ESR spectra of fullerene C_{70} in concentrated sulfuric acid

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It was established by ESR spectroscopy that the reaction of C_{70} with concentrated H_2SO_4 resulted in the formation of isomeric dimers C_{140}^{+}, and the action of H_2SO_4 on a toluene solution of C_{70}^{+} gave the $C_{70}^{\cdot}$ radical cation. The structure of dimers was discussed.

Key words: fullerene, structure, ESR spectra.

We have shown previously[1] by ESR spectroscopy that the action of concentrated H_2SO_4 on a toluene solution of C_{60} results in its oxidation to C_{60}^{+}, whereas dissolution of C_{60} crystals in concentrated H_2SO_4 gives the C_{120}^{+} cation. The validity of this assignment was confirmed by the oxidation of the specially synthesized C_{120} dimer by sulfuric acid. The spectral parameters obtained for the oxidation of C_{60} and C_{120} coincided completely.

In this work, we studied the reaction of fullerene C_{70} with sulfuric acid by ESR spectroscopy.

Experimental

Concentrated H_2SO_4 (0.5 mL) containing SO_3 was used for oxidation of C_{70} (1 mg). For oxidation of a toluene solution of C_{70}, 10 equiv. of H_2SO_4 was taken (0.2 mg of C_{70} per 0.5 mL of the solution).

ESR spectra were recorded on a Varian E-12 spectrometer with a double cavity. One cavity contained the sample under study, and another cavity contained the standard with g = 2.0028, relative to which desired values of g factors were measured.

Each spectrum was recorded during ~4 min, and a change in temperature took approximately the same time. Thus, the total duration of the reaction at variable temperature in the experiments presented in Figs. 1 and 2 was ~1 h.

Results and Discussion

The ESR spectra of solutions of C_{70} crystals in H_2SO_4 at different temperatures are a superposition of two spectra (I and II) attributed to different paramagnetic species (see Fig. 1).

To determine which signals are related to C_{70}^{+} or to possible C_{140}^{+} dimers, a toluene solution of C_{70} was oxidized by sulfuric acid. Under these conditions, toluene forms no noticeable quantities of paramagnetic species.[1]

The recorded spectrum (see Fig. 2) coincides with spectrum I, which thus can be assigned to C_{70}^{+}.

It is of interest that at 77 K anisotropy of the g factor is not manifested, and axial anisotropy, which can be expected reasonably from molecules of the rotation ellipsoid type, is observed in the 90—170 K temperature region.

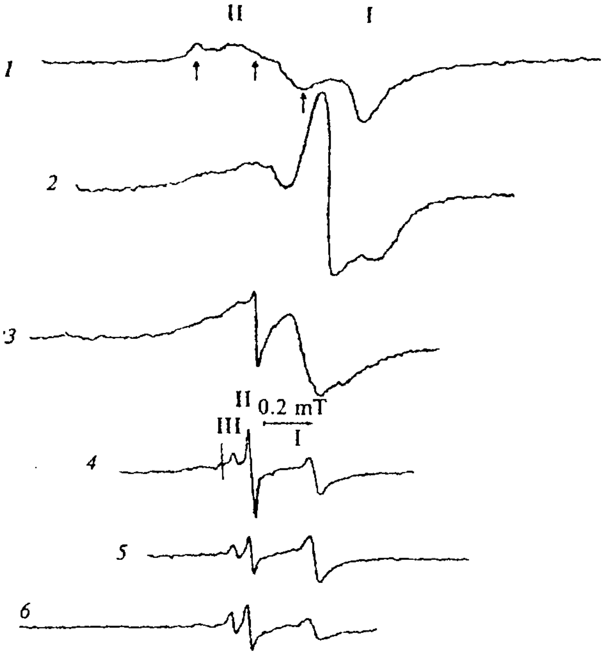

Fig. 1. ESR spectra of C_{70} in concentrated H_2SO_4 at different temperatures: *1*, 77 K; *2*, 170 K; *3*, 240 K; *4*, 260 K; *5*, 273 K; and *6*, 280 K 10 min after recording spectrum *5*. Here and in Figs. 2 and 3, the position of the standard with g = 2.0028 is marked by the vertical line; the positions of lines corresponding to the main values of g tensor are indicated by the arrows; for I—III, see text.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 1, pp. 208—210, January, 1999.

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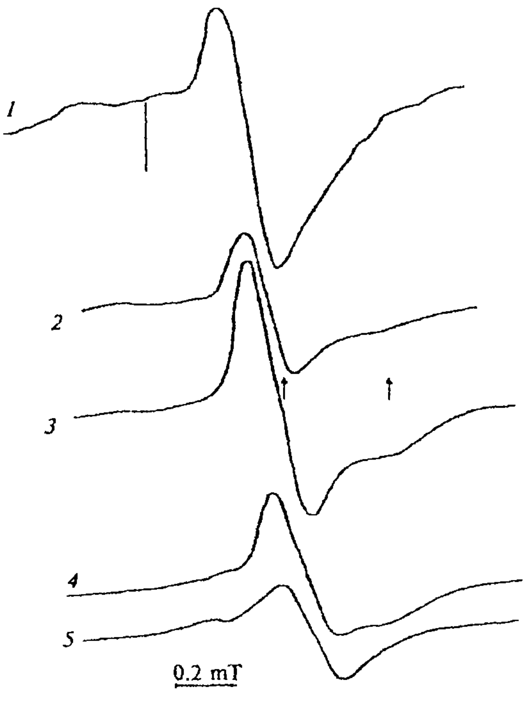

Fig. 2. ESR spectra of C_{70} in a toluene—H_2SO_4 (1 : 10) mixture at different temperatures: *1*, 77 K; *2*, 90 K; *3*, 140 K; *4*, 170 K; and *5*, 210 K.

A possible reason for the appearance of this spectral peculiarity can be associated with triaxial anisotropy of the *g* factor, which is not manifested at 77 K because of the considerable line width. A temperature increase results in averaging of the g_1 and g_2 values (see Fig. 2) to the value of $g_\perp$ due to a faster rotation of the molecule about the long axis of the ellipsoid.

The anisotropy value $\Delta g = g_\perp - g_\parallel$, which is characterized by $g_\parallel = 1.9995$ and $g_\perp = 2.0010$, agrees with the average value of $g = 2.0005$ observed in the solution (see Fig. 1, spectra *4—6* and Fig. 2, spectrum *5*).

Spectra *2—4* in Fig. 2 reflect the dynamics of rotation of $C_{70}{}^+$, which appears as a change in the distance between the lines corresponding to the $g_\parallel$ and $g_\perp$ values.

Noticeable variations in the values of *g* factors and line widths in the $C_{70}{}^+$ and $C_{140}{}^+$ spectra, which are most likely the manifestation of substantial structural distinctions between these species, should be indicated.

Returning to the spectrum of C_{70} in H_2SO_4 (see Fig. 1, spectra *4—6*), we can conclude that lines II and III are related to isomeric $C_{140}{}^+$ dimers. When the temperature and reaction duration increase, the amplitude of line III with respect to line II increases, and the amplitude of line I decreases.

Since line III is virtually absent in spectrum *1* and lines I and II are weakly overlapped, anisotropy of the *g* factor of the isomeric $C_{140}{}^+$ dimer can reliably be determined: $g_1 = 2.0022$, $g_2 = 2.0034$, and $g_3 = 2.0043$.

The reaction conditions do not allow us to conclude whether the thermodynamic or kinetic control occurs in the formation of various $C_{140}{}^+$ dimers, since it is difficult to take into account the influence of their further transformations. Nevertheless, we studied the temperature effect on the formation of isomeric $C_{140}{}^+$ dimers. For this purpose, immediately after dissolution of C_{70} crystals in H_2SO_4 and recording the first spectrum at room temperature, we increased the temperature stepwise to 380 K and recorded successively the ESR spectra (Fig. 3).

As under conditions of the first experiment (see Fig. 1), at first two products are mainly formed: $C_{70}{}^+$ and one of the $C_{140}{}^+$ isomers (see Fig. 3, spectrum *1*). Then the concentration of $C_{70}{}^+$ decreases sharply with time upon heating, and approximately equal quantities of two different $C_{140}{}^+$ isomers (lines II and III) are detected (see Fig. 3, spectrum *2*). At higher temperatures, new lines appear, which are attributed most likely to other isomers, whose number can be very great (see Fig. 3, spectrum *3*).

In terms of discussion of the possible structure of dimers, we should consider the ESR spectrum of $C_{70}H_3$,[2] which contains lines of only one isomer of 2792 possible isomers, whereas the $C_{70}H$ radical is presented in the ESR spectrum by a set of lines related to four ($C_{70}H_A$, $C_{70}H_B$, $C_{70}H_C$, and $C_{70}H_D$) of five possible isomers. The designation of the $C_{70}H$ isomers is determined by the topology of the C_{70} molecule presented in Fig. 4.[2]

The theoretical calculation shows that of all possible isomers of $C_{70}H_3$, the isomer in which hydrogen atoms

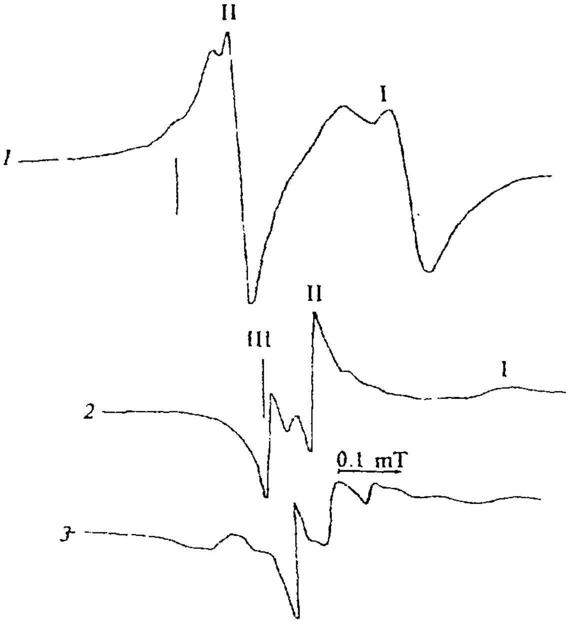

Fig. 3. Effect of heating on ESR spectra of C_{70} in concentrated H_2SO_4: *1*, 300 K; *2*, 350 K; and *3*, 300 K after heating at 380 K for 1 h; for I—III, see text.

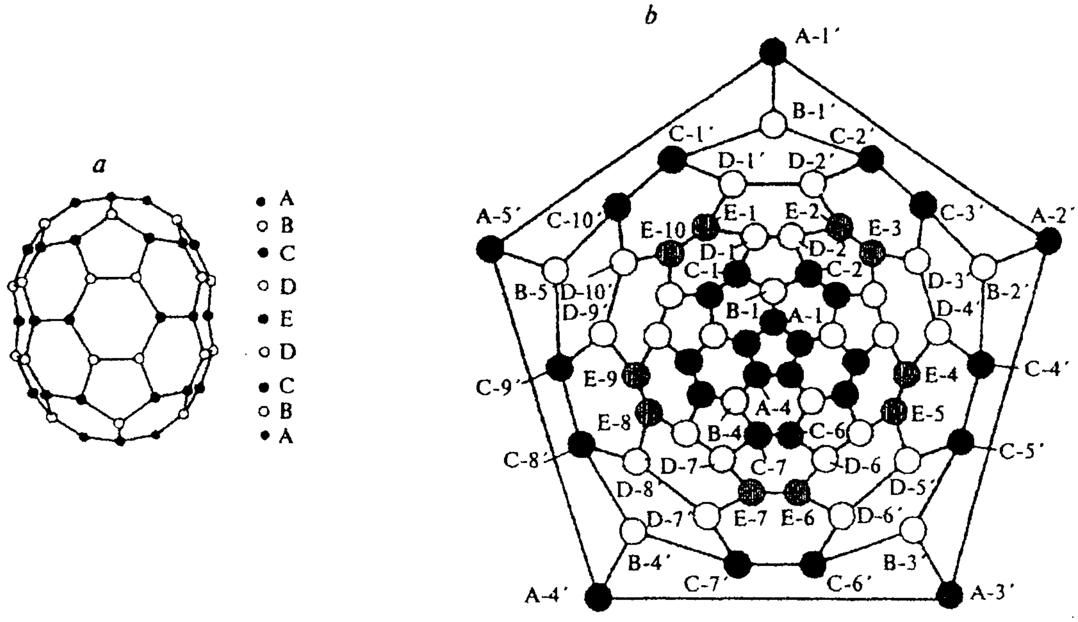

Fig. 4. Structure (*a*) and topology (*b*) of the C_{70} molecule; A—E are the types of atoms of the fullerene skeleton; carbon atoms localized below equator are designated by dashes.

are bound to carbon atoms in positions C-3, A-1, and C-10 is the most stable. Another $C_{70}H_3$ isomer in which hydrogen atoms are bound to carbon atoms in positions C-10, C-1, and A-5 is less stable (by 7 kcal mol^{-1}).

Based on these data, we can assume that the C_{140} isomers in which the bond between fullerenyl fragments occurs through the A-1 and C-3 or A-1 and C-10 atoms are the most stable. An increase in the number of lines in the spectrum of the reaction products as the temperature and process duration increase (see Fig. 3, spectrum *3*) indicates that other C_{140} isomers can be formed. The energies of formation (ΔE) of various C_{140} isomers calculated by the MNDO method were compared:[3] for two *o/o* isomers (*o/o* is "polar/polar") of symmetry C_{2v} and C_{2h}, ΔE = 0; for the *o/t* isomer (*t* is "tropical") of symmetry C_1, ΔE = 4.5 kJ mol^{-1}; and for two *t/t* isomers of symmetry C_{2v} and C_{2h}, ΔE = 9.2 and 9.1 kJ mol^{-1}, respectively.

The results obtained show that the dimerization of fullerenes upon dissolution of their crystals in concentrated H_2SO_4 has most likely the common character.

This work was carried out in the framework of the State Scientific Technical Program "Current Directions in Condensed Matter Physics," direction "Fullerenes and Atomic Clusters" (Grant 98078) and financially supported by the Russian Foundation for Basic Research (Project No. 98-03-3316a).

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Received June 25, 1998
in revised form August 19, 1998