending on the reaction conditions, with a high selectivity. However, a mixture of hydrides $C_{60}H_x$ (x = 0-36, 42–44) is formed by reaction of C_{60} with 9,10-dihydroanthracene at 543 K in the presence of benzanthrene catalyst [14]. Reaction of hydrogenated aromatic compounds with C_{60} under more rigorous condition was studied in [15].

Mass spectra. The toluene-soluble products of reduction of C_{60} Pt with 9,10-dihydroanthracene (see table, sample nos. 4 and 5) were analyzed by field desorption mass spectrometry. It should be noted that the mass spectra of the products of reduction of C_{60} Pt and C₆₀ with dihydroanthracene under similar conditions considerably differ [4, 16]. The peaks with m/z738 and 756 corresponding to $C_{60}H_{18}$ and $C_{60}H_{36}$ are present in the mass spectrum of sample no. 5 prepared at 623 K. The intensity of the peak with m/z 738 is noticeably higher than the intensity of the peak with m/z 756, which agrees with the presence of the absorption at 345 nm ($C_{60}H_{18}$) in the electronic spectrum of the fullerene-containing reaction products. The presence of weak peaks with m/z corresponding to species with a lower hydrogen content can be due to both specific conditions of reduction of the fullerene fragment in the platinum fulleride¹ and degradation of hydrogenated fullerene during prolonged storage of the sample. The mass spectra of the samples contain also the peak of the initial fullerene (m/z 720). Probably, [60]fullerene can be formed both by thermolysis of hydrofullerene in the course of the mass-spectrometric analysis (lower hydrides are less stable [3]) and by dehydrogenation during prolonged storage. De-

¹ In the presence of platinum the onset temperature of reduction of the fullerene fragment with dihydroanthracene decreases, and a greater number of hydrogenated fullerenes are formed, similar to [14]. Platinum may also cause dehydrogenation of the resulting hydrofullerenes; the energy of the C–H bond in $C_{60}H_{18}-C_{60}H_{36}$ (70–71 kcal mol⁻¹) calculated in [17] is close to the energy of the C–H bond at the 9,10-positions of dihydroanthracene.

gradation of hydrofullerene (including $C_{60}H_{36}$) during storage was detected by mass spectrometry [16, 18].

X-ray photoelectron spectra of reduced C_{60} Pt. The $[Pt/C_{60}]_{XPS}$ ratio in $C_{60}Pt$ samples reduced with 9,10-dihydroanthracene on heating is lower than in the initial C₆₀Pt. This ratio regularly increases with increasing reaction temperature or time (see table). The $[Pt/C_{60}]_{XPS}$ ratios are close to those in the samples obtained by reduction of C₆₀Pt with molecular deuterium [5]. This is largely due to thermal stability of the platinum fulleride. As noted above, [Pt/C₆₀]_{XPS} decreases after heating of the platinum fulleride at 523 K in a vacuum (see table, sample no. 7) and reaches 0.5, which agrees with formation of finely divided platinum particles on heating of the platinum fulleride. The onset of platinum crystallization in C_{60} Pt samples treated at 723 K with deuterium is also indicated by an increase in the halfwidth of the Pt 5d peak in the valence band. As determined by TGA, large platinum clusters stable to oxygen are formed on heating of reduced C_{60} Pt at 873 K [5].

The binding energy of Pt $4f_{7/2}$ as well as the ratio $[Pt/C_{60}]_{XPS}$ in reduced $C_{60}Pt$ slightly decrease with increasing temperature and time of reaction of the platinum fulleride with 9,10-dihydroanthracene. The halfwidth of the Pt 4f and C 1s lines increases simultaneously with the decrease in BE of Pt $4f_{7/2}$, which is likely due to continuing growth of platinum clusters and an increase in the degree of fullerene reduction in the $C_{60}Pt$ molecule, respectively. The fact that the Δ C 1s is lower than that in $C_{60}D_{24}$ and $C_{60}H_{36}$ [5, 19] (see table) can be explained by formation of hydrofullerenes with a lower hydrogen content.

The IR, mass, and X-ray photoelectron spectroscopic studies of the products of reduction of the platinum fulleride with 9,10-dihydroanthracene show that the presence of platinum decreases the onset temperature of the reduction of C₆₀ fragment as compared to noncatalytic hydrogen transfer from 9,10-dihydroanthracene to C₆₀ (513 and 623 K, respectively). Simultaneous acceleration of dehydrogenation of 9,10-dihydroanthracene (C₁₄H₁₂ \rightarrow C₁₄H₁₀ + H₂) can change the mechanism of reduction of [60]fullerene with dihydroanthracene and result in the case of the C₆₀Pt-9,10-dihydroanthracene system in formation of hydrofullerenes with a lower hydrogen content (mainly C₆₀H₁₈).

EXPERIMENTAL

The IR spectra were recorded in KBr pellets on a Specord IR 75 spectrophotometer. The X-ray photoelectron and X-ray fluorescence spectra were recorded on Varian IEE-15 and Stearat X-ray laboratory spectrometers, respectively.

The mass spectra were registered on an MAT-731 mass spectrometer. The samples were ionized in the field desorption mode (heating current of the emitter 30 mA). The sample was prepared as follows. Toluene was added to the reaction mixture under argon. The solution separated form the precipitate by centrifuging was concentrated and applied on the emitter. The excess solvent was evaporated. The sample was analyzed by successive scanning of the mass spectrum with gradually increasing heating current of the emitter.

The TLC analysis was performed on Silufol UV-254 plates using toluene–hexane, 1 : 10 (system A) and CH_2Cl_2 –hexane, 1 : 3 (system B) as eluent. The chromatograms were developed by UV irradiation (C_{60}) or with iodine vapor (hydrofullerenes).

We used fullerene C_{60} isolated by column chromatography from a toluene extract of electric arc fullerene black and dried by evacuation at room temperature (the content of crystallization toluene did not exceed 4%). IR spectrum, v, cm⁻¹: 527, 576, 1183, 1429.

Dihydroanthracene (99%, Lancaster) was used as received. As determined by the spectrophotometry, it contained $\sim 1\%$ of anthracene. Toluene, hexane, and methylene chloride were purified by the known procedures and freshly distilled before use.

The complex $Pt(dba)_2$ was prepared by the procedure in [20]; the elemental analysis and IR spectrum of the prepared $Pd(dba)_2$ agree with the published data.

Platinum fulleride C_{60} Pt was prepared by reaction of C_{60} with Pt(dba)₂ in toluene [7]. The precipitate was repeatedly washed with toluene and ether to remove unreacted initial reagents and liberated dba and evacuated at 323 K for 6 h. IR spectrum, v, cm⁻¹: 486, 525, 578, 666, 697, 726, 736, 755, 1183, 1425, 1460. Found, %: C 78.96; Pt 20.4. C_{60} Pt. Calculated, %: C 78.68; Pt 21.3.

Dehydrogenation of 9,10-dihydroanthracene with platinum fulleride C_{60} Pt was studied in evacuated glass ampules. The typical procedure was as follows. An ampule containing C_{60} Pt (10 mg) and 9,10-di-hydroanthracene (0.22 g, ~100-fold excess) was evacuated to a residual pressure of 10^{-2} mm Hg and sealed. The ampule was placed in an air thermostat and thermostated at 513 ± 5 K. The reaction time was

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0.4, 1.0 and 1.8 h (the control experiment is reaction of [60]fullerene with 9,10-dihydroanthracene at 513 K for 1.8 h). The initial dark brown suspension of C_{60} Pt in a 9,10-dihydroanthracene melt appreciably lightened during prolonged heating. After reaction completion the reaction mixture was cooled to room temperature. The unchanged 9,10-dihydroanthracene, anthracene, and other reaction products were sublimed in a vacuum at 373 K for 1 h and then at 443 K for 0.25 h.

To compare with results of [4], we performed hydrogenation of C_{60} Pt with dihydroanthracene at 623 ± 5 K for 0.4 h. After reaction completion the reaction mixture in the ampule consisted of a yellowbrown solution and a dark precipitate. Hydrogen was detected in the gas phase. The reaction mixture was worked up by the above procedure.

The anthracene concentration in the sublimate was determined spectrophotometrically by the absorption at λ 354 nm (alcohol, ε_{354} 7250 l mol⁻¹ cm⁻¹); the presence of C₆₀ in reduced C₆₀Pt samples was determined by TLC (Silufol UV-254, system A) and spectrophotometry (λ 330 and 406 nm).

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