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Dehydrogenation of Compounds with Weakened C–H Bonds in the Presence of Platinum and Palladium Fullerides

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Abstract — Coordinated fullerene acts as a hydrogen acceptor in reactions with compounds having weakened C–H bonds (1,4-dihydropyridine and 9,10-dihydroanthracene). Metal fullerides are the dehydrogenation catalysts. They activate the C–H bonds of dihydroanthracene and diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate in positions 9,10 and 1,4, respectively. No activation of norbornane carbon–hydrogen bonds with metal fullerides was observed under mild conditions.
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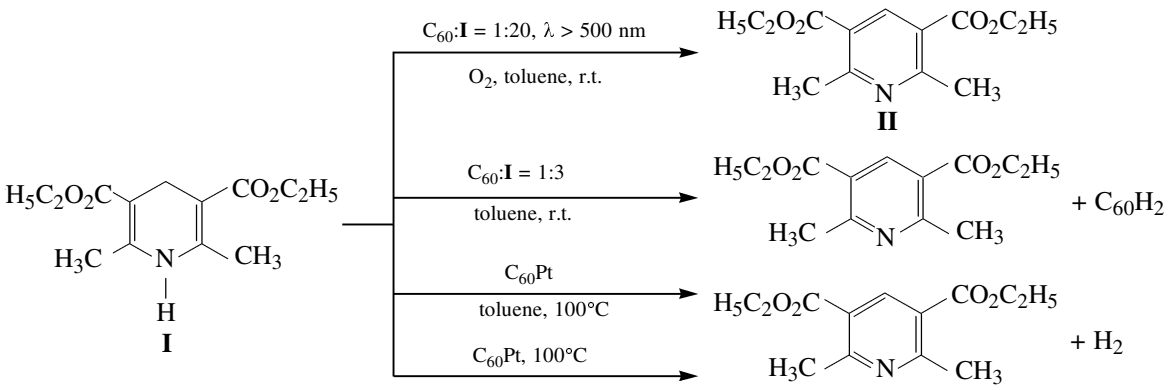
Physicochemical properties of C_{60} such as thermal stability, electron-withdrawing power, high capacity for hydrogen, capability for various types of coordination, etc. [1], allow fullerene to be considered as possible polyfunctional ligand in reactions of metal complexes with hydrocarbons. It can play the role of the electron and/or hydrogen acceptor in reactions with hydrogen donors [2] and other related processes. Fullerenes, including [60]fullerene, are strained alkenes with a high degree of unsaturation, which allows us to expect that fullerene ligands will participate in multiple hydrogen transfer processes during one event of the C–H bond activation with a metal complex.

In this study, fullerene-containing complexes and platinum group metal fullerides are used as components of systems activating C–H bonds. 9,10-Dihydroanthracene, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **I**, and norbornane are chosen as substrates. It was shown previously [3] that, in the presence of C_{60}, compound **I** modeling the effect of dihydronicotinamide adenine dinucleotide transforms under the anaerobic conditions at room temperature and natural illumination into the oxidized species, diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (see scheme).



It is known that platinum fulleride $C_{60}Pt_x$ ($x \sim 1$) under mild conditions is an active catalyst of hydrogenation of unsaturated compounds [4]. In this connection, it was interesting to examine the possibilty of participation of platinum fulleride also in the C–H bond activation. The possibility of intermediate formation of the hydrocarbon–metal σ complex [5] containing a five-coordinate carbon atom was considered

X-ray photoelectron spectral parameters of rhodium complexes

Comp. no.	Complex	E_bRh3$d_{5/2}$, eV
III	$(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$	308.6
IV	$RhH(CO)(PPh_3)_3$	308.1
V	$RhCl(PPh_3)_3$	307.6
VI	$Rh(CO)Cl(PPh_3)_2$	308.5
VII	$Rh(CO)Br(PPh_3)_2$	308.8
VIII	$RhBr(PPh_3)_3$	308.1

as the main hypothesis. The reaction of platinum fulleride $C_{60}Pt$ with *exo*,*exo*,*exo*,*exo*-2,3,5,6-norbornane-d_4 ($C_{60}Pt$: *nb*-d_4 ~1 : 100, 2 h, 100 or 180°C) was carried out in a sealed glass ampule. However, we found that the ^1H NMR spectra of norbornane-d_4 (integral intensity ratio $H_d : H_{a+c} : H_b$ 2 : 6 : ~0.22) isolated from the reaction mixture were essentially similar to that of the starting compound. That is, no *endo–exo* isomerization (deuterium transfer from the *exo* to *endo* position) or dehydrogenation takes place. Note that platinum fulleride under these conditions is stable, because the IR spectra of $C_{60}Pt$ before and after the experiment are identical (525, 578, 666, 726, 755, 1183, 1425, 1460 cm^{-1}). No catalysis of the H–D exchange in norbornane-d_0 with platinum fulleride at 100°C was observed (integral intensity ratio in the ^1H NMR spectrum $H_d : H_{a+c} : H_b$ = 2 : 6 : 4) when CF_3COOD and acetic acid-d_4 were used as the deuterium sources. This means that the hydrocarbon–metal σ complex [5] under these conditions is not formed as an intermediate. It is possible that such a behavior of $C_{60}Pt$ in the interaction with norbornane C–H bonds at low temperatures and in the absence of reducing agent (hydrogen) is caused by the platinum valence configuration in C_{60} (partial transfer of electron density from platinum to C_{60} [6, 7]) or by steric inaccessibility of the active center (platinum atom).

At the same time, under the anaerobic conditions at room temperature and natural illumination, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate reduces C_{60} (**I** : C_{60} ratio 3 : 1) in toluene, which is accompanied by the appearance of signals at δ 5.92 ppm, s (2H) and δ 9.020 ppm, s (1H, $C_{arom}H$) in the ^1H NMR spectrum (toluene-d_8). These signals are characteristic of $C_{60}H_2$, the fullerene hydrogenation product, and of the substituted pyridine, the product of dehydrogenation of **I** (see scheme). Heating of $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$ in toluene-d_8 to 80°C leads to disappearance of the Rh–H triplet at 9.2 ppm ($^2J_{PH}$ 9.7 Hz) and to simultaneous appearance of a new signal characteristic of $C_{60}H_2$ (s, 5.95 ppm). Addition of **I** to a solution of $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$ increases the degree of reduction of the fullerene, and the signals at 4.7 and 9.02 ppm characteristic of $C_{60}H_x$ ($x > 2$) and of substituted pyridine **II**, respectively, appear in the ^1H NMR spectrum. Note that the Rh3$d_{5/2}$ binding energy (E_b) in $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$ is 308.6 eV (see table), which is 0.5 eV higher than the corresponding value in $RhH(CO)(PPh_3)_2$. In platinum group metal complexes, the partial shift for the triphenylphosphine is accepted to be $\Delta(PPh_3) = 0$ (see [8] and references therein). Then, comparison of the E_b values for **V** and **VI** (see table) gives Δ(CO) 0.9 eV, and from the comparison of **VII** and **VIII** follows Δ(CO) 0.7 eV. From the E_b data for **III** and **IV**, it follows that $\Delta(\eta^2\text{-}C_{60})$ is 0.5 eV. This means that the acceptor power of $(\eta^2\text{-}C_{60})$ in rhodium complexes does not exceed that of the coordinated CO.

Thus, in both cases [compound **I**–C_{60} and $(\eta^2\text{-}C_{60})\cdot RhH(CO)(PPh_3)_2$], hydrogenation of C_{60} to $C_{60}H_2$ takes place. In the first case it is provided by the hydrogen transfer from 1,4-dihydropyridine, an organic reducing agent, whereas in the second case C_{60} is reduced with the complex-bound hydride hydrogen.

Under the anaerobic conditions, heating of **I** in the solid state or in toluene (100°C, 1 h) leads to the dehydrogenation of 1,4-dihydropyridine (see scheme) accompanied by the liberation of molecular hydrogen and formation of pyridine **II**. This was shown by mass spectrometry (hydrogen), ^1H NMR spectroscopy, and spectrophotometry (pyridine). Analysis shows that, under these conditions, about 50% of dihydropyridine **I** is consumed. At the same time, the reaction of C_{60} with excess **I** in toluene at 100°C yields a mixture of lower fullerene hydrides [3].

Dehydrogenation of 9,10-dihydroanthracene (350°C, 0.5 h) in the presence of palladium fullerides $C_{60}Pd$ or $C_{60}Pd_{4.9}$ (dihydroanthracene : $C_{60}Pd_n$ = 100 : 1), as in the case of platinum fulleride [9], is accompanied by liberation of molecular hydrogen by the reaction $C_{14}H_{12} \rightarrow C_{14}H_{10} + H_2$ and formation of hydrofullerides having lower hydrogen content as compared to the noncatalyzed hydrogen transfer from dihydroanthracene to C_{60} [10, 11]. After heating of the $C_{60}Pd$–dihydroanthracene sample, a new absorption band at 345 nm appears in the electronic spectrum. It is indicative of the presence of hydrofullerene $C_{60}H_{18}$ in the sample, which was also confirmed by TLC data (R_f 0.1, system B). With an increase in the Pd : C_{60} ratio, the H_2 content in the gas phase increases. At the same time, the anthracene content is 18 and 29% for $C_{60}Pd$ and $C_{60}Pd_{4.9}$, respectively. Note that about 50% of the converted dihydroanthracene forms anthracene by palladium-catalyzed de-

hydrogenation. Formation of $C_{60}H_{18}$ as the most stable molecule under the chosen conditions of the reaction of metal fulleride with dihydroanthracene is confirmed by the studies of the catalytic dehydrogenation of $C_{60}H_{36}$ in presence of $IrCOCl(PPh_3)_2$, Pd/C, etc. The 10% Pd/C catalyst appeared to be the most active [12].

In the sample isolated after heating of the dihydroanthracene–C_{60}Pt mixture at 623 K, the following compounds were identifie-d [1] by their ^{1}H NMR parameters (toluene-d_8, TMS), δ, ppm: $C_{60}H_{18}$: 4.27 br.d (1H, *J* 12.6 Hz), 3.86 br.m (2H, *J* 8.6 Hz), 3.52 br.d.d (1H, *J* 8.1 Hz, *J* 12.6 Hz), 3.13 br.m (2H, *J* 8.6 Hz); 4.20 s ($C_{60}H_6$); 2.70–4.4 br.s ($C_{60}H_{36}$). The ^{1}H NMR spectra obtained and the signal assignment agree (considering the correction for the solvent) with the spectra presented in [11, 13, 14]. According to the ^{1}H NMR data, the main product of the C_{60} reduction in the case of C_{60}Pt is $C_{60}H_{18}$, which agrees with the data of field desorption mass spectrometry [9].

A specific feature of the component interaction in the dihydroanthracene–C_{60}Pt system as compared to the noncatalytic dihydroanthracene–C_{60} system [10, 11] is the presence of platinum and the preservation of heterogeneity in the course of the reaction. These factors may change the hydrogen transfer mechanism (from dihydroanthracene to coordinated C_{60} and to anthracene formed by dehydrogenation of dihydroanthracene, respectively), and also cause the component adsorption on the catalyst surface. Purification of the hydrofullerene $C_{60}H_{36}$ formed by the noncatalytic hydrogen transfer from dihydroanthracene to C_{60} required prolonged heating of the sample to 573 K in a high vacuum [11]. Note that sublimation of the reaction mixture obtained in the reaction of dihydroanthracene with C_{60}Pt was carried out at lower temperatures to avoid the platinum-catalyzed dehydrogenation of hydrofullerenes $C_{60}H_x$ [15]. The mixture obtained by such procedure and consisting mainly of C_{60} and Pt, according to the ^{1}H NMR data, is contaminated with anthracene [^{1}H NMR spectrum, δ, ppm: 8.30 s (2H, H^1), 7.97 m (4H, H^2), 7.43 m (4H, H^3)], dihydroanthracene [7.27 s (8H, Ph), 3.84 s (4H, CH_2)], and, probably, tetrahydroanthracene [7.80 m (2H, Ph, H^d), 7.55 br.s (2H, Ph, H^c), 7.44 br.m (2H, Ph, H^e), 2.95 br.m (4H, CH_2^b), 1.85 br.m (4H, CH_2^a)]. In this case, the product ratio $C_{60}H_{18}:C_{60}H_6:C_{14}H_{10}:C_{14}H_{12}:C_{14}H_{14}$ is 54:9:2:7:28. High-temperature treatment of the sample (thermogravimetry, 20–1000°C) yields a material of the composition $C_{69}Pt_2$ in which fullerene is determined neither chramatographically nor spectroscopically. This sample exhibits complete absorption in the IR range. The presence of metallic platinum in it was proved by X-ray diffraction. The data obtained agree with the formation of graphite and crystalline platinum in the course of thermal decomposition of the $\{C_{60}H_xPt\}$ mixture.

Thus, coordinated fullerene acts as hydrogen acceptor in reactions with compounds containing weakened C–H bonds (1,4-dihydropyridine and 9,10-dihydroanthracene). Metal fullerides are the dehydrogenation catalysts. They activate C–H bonds of dihydroanthracene and diethyl 2,6-dimethyl-1,4-dihydropyridine-3,4-dicarboxylate in positions 9,10 and 1,4, respectively.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75 IR spectrometer. The electronic absorption spectra were obtained on a Specord UV-vis spectrophotometer.

The mass spectra of hydrofullerenes were measured on an MAT-731 mass spectrometer in the field desorption ionization mode. Hydrogen was determined on an MI-1201V mass spectrometer. The ^{1}H NMR spectra were taken on a Bruker AC-200P (200 MHz) spectrometer; the X-ray photoelectron spectra were recorded on a VARIANIEE-15 spectrometer.

TLC analysis of samples after the experiments was carried out on Silufol UV-254 plates, elution with 1:10 toluene–hexane (A) or 1:3 methylene chloride–hexane (B). Compounds were detected by UV irradiation (C_{60}) or by treatment with iodine vapor (hydrofullerenes). The presence of C_{60} in the solid phase was checked spectrophotometrically (toluene, λ 330 and 406 nm).

Fullerene of 99.5% purity was used; IR spectrum, ν, cm^{-1}: 527, 576, 1183, 1429.

Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate was prepared according to [16], mp 175°C (175–180°C [16]). IR spectrum (Vaseline oil), ν, cm^{-1}: 3350 (N–H). UV spectrum (EtOH): λ 375 nm (ε 6500 $l\,mol^{-1}\,cm^{-1}$). 9,10-Dihydroanthracene (99%,

[1] The ^{1}H NMR analysis of the reaction products was carried out taking into account the reference data on the chemical shifts and the spectra of structural fragments of model compounds. The data obtained were also compared with the spectra of individual compounds recorded under the comparable conditions (solvent, concentration, temperature). The quantitative composition of the reaction products (mol %) was evaluated from comparison of the integral intensities of the characteristic signals in the ^{1}H NMR spectra of these compounds.

Lancaster) was used without additional purification (anthracene content 1%). *exo*,*exo*,*exo*,*exo*-2,3,5,6-Norbornane-d_4 was prepared according to [17]. ^{1}H NMR data show that the degree of deuteration of the *exo*-position was 94.5%; integral intensity ratio $H_d : H_{a+c} : H_b$ 2 : 6 : ~0.22; IR spectrum (film), ν(C–D), cm^{-1}: 2160. $(\eta^2\text{-}C_{60})RhH(CO)(PPh_3)_2$ was prepared according to [18]. $Pt(dba)_2$ and $Pd_2(dba)_3 \cdot CHCl_3$ (dba is dibenzylideneacetone, $C_{17}H_{14}O$) were prepared according to [19, 20]. The elemental analysis data agree with the empirical formula. Platinum fulleride $C_{60}Pt$ was prepared by the reaction of C_{60} with $Pt(dba)_2$ in toluene [4]. Palladium fullerides $C_{60}Pd$ and $C_{60}Pd_{4.9}$ were prepared by the reaction of C_{60} with $Pd_2(dba)_3 \cdot CHCl_3$ in toluene [$C_{60} : Pd_2(dba)_3$ ratio 1 : 1 and 1 : 10, respectively] [21].

The reaction of dihydropyridine **I** with metal fullerides was carried out in evacuated ampules similarly to the dehydrogenation of 9,10-dihydroantracene in the presence of $C_{60}Pt$ [9]. The thoroughly blended mixture of 10 mg of $C_{60}Pt$ and a 25-fold molar excess of ester **I** was placed in an ampule, evacuated to 10^{-2} mm Hg, and sealed. The ampule was placed on a boiling water bath. The reaction time was 1.0 h (control experiment: reaction of [60]fullerene with **I**, 100°C, 1.0 h). After the reaction completion, the mixture was cooled to room temperature, the gas phase was analyzed, and the solid residue was repeatedly extracted with alcohol.

The concentrations of diethyl 2,6-dimethylpyridine-3,5-dicarboxylate **II** and unchanged ester **I** in the alcoholic extract (experiments on reactions of **I** with metal fullerides) and of anthracene in the sublimate (dihydroanthracene–metal fulleride experiments) were determined spectrophotometrically in ethanol: pyridine **II**, λ 274 nm (ε_{274} 3200 l mol^{-1} cm^{-1}); compound **I**, λ 375 nm (ε_{375} 6500 l mol^{-1} cm^{-1}); anthracene, λ 354 nm (ε_{354} 7250 l mol^{-1} cm^{-1}).

Toluene, hexane, and methylene chloride were purified by standard procedures. Freshly distilled solvents were used.

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