Brief Communications

Interaction of fullerene C_{60} with 3-amino-1-propanol

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The C_{60} radical anions formed in the interaction of C_{60} with 3-amino-1-propanol under a vacuum were characterized by ESR and near-IR spectroscopy. In the air, a compound was obtained whose composition corresponds to the C_{60}:$NH_2CH_2CH_2CH_2OH$=1:3.

Key words: fullerene, radical anion, 3-amino-1-propanol, ESR-, IR-, X-ray photoelectronic spectroscopy.

The discovery of carbon clusters (fullerenes)[1] has given rise to the intense study of their chemical properties[2], including the interaction of C_{60} with primary and secondary amines. This interaction was shown to proceed stepwise. According to Ref. 3, the first stage is the transfer of an electron from the nucleophile to C_{60} to form a radical ionic salt which is transformed to the reaction products in the second stage.

We have studied the interaction of C_{60} with 3-amino-1-propanol (AP). It is known that the basicity of nitrogen in 2- and 3-aminoalcohols is decreased due to the electron-withdrawing effect of the hydroxyl group. On the one hand, this can decrease the rate of the interaction between C_{60} and aminoalcohol, but on the other hand, this may stabilize the radical ionic salt formed in the first stage.

We found that at room temperature fullerene C_{60} dissolves slowly in freshly distilled AP to give a reddish-brown (under a vacuum) or yellowish-orange (in the air) solution. In the former, an ESR signal appears and increases with time, whereas in the solution obtained in the presence of oxygen no ESR signals are detected. Originally, the signal consists of two singlets with g = 2.0004 (ΔH = 0.22 G) and g = 2.0000 (ΔH = 1.0 G) (Fig. 1, *a*). A similar situation was observed when morpholine was substituted for AP. The rate of radical formation increases with temperature. After 5 h at 77 °C only one line with g = 2.0004 (ΔH = 0.22 G) remains in the ESR spectrum; weak symmetrical satellites are also observed (Fig. 1, *b*). In this case the concentration of free radical species attains ~25 % based on the initial amount of C_{60}. As the temperature increases, the ESR signals are broadened (by 0.2 G when heated to 40 °C). At the first stages the ESR spectrum observed (Fig. 1, *a*) is similar in several parameters (the signal shape and *g*-factor value) to the spectra obtained in the initial stages of the reaction between C_{60} and metallic sodium in THF[4], whereas the final ESR spectrum (Fig.1, *b*) is similar to the spectra of the radical anion of C_{60} generated electrochemically in toluene-dichloromethane[5]. As

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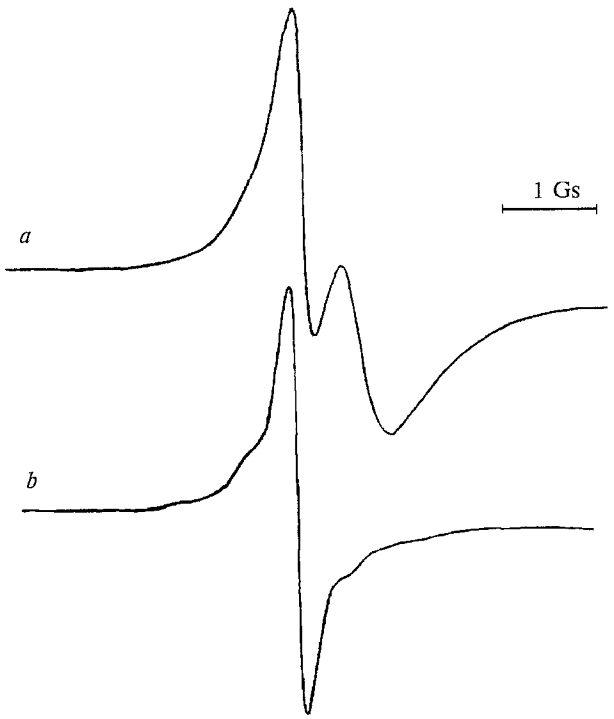

Fig. 1. The ESR spectra of the product obtained in the interaction of C_{60} with 3-amino-1-propanol under a vacuum: after 2 h of the reaction at room temperature (*a*); after heating the reaction solution at 77 °C for 5 h (*b*).

the temperature increases the ESR spectra of $C_{60}^{-\cdot}$ anions are broadened[6] which is in agreement with our observations.

In the spectrum of the solution formed by the interaction of C_{60} with AP absorption bands appear in the near-IR region at λ = 930, 994, 1030 and 1076 nm (Fig. 2). This may indicate the existence of mono- and dianions of C_{60} in the solution, which is in accord with earlier data[7]. It should be mentioned that the solution obtained from C_{60} and AP under a vacuum can be stored for a long time without showing any changes in the spectrum . At the same time, when the ampule is filled with air, a short-lived compound with λ = 650 nm is formed and the ESR signal and absorption bands in the near-IR region disappear.

The solutions obtained in the interaction of C_{60} with AP or morpholine in the air display weak, but characteristic absorption bands in the region of 350 and 400 nm; at the same time, the adsorption bands in the near-IR region are absent. It should be noted that the reaction of C_{60} with AP in the presence of air oxygen proceeds with complete consumption of the former (TLC, Silufol-254, benzene:hexane = 1:10). The corresponding reaction product, **1**, was isolated as a fine brown crystalline powder when acetone was added directly to the reaction solution. After drying, compound **1** becomes weakly soluble in organic solvents, but it dissolves well in

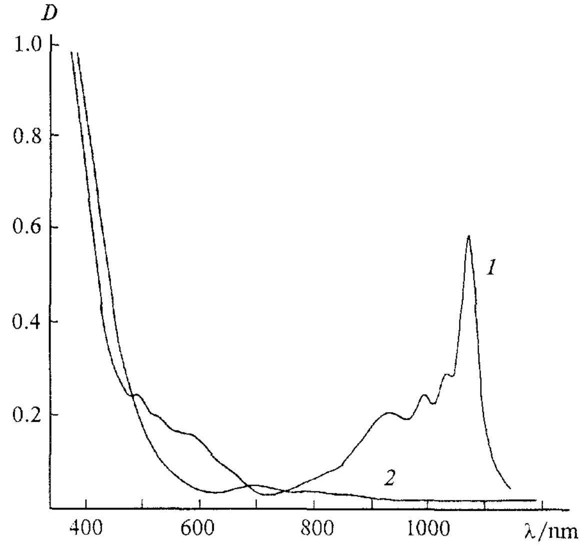

Fig. 2. Electron absorption spectra: interaction of C_{60} with 3-amino-1-propanol (under a vacuum) for 2 weeks (*1*); the same solution, after aeration (*2*).

aqueous hydrochloric acid. The data* of the elemental analysis of nitrogen are in accordance with the composition with a C_{60}:$NH_2CH_2CH_2CH_2OH$ = 1:3 ratio.

The IR-spectrum of **1** indicates the presence of associated N—H and OH groups (Fig. 3). When **1** is treated with CF_3COOH, the IR-spectrum of the compound obtained contains new bands which can be attributed to ν(C=O), $\nu^s(CF_3)$ and ν(C—O) of trifluoroacetic 3 group at 1780, 1200—1165 cm^{-1}, and, possibly, to ν(C=O) of the tertiary amide (1670 cm^{-1}).

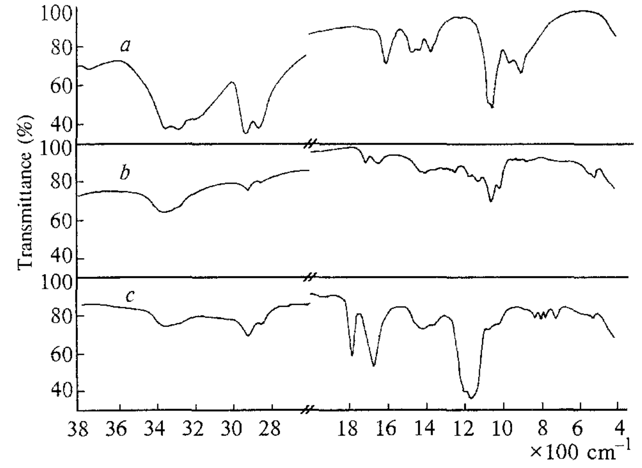

Fig. 3. The IR absorption spectra of 3-amino-1-propanol (*a*), compound **1**, *i.e.*, $C_{60}(NH_2CH_2CH_2CH_2OH)_3$ (*b*) and the product of its interaction with CF_3COOH (*c*).

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* It is well known[2,3] that for fullerenes and their derivatives the %C found deviates 1—10 % from the calculated value.

The X-ray photoelectron spectrum (XPS) of **1** shows a quite intense N1s line in addition to C1s and O1s peaks. The position of the N1s peak (398.45 eV) determined by calibration with C1s (285.0 eV) is characteristic of an amino group[8]. The full width at half maximum (FWHM) of the N1s peak (2.6 eV) is somewhat larger than that of the C1s peak (2.3 eV). This testifies to different environments in the vicinity of all of the nitrogen atoms. The observed $[C/N]_{at}^{XPS}$ ratio is equal to 22, which corresponds to approximately three molecules of $NH_2(CH_2)_3OH$ per one molecule of C_{60} and agrees well with the data of elemental analysis. The value of $(\sigma + \pi)$-plasmon energy determined according to Ref. 9 was found to be equal to 23 eV. This value is smaller than that for C_{60}. This fact can be interpreted as a decrease in the density of valence electrons. The satellite peak due to the plasma oscillations of only π-electrons is practically absent in the XPS near the C1s peak. If the interaction of the fullerene molecule with one amino group of AP decreases the number of its π-electrons by exactly unity, we should not observe such a sharp decrease in this peak. It is possible that the addition of AP to C_{60} in the air is accompanied by the oxidation of the reaction product. This would lead to a decrease in the number of valence π-electrons. Also, the cause of the decrease in π-plasmon intensity may not lie only in a simple decrease in the number of π-electrons but, possibly, also in an increase in the FWHM of this peak.

The nature and mechanism of the formation of the intermediates observed in the reaction of C_{60} with AP deserve more detailed studies. It should be mentioned that the direct transfer of an outersphere electron from the amine molecule to C_{60} giving rise to $C^{-\cdot}_{60}$ and the radical cation $RNH^{+}{}_{2}{}^{\cdot}$ is thermodynamically difficulty; for this process $\Delta G > +2.0$ eV ($E^0{}_{RNH^{+\cdot}}/E^0{}_{RNH} > 1.8$ V; $E^0{}_{C_{60}}/E^0{}_{C_{60}^{-\cdot}} = -0.3$ V). Therefore, this reaction can not be a source of free radicals in the systems studied. In order to clarify the mechanism, it is essential to establish the plausibility of the photochemical stages, the reactions involvng the surfaces of the C_{60} crystallites, and thermodynamically more favorable multielectron processes. Studies in these directions are in progress.

Thus, we have shown that fullerene C_{60} can be reduced by 3-amino-1-propanol to form the radical anion and, subsequently, a C_{60}—AP adduct, the molecular composition of which is C_{60}:$NH_2CH_2CH_2CH_2OH$ = 1:3.

Experimental

ESR spectra were recorded on a Radiopan SE/X-2544 radiospectrometer at the modulation of 0.1 G and microwave power of 10 mW. Electron absorption spectra were registered on an SF-8 spectrophotometer: spectra in the IR range — on a Specord 75-IR spectrophotometer. The X-ray photoelectron spectra were measured by using an ES-200B spectrometer with a magnesium anode ($h\nu = 1253$ eV).

Fullerene C_{60} (10 mg, $1.39 \cdot 10^{-5}$ mol) was slowly dissolved in freshly distilled AP (1.5 mL) at room temperature to produce a yellowish-orange (in the air) solution. Compound **1** precipitated as a fine brown powder by adding acetone to the reaction solution either directly or when most of the AP was removed under a vacuum (65 °C, 2 mm Hg). After centrifugation the precipitate was washed many times with acetone, water, ethanol, and hexane and dried *in vacuo* (24 h, 60 °C). Anal.: Calculated (%) for $C_{69}H_{35}N_3O_8$: C, 77.6; H, 3.38; N, 4.06. Found (%): C, 79.8; H, 3.80; N, 4.46. Selected spectroscopic data: IR (Nujol mull), ν/cm^{-1}: broad band with inflections at 3350 and absorption bands at 2950, 2920, 2850, 1705, 1640, 1525, 1430, 1365, 1240, 1170, 1120, 1055, 1015, 550, 520. UV-Vis (ethanol, λ/nm) 250 sh. Yield 60 %.

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