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Near-IR and ESR studies of the radical anions of C_{60} and C_{70} in the system fullerene–primary amine

A.S. Lobach, N.F. Goldshleger, M.G. Kaplunov, A.V. Kulikov

The Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation

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Abstract

It is shown by near-IR that the anion radicals C_{70}^{-} and C_{70}^{2-} are formed in vacuum by interaction between the fullerenes C_{70} and 1-amino-3-propanol (AP) and 1,5-diaminopentane (DAP). The temperature dependence of the ESR spectra for the systems C_{60}–AP, C_{70}–AP and C_{70}–DAP were studied. At low temperature (15–45 K) the ESR spectrum for C_{60}^{-} is similar to that for species with an axially symmetric g-factor. The anisotropy of the signals is averaged out with increasing temperature. The averaged line broadens with further temperature growth, the sharp signal at $g = 2.0001$ being superimposed on this wide line. The ESR spectrum in the system C_{70}–AP at 12.5 K may be tentatively described as a superposition of two ESR spectra, namely the ESR of a radical (assumed to be a cation radical) and of C_{70}^{-}.

1. Introduction

Fullerenes have pronounced electron affinity and are reduced by amines as electron donors [1]. The treatment of C_{60} with the tertiary amine tetrakis(dimethylamino)ethylene (TDAE) leads to the salt TDAE^{+}C$_{60}^{-}$ which reveals an unusual molecular ferromagnetism [2]. Treatment of C_{60} with primary amines and their derivatives results in reduction of the fullerene to anions with subsequent formation of fullerene amino derivatives which are potential monomers for the formation of fullerene-containing polymers [3,4]. The first step of the reaction of fullerene with amines is the single electron transfer from the amine to the fullerene with formation of fullerene anions. Therefore, it is interesting to investigate the reduction of fullerenes C_{60} and C_{70} by amines and their derivatives.

Recently we reported that 1-amino-3-propanol (AP) reduces fullerene C_{60} in an inert atmosphere to the monoanion C_{60}^{-} and the dianion C_{60}^{2-} which were characterized by absorption spectra in the near-IR range ($\lambda = 930$, 994, 1030, 1076 nm) and by the appearance of an ESR signal [3,4]. Now there are a number of papers confirming the reduction of C_{60} by various amines [5,6]. For example, it was reported [5] that C_{60} is reduced to the monoanion radical ($\lambda = 1073$ nm, ESR signal with $H = 0.14$ mT) by the tertiary amine 1,8-diazabicyclo[5.4.0]undec-7-ene in benzonitrile. The formation of C_{60}^{-} was also observed under a reductive quenching of a triplet state of C_{60} by an electron donor (tertiary amine diazabicyclooctane) in an aqueous solution of C_{60} complex with γ-cyclodextrin, in an aqueous micellar solution of triton X-100, and in aliphatic alcohols. C_{60}^{-} was identified by the appearance of the absorption band at $\lambda = 1080$ nm [6].

In contrast to fullerene C_{60}, there are only a few

reports on the formation of anion radicals of C_{70} and their characterization by various methods, apparently because of a smaller accessibility of C_{70}. Table 1 summarizes the data on the reduction of C_{70} by various methods and the characterization of its anions by optical means. It is seen from Table 1 that the anions C_{70}^{n-} ($n = 1-4$) have characteristic absorptions in the near-IR range, the location of the peak maximum for C_{70}^{-} being independent of solvent polarity and the type of the counter-ion [7,8] and it is characteristic only of C_{70}^{-}. One cannot observe the chemical reduction of C_{70}.

The present work continues the study of fullerene reduction by primary amines and their derivatives. It presents the results of the study of C_{70} reduction by 1-amino-3-propanol and 1,5-diaminopentane (DAP) by using optical spectroscopy, electron spin resonance (ESR) and temperature dependence of the ESR lineshape for the C_{60}–AP, C_{70}–AP and C_{70}–DAP systems.

2. Experimental

The pristine C_{60} and C_{70} were obtained as described in Ref. [9]. The high purity of C_{70} was achieved by multiple chromatography of the fullerene mixture and was equal to 99.0% according to the spectroscopic and high-performance liquid chromatography data.

1-amino-3-propanol (Reachim) and 1,5-diaminopentane (Fluka, purum) were used in situ after distillation.

The experiments were carried out in quartz evacuated cells for spectrophotometry with the attached quartz tube for ESR measurements and with the additional volume for solvent freezing. The experimental procedure was as follows: 0.7 mg (8.2×10^{-7} mol) of fullerene and 1.5 ml of amine were put into the cell and the additional volume, respectively. The cell was evacuated, degassed by three freeze–pump–thaw cycles after which the components were mixed under vacuum. After complete fullerene dissolution the ESR spectra and electron absorption spectra were recorded.

The absorption spectra were obtained on a SF-8 spectrophotometer at 1 nm resolution and a cell filled with the corresponding amine used for the reference. The optical path length for the cell was 0.2 cm. The ESR spectra were recorded with a Radiopan SE/X-2544 spectrometer at 0.01 mT modulation and 10 mW power.

Table 1
Optical spectroscopy data for C_{70} anions in the visible and near-IR ranges

Anion	Solvent (electrolyte)	T (K)	Preparation	λ (nm)	ϵ (M^{-1} cm^{-1})	Ref.
C_{70}^{-}	benzonitrile (0.1 M Bu$_4$NPF$_6$)	293	electrochemical reduction	1368	4000	[7]
C_{70}^{2-}				670	2600	[7]
				1170	7200	
C_{70}^{3-}				670	4600	[7]
				1170	5800	
C_{70}^{4-}				670	6000	[7]
				1170	3000	
C_{70}^{-}	Ne matrix isolated	5	NeI irradiation	1363		[8]
C_{70}^{-}	methylcyclohexane	77	γ irradiation	1386		[10]
C_{70}^{2-}	methyltetrahydrofurane	77	γ irradiation	1377		[10]
				1184		
C_{70}^{-}	CH$_2$Cl$_2$ (0.05 M Bu$_4$NBF$_4$)	293	electrochemical reduction	340		[11]
				386		
				483		
C_{70}^{2-}				609		[11]
C_{70}^{-}	AP	293	chemical interaction	1372		this work
	DAP			1370		
C_{70}^{2-}	AP			1172		this work
	DAP			1176		

3. Results and discussion

3.1. Optical spectra in C_{70}–AP and C_{70}–DAP systems

On adding solid C_{70} to neat AP or DAP under vacuum at room temperature a slow dissolution of the fullerene proceeds, the total dissolution being attained in 8–10 h after which the solution turns brown. After that the solution spectra show absorption bands in the UV, visible and near-IR ranges (see Fig. 1, spectrum (1) for C_{70}–AP, that for C_{70}–DAP is given in brackets): two wide bands with maxima at ≈ 320 and ≈ 405 nm (not shown in Fig. 1), 625 nm (shoulder), a wide absorption band in the $\approx$ 700–1000 nm range, 1076 (1078) nm, 1172 (1176), 1372 (1370) nm. These spectra differ from that for C_{70} and from those for neat amines, thus giving evidence for the formation of new compounds. The spectra of the solutions obtained change with time (see Fig. 1), these changes are rather slow. It can be seen in Fig. 1 that the peak intensity at $\lambda = 1372$ (1370) nm grows with time (spectra (1) and (2)), attains a maximum and then diminishes (spectra (3)). The peak intensity at $\lambda = 1172$ (1176) nm grows

with time concomitant with the decrease of the peak intensity at $\lambda = 1372$ (1370) nm and one observes an isobestic point at $\lambda \approx 1220$ (1240) nm.

We attribute the absorption bands obtained at $\lambda = 1372$ (1370) nm to the monoanion C_{70}^-, since they are in agreement with the well-known absorption bands for the monoanion (see Table 1) and are independent of the amine. Analogously, the absorption bands at $\lambda = 1172$ (1170) nm may be attributed to C_{70}^{2-}. The absence of absorption bands in the visible range at $\lambda = 670$ nm, observed in Ref. [5] for C_{70}^{2-}, is probably associated with overlap by a wide band at $\lambda = 700–1000$ nm. Additional confirmation of this is that the exposure of the solutions to air results in the disappearance of the absorption band in the near-IR range and the spectrum changes to a featureless curve (see Fig. 1, spectrum (4)).

A wide absorption band at $\lambda = 700–1000$ nm changes with time both in shape and intensity, the decrease of peak intensity at $\lambda = 806$ and the increase at $\lambda = 936$ nm taking place in the case of AP. This band was not observed earlier in the spectra of C_{70}^- and C_{70}^{2-}, so we attributed it to the products of the fullerene interaction with amines. It should be noted that the shape of this absorption band depends on the type of amine in contrast to the bands attributed to C_{70} anions. The absorption band at $\lambda = 1076$ (1078) nm remains practically unchanged with time both in intensity and in shape. One can assume that this absorption band is associated with C_{60}^- which is present in C_{70} as an impurity ($\approx 1\%$) [12].

We can estimate the concentration of mono- and di-anions of C_{70} from our experimental data using the molar absorption coefficient given in Table 1. Therefore, the maximum absorption for C_{70}^- (Fig. 1, spectrum (2)) corresponds to a concentration of 3.4 $\times 10^{-4}$ M, which constitutes 60% of the initial concentration of C_{70} ($[C_{70}]_0 = 5.5 \times 0^{-4}$ M), i.e. practically all the C_{70} is transformed to anions. After 15 days (see spectrum (3)) the concentration ratio was $[C_{70}^-]/[C_{70}^{2-}] = 1:4$.

3.2. ESR spectra in C_{60}–AP system

We found that at room temperature fullerene C_{60} dissolves slowly in freshly distilled AP to give a reddish-brown (under vacuum) solution. In this solution the ESR signal appears and increases with time
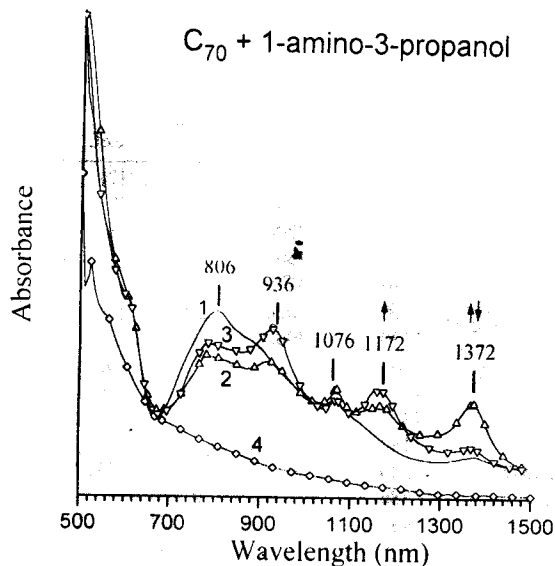

Fig. 1. Visible and near-IR absorption spectra of solutions obtained by the interaction of C_{70} with 1-amino-3-propanol under vacuum; (1) after 8 h; (2) after 6 days; (3) after 21 days of interaction; (4) after exposure to the air.

[3,4]. Originally, the signal consists of two singlets with $g = 2.0004$ ($\Delta H = 0.022$ mT) and $g = 2.0000$ ($\Delta H = 0.1$ mT) (Fig. 2, spectrum at 290 K). A similar situation was observed when morpholine was used instead of AP. We investigated the temperature dependence of the ESR spectra for two C_{60} samples in 1-amino-3-propanol at an early stage of the reaction (5 h at room temperature, sample 1) and after a longer reaction at 70°C (sample 2).

The ESR spectra of sample 1 are shown in Fig. 2. At low temperatures (15–45 K) the ESR spectrum is close to that for species with axial symmetry for the g-factor ($g_\perp = 1.995$ and $g_\parallel = 2.000$). At 15.6 K a weak line was also observed at low field. The anisotropy of the g-factor is averaged with temperature increase (see the spectra at 75 and 109 K). With further temperature increase this averaged line broadened, a narrow signal being superimposed on this wide line at $g = 2.0001$ (see the spectrum at 148 K). The intensity of this narrow line increases with temperature. At 250 K only this narrow line with a width of ≈ 0.1 mT was observed and the main line was so broad that it was not observed. At room temperature the double integration of the spectrum allows one to conclude that the narrow line corresponds only to 25% of the total amount of C_{60}. The other 75% probably corresponds to the wide non-observed line. With further temperature increase the narrow line was split into a narrower line at $g =$
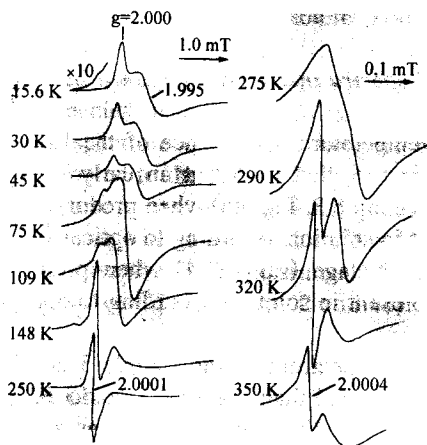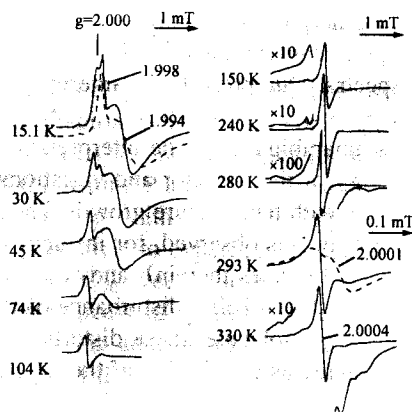

Fig. 3. Temperature dependence of the ESR spectrum of C_{60} in 1-amino-3-propanol under vacuum after heating at 70°C for 5 h.

2.0004 and a width of ≈ 0.15 mT and a wider line at $g = 2.0001$ and a width of ≈ 0.1 mT (see spectrum at 350 K).

The spectra for sample 2 are given in Fig. 3. They are in general similar to those for sample 1; however, new lines were observed. At low temperature (15.1–30 K) an additional line was observed at $g = 1.998$, the intensity of which sharply decreases with temperature increase in such a way that it is not observed at 45 K. It is interesting that at 15.1 K at high microwave power (the spectrum is depicted with a dashed line) the shoulder at $g = 2.0000$ vanishes. Analogously to sample 1 the temperature increase up to 45–74 K results in averaging of the anisotropy of the g-factor, the main line is broadened, and the narrow line is superimposed on it at $g = 2.0000$. Only this narrow line is observed at 104 K and the main line is broadened so much that it is not observed. Four additional satellites with splitting of ≈ 1 mT between them appear at 150–280 K as compared with the spectrum for sample 1. The satellites are most intense at 240 K and are hardly discernible at 280 K. At 293 K the ESR line appears as a superposition of a narrow and a wide line as in the case of sample 1 which have almost the same widths and g-factors. The dashed line at 293 K corresponds to measurement at high microwave power (100 mW). Further temperature increase up to 330 K again results in the appearance of satellites with a splitting of ≈ 0.2 mT.

Fig. 2. Temperature dependence of the ESR spectrum of C_{60} in 1-amino-3-propanol under vacuum after 5 h from the beginning of the interaction.

Despite numerous investigations, it is now difficult to explain unambiguously all the peculiarities of the ESR spectra. Our preliminary interpretation follows.

The most unambiguous is the interpretation of the axial symmetry of the g-factor and variations of the ESR lineshape with temperature growth. The averaging of anisotropy was observed, for instance in Refs. [13–18] (and references therein), and was explained by the so-called Jahn–Teller disturbance of the symmetry of the C_{60}^- molecule, these disturbances (they may be considered as a wobbling of the sphere of the C_{60} molecule) increased with temperature. The anisotropy of the g-factor itself is probably caused [14] by the interaction of C_{60}^- with a countercation. At low temperature the anisotropy is not observed for some countercations [14]. In our case it is not clear why the ESR spectrum of the AP cation radical is not observed. Note that the cation radical is seen in some cases (see, for example, Ref. [19]). The broadening of the main line with temperature increase seems to be attributed not to a dynamic broadening of the ESR lines but mainly to the appearance of a great number of structures at elevated temperatures [18].

It is more difficult to elucidate the origin of the narrow line, which appeared at temperatures greater than 70 K. According to Ref. [14], this narrow line is stipulated by the exited states, the population of which increases with temperature. The authors of Ref. [18] think that in Ref. [14] the intensity of this narrow line was measured incorrectly due to the use of high microwave power, resulting in wrong conclusions on the growth of the intensity of this line with temperature. We paid special attention to this in our measurements, but also observed the growth of the intensity with temperature for this narrow line. The authors of Ref. [18] attribute sharp lines to C_{60} derivatives with a lower symmetry and higher barriers of molecular rotation than C_{60}. The splitting of this narrow line to a narrower and a wider one is not elucidated enough. According to Ref. [20], the narrow line is attributed to free C_{60}^- and the wide one is attributed to a C_{60}^- complex with a countercation. The appearance of satellites could be explained by C_{60}^{2-} as an impurity [21]; however, it is assumed in Ref. [18] that C_{60}^{2-} is diamagnetic and the satellites are caused by species of unknown nature. The disap-
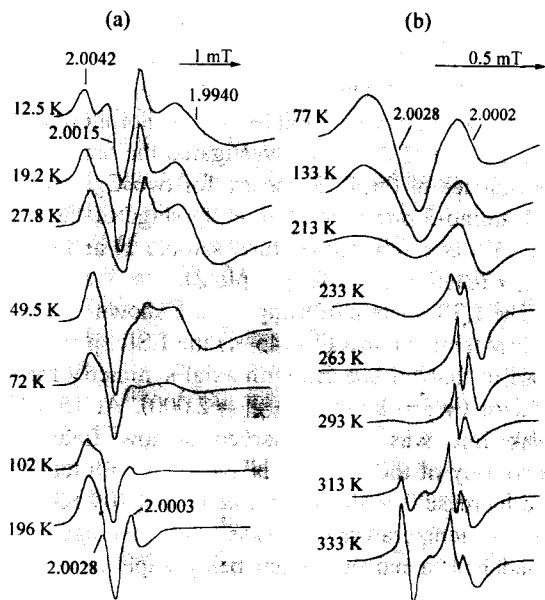

Fig. 4. Temperature dependence of the ESR spectrum of C_{70}: (a) in 1-amino-3-propanol under vacuum after 6 days of interaction; (b) in 1,5-diaminopentane under vacuum after 51 h of interaction.

pearance of the shoulder at $g = 2.000$ in the ESR spectrum at 15.1 K and high microwave power can be explained in the following way. According to Ref. [18], the rates of spin–spin and spin–lattice relaxation of C_{60}^- are strongly dependent on the magnetic field and increase with the field, therefore the line at $g = 2.0000$ must be more strongly saturated than the lines at higher fields.

3.3. ESR spectra in C_{70}–AP system

The temperature dependence of the ESR spectra of C_{70} was studied in AP at an early stage of the reaction (sample 3, Fig. 4a) when predominantly C_{70}^- is present in solution according to optical spectra and at the final stage (sample 4) when predominantly C_{70}^{2-} is present in solution according to optical spectra.

The ESR spectrum of the sample 3 at 12.5 K is more complicated than that of C_{70}^- at 15 K (see Fig. 2) and may tentatively be described as a superposition of two ESR spectra, namely the ESR spectra of a radical with $g_{\parallel} = 2.0042$ and $g_{\perp} = 2.0015$ and that of C_{70}^- with $g_{\parallel} = 2.000$ and $g_{\perp} = 1.994$ which

are close to the g-factors of C_{60}^-. It should be noted that the ESR spectrum of C_{70}^- was interpreted in Ref. [21] as a spectrum with three different g-factors. With temperature growth up to 196 K the spectrum changes to that consisting of two lines, namely the line attributed to the radical with $g = 2.0028$ and that attributed to C_{70}^- with $g = 2.0003$. The spectra of C_{70}^- are characterized by a weaker temperature dependence as compared with those of C_{60}^- (the broadening of lines at $g = 2.0000$ is less and the averaging of the anisotropy of the g-factor is attained at higher temperatures). This observation is in accordance with Ref. [21] and may be explained by greater Jahn–Teller distortions from the geometry of the C_{70} molecule and consequently by slower thermally induced transitions between these distorted structures.

The spectra of sample 4 in which C_{70} is present mainly as C_{70}^{2-} shows only the line with $g = 2.0004$, two satellites being observed at 293 and 313 K. The presence of the satellites in the ESR spectra of C_{70}^{2-} were also reported in Ref. [21]. Their presence in the ESR spectra for both C_{60}^{2-} and C_{70}^{2-} is probably explained by the triplet state of these fullerenes. It is interesting that no ESR signal of the radical found in sample 3 is observed in the ESR spectrum of sample 1; this radical (assumed to be a cation radical) seems to be reduced to a diamagnetic species in sample 4.

3.4. ESR spectra in the C_{70}–DAP system

The ESR spectra of C_{70} in diamine (see Fig. 4b) are similar to those for sample 3 (see Fig. 4a) and are characterized by the presence of two types of paramagnetic species, namely radical ones and C_{70}^-. At 333 K the spectrum consists of the line with $g = 2.0021$ attributed to the radical and two lines of C_{70}^-, namely a narrow one with $g = 2.0004$ and a relatively wide one with $g = 2.0001$. It should be noted that in this case the ESR spectrum of C_{70}^- is rather similar to that of C_{60}^- (see Figs. 2 and 4b).

4. Conclusions

The reaction of fullerenes C_{60} and C_{70} with primary amines and their derivatives in the absence of oxygen (under vacuum) was studied by near-IR and ESR spectroscopies. In all cases predominantly monoanion radicals, C_{60}^- or C_{70}^-, are formed at an early stage of the reaction. At later stages of the reaction, dianion radicals, C_{60}^{2-} or C_{70}^{2-}, are formed. Formation of C_{70}^- and C_{70}^{2-} was found for the reaction of C_{70} with AP and DAP; in addition, a reaction product of C_{70} with AP ($\lambda = 700$–1000 nm) was found. In contrast to experiments with C_{60}, in experiments with C_{70} free radicals, attributed tentatively to cation radicals of amines, were revealed by the ESR method, in addition to C_{70}^- and C_{70}^{2-} species. At later stages of the reaction of C_{70} with AP the cation radical is not observed, presumably because of reduction of this cation radical to a diamagnetic species. The reason why the cation radical is not observed in the reaction with participation of C_{60} is not clear.

The ESR spectra of all samples were recorded within the 12–350 K temperature range. For all the samples the temperature dependence of the ESR spectra of C_{60}^- or C_{70}^- have common features. At the lowest temperatures an axial anisotropy of the g-factor is observed; the anisotropy may be caused by an interaction between anion and cation radicals. At higher temperatures (above 70 K) the anisotropy is averaged out, presumably by Jahn–Teller distortions, for C_{70}^- the averaging being achieved at higher temperature than for C_{60}^-, in accordance with the lower symmetry of C_{70} molecules. On further increase of temperature the averaged line broadens, and a narrow line, presumably due to excited states of fullerene anions, is superimposed on the broad line. This narrow line splits into two lines at room temperature; the narrower line is attributed to free fullerene anion and the wider line to a complex fullerene anion–amine cation. In some samples satellites are observed, presumably attributed to dianions of fullerenes. It should be noted that at present it is difficult to give an unambiguous interpretation of the temperature dependence of the ESR spectra of fullerenes and further experiments are required.

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