Brief Communications

Catalytic polyaddition of benzene to fullerene and properties of the reaction product

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The use of a catalyst based on aluminum trichloride and copper dichloride in the reaction of fullerene with benzene afforded $C_{60}Ph_{19}H_{19}$. At 400 °C, this compound eliminates hydrogen to form $C_{60}Ph_{19}$. The compounds obtained are characterized by their high solubility in organic solvents, film-forming properties, and photoluminescence at 520 nm.

Key words: fullerene; benzene; polyaddition, photoluminescence.

Synthesis of novel film-forming materials based on fullerene is of interest because they can be used as semiconducting films, for example, for the production of diodes.

The compound $C_{60}Ph_5H$ obtained by the reaction of fullerene hexachloride with benzene in the presence of $FeCl_3$ followed by reduction has been described.[1] The possibility of the synthesis of $C_{60}Ph_{12}H_{12}$ using $AlCl_3$ as the catalyst has been shown.[2]

In the present work, the possibility of preparing soluble compounds by adding benzene to fullerene is studied. It is established that the catalytic polyaddition of benzene to fullerene in the presence of $AlCl_3$ and $CuCl_2$ makes it possible to add up to nineteen phenyl rings to form $C_{60}Ph_{19}H_{19}$, and thermolysis of the latter at 400 °C results in the elimination of hydrogen to form $C_{60}Ph_{19}$.

Experimental

IR and UV spectra were recorded on IKS-29 and Specord M-40 spectrophotometers. Photoluminescence spectra were recorded on an Aminco Bowman spectrofluorimeter. Dynamic thermogravimetric analysis was carried out on a Q-1500 derivatograph in an atmosphere of argon at a heating rate of 7.5 deg min^{-1}. Mass spectra were recorded on an MSBC time-of-flight mass spectrometer (Electron plant) (ionization by ^{252}Cf decomposition products with an accelerating voltage of 15 kV).

Aluminum trichloride (analytical purity grade) was purified by sublimation *in vacuo*. Admixtures were removed from benzene by heating with KOH and triple distillation. Copper dichloride (analytical purity grade) was used without additional purification.

The synthesis was carried out in an atmosphere of argon in a three-necked flask equipped with a stirrer. Fullerene (30—60 mg) was dissolved in benzene (10 mL), $CuCl_2$ and $AlCl_3$ were added in a molar ratio of 1 : 2, and the mixture was stirred for 4 h. After the reaction was complete, the mixture was treated consecutively with 5 *M* HCl and water to remove metal chlorides, and the fraction soluble in benzene was separated by filtration and decanted. After evaporation of benzene, the reaction product (brown powder) was obtained and dried at room temperature in a dynamic vacuum. Thermolysis was performed in a dynamic vacuum (~1 Pa) at 400 °C for 1 h.

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Results and Discussion

The character of the IR spectrum of the reaction product depends substantially on the amount of $AlCl_3$ (the $AlCl_3$: $CuCl_2$ ratio was maintained constant). When the $AlCl_3$: C_{60} ratio was low (~ 2 : 1), a product was isolated (compound **1**, ~8 mg per 30 mg of the initial C_{60}) whose spectrum is presented in Fig. 1 (spectrum *1*). Along with the peaks at 526, 577, 1183, and 1425 cm^{-1} corresponding to the unconsumed fullerene,[3] absorption at 2845 and 2920 cm^{-1} and a shoulder at 1446 cm^{-1}, which can be assigned to the stretching and bending vibrations of the saturated C—H bond, are observed. The peak at 1370 cm^{-1} is close to a frequency of 1382 cm^{-1} corresponding to the bond of an O atom with the fullerene molecule.[3] It should be mentioned that broad absorption at frequencies higher than 1600 cm^{-1} and a broad peak at 3450 cm^{-1} are observed (similar absorption is also observed in the spectra of other samples, but is not shown in Fig. 1), which indicate that H_2O is present. The peak at 725 cm^{-1} can be assigned to the C—Cl bond.

When the $AlCl_3$: C_{60} ratio was 10 or greater, the yield of the product (compound **2**) was ≥90 mg per 30 mg of the fullerene. The IR spectrum of this compound contains absorption bands at 3030 and 3065 cm^{-1} corresponding to the stretching vibrations of the C—H bonds of the aromatic ring. The presence of the phenyl group is also confirmed by the existence of the bands of the stretching vibrations of the C—C bond at 1450, 1500, and 1600 cm^{-1}, as well as by the nonplanar vibrations of the C—H bond at 690 and 755 cm^{-1}, which indicate that the phenyl group is monosubstituted. This is also supported by the presence of four small peaks in the Raman spectrum in the region of 1700—2100 cm^{-1}.[4] For compound **2**, found (%) : C, 94.81; H, 5.20; Cl, ≤0.3; Cu, Al, <0.01. $C_{60}Ph_{19}H_{19} = C_{174}H_{114}$. Calculated (%): C, 94.79; H, 5.21. When product **2** is heated at 400 °C for 1 h, compound **3** forms. In its IR spectrum, the bands in the region of 2800—3000 cm^{-1} corresponding to the C—H bond of fullerene with hydrogen[5] no longer appear (see Fig. 1, spectrum *2*). Compounds **2** and **3** are highly soluble in organic solvents: benzene, toluene, chloroform, ether, acetone, *etc.*), but are insoluble in water. A uniform amorphous film ~0.1 mm thick is formed from a solution of compound **2** or **3** in toluene transferred onto a substrate rotating with a velocity of ~1000 rpm.

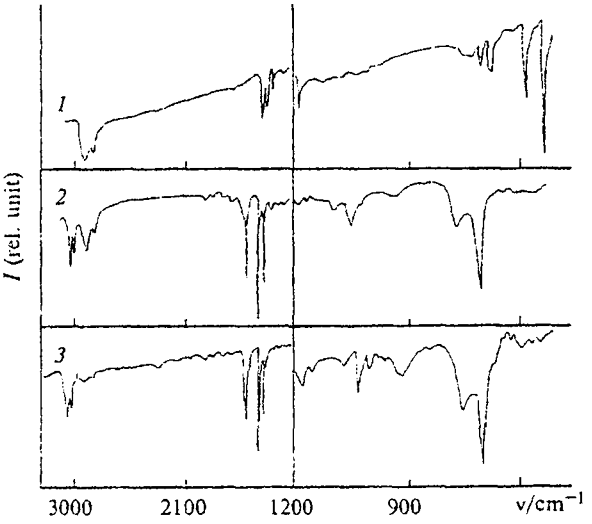

Fig. 1. IR spectra of the products of the reaction of benzene with fullerene in the presence of $AlCl_3$ and $CuCl_2$ (2 : 1): *1—3*, spectra of compounds **1**, **2**, and **3**, respectively.

In the UV spectral region, the absorption of solutions of compounds **2** and **3** in methanol begins at 500—530 nm and gradually increases to 200 nm without any specific features. The absorption curve of compound **3** can be linearized with an accuracy of ±3% in the coordinates log*D*—ν, where *D* is the optical density and ν is the frequency.

The luminescence spectra of compounds **1** and **3** presented in Fig. 2 exhibit peaks at 450 and 490 nm (spectra *1* and *2*, respectively). In both cases, the maximum of the excitation spectrum is located at 390 nm. For compound **2**, the position of the luminescence maximum changes from 450 to 510 nm when the wavelength of the exciting radiation is shifted from 400 to 450 nm. It can be assumed that compound **2** consists of several compounds or contains additional functional groups that are eliminated when it is heated to 400 °C.

The mass spectral data confirm the composition of compound **3**. A peak with a mass of ~720 corresponding to the fullerene fragment and 19 equally separated peaks with a maximum mass of 2182 can be seen in Fig. 3. If the weight of the fullerene moiety (720) is subtracted from the latter value and the result is divided by 19 (assumed number of functional groups), we obtain a value equal to 76.9, *i.e.*, a value close to 77, the weight of a monosubstituted phenyl group. Compound **2** is characterized by the same set of peaks, but with a higher level of background components, which is likely related to the presence of protons and, perhaps, other admix-

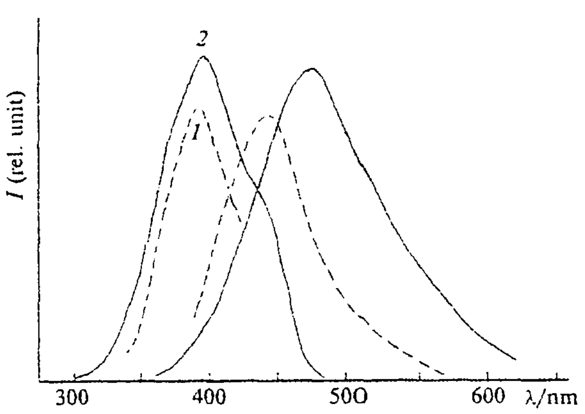

Fig. 2. Luminescence excitation and emission spectra of compounds **1** (*1*) and **3** (*2*) in toluene.

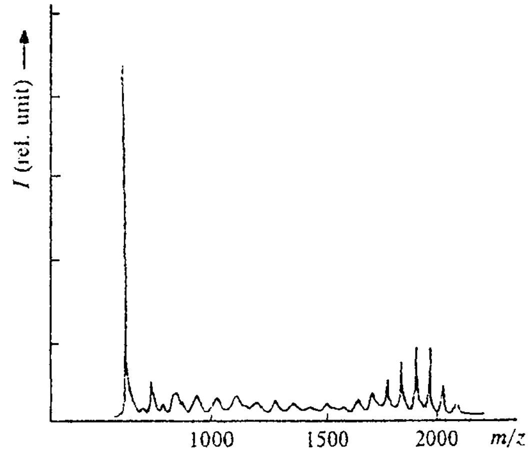

Fig. 3. Mass spectrum of compound 3.

ture groups giving an almost continuous mass spectrum in the region of 720—2182.

The results obtained suggest that at the initial stage of the reaction, $AlCl_3$ reacts with microadmixtures of water to form HCl, which is added to the double bond of C_{60}. This supposition is confirmed by the data of chemical analysis and IR spectroscopy, and the addition of H_2O molecules is also possible. However, when the concentration of $AlCl_3$ is low, the process is complete at this stage. When the amount of the catalyst is increased, the protonation of C_{60} and the reaction with benzene according to the scheme presented in the previously published work become possible.[2]

The $AlCl_3$+$CuCl_2$ mixture is known as the Kovachik catalyst and is used for the polymerization of benzene to polyparaphenylene. In fact, a small amount of insoluble polyparaphenylene was found as a by-product of the reaction studied. Perhaps this catalyst favors an increase in the average number of added phenyl rings due to the presence of $CuCl_2$. However, this process is not the major one. If the benzene rings were joined to form the polyphenylene chain to a considerable extent, the appearance of an absorption peak in the UV region (~330 nm) and the corresponding peaks in the IR spectrum that indicate disubstitution of benzene would be expected. No intense absorption is observed in the region of 800 cm^{-1}, which indicates the absence of *para*-substitution of the benzene rings linked with the fullerene molecule. It is more difficult to rule out *meta*-substitution since the corresponding peaks should appear in the same region as the peaks of the monosubstituted benzene ring. In this case, the absorption in the region of 1700—2100 cm^{-1}, whose character indicates the monosubstitution, is relevant.

Thus, the presence of $CuCl_2$ in the composition of the catalyst increases the maximum number of added phenyl groups to 19, and the compound obtained (**2**) possesses high solubility and film-forming properties. Heating at 400 °C makes it possible to remove hydrogen atoms and other admixture groups to form polyphenylated fullerene **3** with pronounced photoluminescence properties in the blue-green spectral region.

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