

Spectral studies of chemically generated C_{60}^{n-} and C_{70}^{n-} anions; $n=1,2$ and 3

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Abstract

For the first time the spectra of the fullerene anions C_{60}^{n-} and C_{70}^{n-} , for $n = 1, 2$, and 3, in benzonitrile, in the presence of three reducing agents: Na, K and TDAE, were studied. The fullerene anions reveal characteristic, near IR absorption bands, similar to those observed in electrogenerated anions.

Keywords: Fullerene, C_{60} anions, C_{70} anions, optical spectra

1. Introduction

The fullerenes anion radicals can be generated relatively easy by the electrochemical method. Electrochemically generated C_{60}^{n-} anions ($1 \leq n \leq 6$) have been spectrally characterized by many authors [1–5]. On the other hand the chemical method is confined to only two solvents: THF or liquid ammonia. Small solubility of C_{60} and C_{70} in THF as well as of their anions C_{60}^{n-} and C_{70}^{n-} confines the chemical procedure to generation of monoanions or sometimes dianions. Only few papers report the successful synthesis and isolation of discrete salts of the highly reduced C_{60}^{n-} anions [6–8].

In this paper we perform a systematic spectral study of redox states of C_{60} and C_{70} produced in benzonitrile solution by contact on Na, K or TDAE. For the first time the generation of the two-fullerene anions, in the same solvent, has been performed using the same procedure. The features of fullerene anions optical spectra in the near IR region are discussed.

2. Experimental

Absorption spectra of C_{60} or C_{70} solution in the benzonitrile, in the presence of Na, K or TDAE were recorded in the air-tight quartz cell with a Perkin Elmer UV – VIS – NIR Lambda 19 spectrometer, at room temperature. In the reference beam the similar absorption cell with alkali metal solution in the benzonitrile was placed. All the manipulations were carried out under the inert atmosphere conditions of a glovebox under argon. Progress of the reaction of the fullerene with a reducing agent was observed by spectral method, recording the absorption spectra every 5 to 20 minutes, with resolution of 0.1 nm

3. Results and Discussion

Reaction of fullerene reduction by the alkali metal in benzonitrile runs in two stages. On the first stage of the reaction

the benzonitrile molecule receives an electron from an alkali metal and benzonitrile anion-radical forms on the alkali metal surface. Then the anion radical diffuse to the solution forming a salt with the alkali metal. This compound is red-colored and has a strong absorption maximum at 550 nm; the absorption decreases quickly in the 600–620 nm range. Thus the spectral study of the fullerene reduction in the benzonitrile is possible only for wavelengths longer than about 650 nm.

Rates of the reactions of fullerenes C_{60} and C_{70} reduction are nearly the same at room temperature and decrease with the number of charges on fullerenes. Production of the monoanions C_{60}^{1-} and C_{70}^{1-} was observed in 10–15 minutes, C_{60}^{2-} and C_{70}^{2-} in 45 minutes – to one hour and C_{60}^{3-} and C_{70}^{3-} in about 3–4 h after start of the reaction. Due to different reaction rates of formation of benzonitrile and fullerene anion-radicals an accumulation of benzonitrile ion occurs and gets very intensive after C_{60}^{3-} and C_{70}^{3-} formation. It leads to an increase of the absorption in the region of 550–650 nm and in about 5–6 h the solution is not transparent at visible region; the spectra in 550 to 900 nm range become distorted. Thus, the fullerene anions spectra can only be analyzed when the reaction is far from such saturation.

An evolution of the absorption spectra of the C_{60} anion generated in the benzonitrile solution by contact on sodium mirror is shown in Fig. 1. The C_{60}^{1-} fullerene monoanion exhibits strong absorption at 1081 nm together with additional fine structure at 1042 nm, 1001 nm and 940 nm. Upon charging to dianion the C_{60}^{1-} bands disappear while strong absorption bands at 844 nm and 957 nm gain in intensity together with a weak band at 1322 nm. The next reduction state (C_{60}^{3-}) is characterized by relatively intense NIR transitions at 1378 nm and 1012 nm with another band at 878 nm, while the dominant absorption is shifted to 796 nm. The obtained spectra are similar to the spectra of electrochemically generated C_{60} anions that have been observed by other authors [3–5]. The wavelengths corresponding to the main and supplementary maxima in the spectra of C_{60} anions chemically generated by contact on three different reducing agents are collected in the Table I.

Table I
Wavelengths of the absorption bands of C_{60} and C_{70} anions

Species	Wavelengths [nm]			Species	Wavelengths [nm]		
	Reducing agents				Reducing agents		
	Na	K	TDAE		Na	K	TDAE
C ₆₀ ¹⁻	1081	1080	1080	C ₇₀ ¹⁻	1374	1373	1379
	1042	1042	1042				
	1001	1001	998				
	940	936	940				
C ₆₀ ²⁻	1332	1321		C ₇₀ ²⁻	1182 670	1182 670	
	957	955					
	844	840					
C ₆₀ ³⁻	1378	1378		C ₇₀ ³⁻	1172 759 675	1171 759 670	
	1012	1002					
	878	868					
	796	796					
				C ₇₀ ⁴⁻		1160 759 674	

All the maxima are observed at nearly the same lengths of the wave for K, Na and TDAE, but they are red-shifted by 5–20 nm in comparison with the spectra observed in other solutions. Obviously it is caused by universal solvent effect. Lawson et al. [9] have proposed the schematic molecular orbital and optical transition diagrams for C_{60}^{n-} anions; these diagrams suggest the origin of the observed absorption bands in the solution of chemically generated anions.

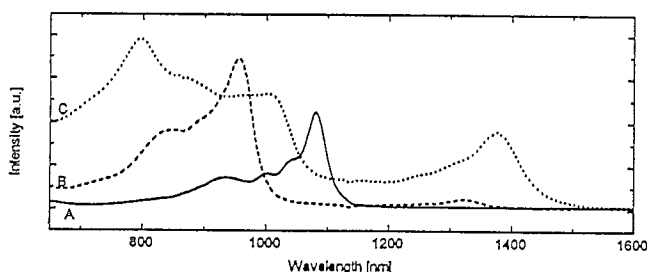


Fig. 1: Optical absorption spectra of the C_{60} anions generated in the benzonitrile solution; the abundances of particular anions are given: (A) – 72% of the C_{60} molecules in the monoanion state, (B) – 100% of the di-anions C_{60}^{2-} , and (C) – 100% of the tri-anions C_{60}^{3-} .

The spectra of the C_{70} anions produced under the same conditions as C_{60}^{n-} are shown in Fig. 2; their maxima are listed also in Table I. Monoanion C_{70}^{1-} shows an absorption band at 1374 nm. Further reduction of C_{70} reduces the intensity of this band, and a new strong band at 1182 nm and a weak one at 670 nm gain their intensities. Mono- and di-anion bands of C_{70} that are red-shifted by 5–17 nm from these positions have been reported [10], similarly to anion bands in the C_{60} spectra and it can also be attributed to the universal solvent effect. With C_{70}^{3-} formation the band at 1182 nm shifts to 1172 nm and its width considerably increases. Simultaneously a distinct band at 769 nm appears. The obtained spectra are similar to the spectra of C_{70} reduced electrochemically in benzonitrile [10]. Only the C_{70}^{4-} spectrum differs considerably from the analogous spectrum obtained for C_{70} reduced in THF by contact on a potassium mirror which shows only one maximum at 1048 nm [11].

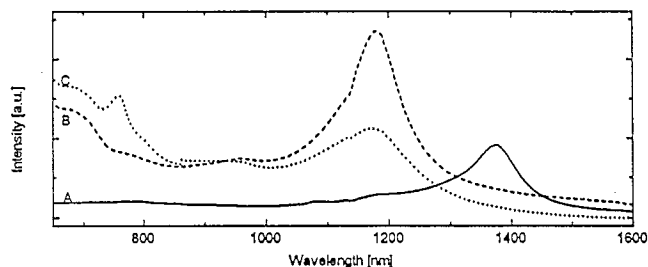


Fig. 2: Optical absorption spectra of the C_{70} anions, generated in the benzonitrile solution; contents of particular anions are given: (A) – 85 % of the C_{70} molecules in the monoanion state, (B) – 100% of the di-anions C_{70}^{2-} , (C) – 100% of tri-anions C_{70}^{3-} .

In conclusion, we would like to stress, that in this paper the chemically generated anions of the fullerenes C_{60} and C_{70} in the benzonitrile solution of three reducing agents (Na, K, and TDAE) were spectrally characterized. It was demonstrated that the spectra of chemically generated anions are similar to that observed for the electrochemically produced fullerene anions. Reduction of C_{60} in oxygen-containing solvent showed that the monoanion is relatively stable against oxidation while its dianion is oxidized quickly with formation of $C_{60}(O_2)_n$, leading to a broad absorption band in 900–1000 nm region.

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