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On the Radical Anion Spectra of Fullerenes

C60 and C70

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The radical anion spectra of C60 and C70 can be easily generated and studied in primary aliphatic amines. In these conditions the C60− and C70− species are accompanied by the dianions C602− and C702−. In the near infrared region the electronic transitions at 1075, 1058 and 991 nm were assigned to C60− while those at 1020–1030 nm and at 933 nm were assigned to the fullerene dianion C602−. The electronic transition of C70− occurs at 1370 nm and that of C602− at 1170 nm, but in primary aliphatic amines C70 also display a broad absorption band at 814–820 nm with other features certainly due to a specific interaction of the amine with C70.

The behavior of C60 was studied with primary aromatic amines, but no interaction was found. Furthermore, solutions of C60 and C70 were studied with the secondary amine dioctylamine and with the tertiary amines triethylamine and N,N,N’,N’-tetramethylethylene diamine (TMEDA). FT-IR spectra of selected fullerene-amine adducts were reported.

Keywords Fullerenes, C60, C70, radical anion, aminolysis, electronic spectroscopy, adducts

1. Introduction

The interest on the radical cation and radical anion spectra of fullerenes is linked to the study of the earlier intermediates in the chemical reactions of these molecules, which may lead to interesting new fullerene derivatives with practical applications (1), and to have reference spectra for the astrochemical search of these molecules in the interstellar medium (2) and in certain circumstellar environment (3,4). The most common methodologies to produce the radical anion of fullerenes involve the electrochemical reduction (5,6) or the γ irradiation of C60 and C70 in frozen matrices (7).

Since the radical cation spectra of a series of fullerenes (6), fulleranes (8,9) and polycyclic aromatic hydrocarbons (10) can be generated chemically and studied in a superacid medium, we were interested in using a similar approach in the synthesis of the radical anion of fullerenes. Indeed, the radical anion spectra of fullerenes were detected by electron spin resonance as a result of the early stages of the reaction of C60 and C70 with amines (11–18). Consequently, the present paper is dedicated to the chemical synthesis of the C60− and
C$_{70}$• in different matrices and to the study of the resulting spectra especially in the visible and in the near infrared.

2. Experimental

2.1. Materials and Equipment

Fullerenes C$_{60}$ and C$_{70}$ were high purity grades (99.95% and 99.0+%, respectively) from MTR Ltd. (Cleveland, OH, USA). n-Propylamine, n-butylamine, N,N-dioctylamine (DOA), 1,3-diaminepropane (DAP) and N,N,N',N'-tetramethylethylenediamine (TMEDA), triethylamine, aniline and 4-ethylaniline were obtained from Aldrich (St. Louis, MO, USA) or Fluka (Buchs, Switzerland). The chemical structures of all amines used in the present work are listed in Scheme 2. The electronic absorption spectra of the radical anion were recorded on a Shimadzu UV2405 spectrometer in the range of 190–1100 nm (6.53–1.13 eV). Optical grade quartz UV cuvettes were used for recording the spectra. The Fourier Transform Infrared (FT-IR) spectra were recorded on an IR300 spectrometer from Thermo-Electron Corp. using KBr pellets in transmission mode.

2.2. Generation of Fullerene Radical Anion by Aminolysis

The synthesis of C$_{60}$• and C$_{70}$• was conducted in a quartz-cuvette reactor described in ref. (19). Essentially the quartz cuvette-reactor is a common cuvette connected with a flask equipped with evacuation valve. The common procedure involves the use of about 1 mg of fullerene (either C$_{60}$ or C$_{70}$) and 3–4 ml of amine and a small magnetic stirring bar. As soon as the amine was added to the fullerene contained in the cuvette-reactor, the latter was immediately sealed and evacuated. The reaction mixture was stirred magnetically at room temperature and the spectra taken periodically. Only in the case of N,N-dioctylamine (DOA) were the spectra taken at 30° C due to the high melting point of DOA.

As a general rule, C$_{70}$ is more readily soluble in the amines than C$_{60}$. In fact the latter requires in general more stirring time than the former fullerene. When the radical anion is formed in the early stages of dissolution, the amine appears usually greenish; on standing and on further dissolution of more fullerene, the amine usually becomes completely brown.

2.3. Isolation of Fullerene-amine Primary Adduct

At times, the amine fullerene adduct resulting from the interaction between the amine and fullerene was isolated. The general procedure adopted was the following: the fullerene-amine mixture consisting of 50 mg of fullerene and amine 10–20 ml was stirred under vacuum for 2–3 hours at room temperature. The resulting dark-brown solution was poured into an excess of distilled water 60–80 ml and stirred for 10 minutes at room temperature and then left to settle overnight. The brown precipitate at the bottom of the flask can be isolated by centrifugation, decantation of the aqueous phase.

2.4. Attempt to Produce Fullerene Aromatic Amine Adduct

The procedure described in section 2.3 failed to produce the fullerene-amine adduct when C$_{60}$ (50 mg) was stirred at room temperature with 10 ml of aniline or 4-ethylaniline. With the addition of methanol, a black precipitate was collected that was identified as pure, pristine C$_{60}$. Therefore, no reaction occurred between fullerene and aniline or 4-ethylaniline.
3. Results and Discussion

3.1. Radical Anion Spectra of C\textsubscript{60} in Primary Amines

The radical anion near infrared (NIR) spectrum of C\textsubscript{60}\textsuperscript{−} generated electrochemically consisted of an intense absorption band in the NIR, at 1064 nm accompanied by a shoulder at 995 nm and a broad peak at 917 nm (5,6). The electron spin resonance (ESR) spectrum recorded simultaneously with the NIR spectrum of C\textsubscript{60}\textsuperscript{−} confirms its radical anion nature (5). Indeed similar near infrared spectrum was reported by Kato, Kodama and Shida when C\textsubscript{60} is irradiated with γ rays in frozen matrices at 77 K (7). The C\textsubscript{60}\textsuperscript{−} spectrum was reported as characterized by two NIR absorptions at 1076 and 952 nm (7). The difference in band position between the C\textsubscript{60}\textsuperscript{−} prepared by electrochemical reduction and γ irradiation is due to the different temperature and matrices used. Figure 1 shows the electronic absorption spectrum of C\textsubscript{60} in n-propylamine. In the earlier dissolution stages, at low concentration the spectrum is characterized by a strong absorption band in the UV, at 256–264 nm, and by another absorption feature at 335 nm followed by a shoulder at about 620 nm. On further C\textsubscript{60} dissolution, the spectrum of Figure 1 shows that the UV absorption band goes out of scale and the band at 335 nm undergoes a shift to 397 nm while the shoulder at longer wavelength is shifted to 633 nm. An additional new broad absorption feature appears at about 975 nm. In the final stages of dissolution, a series of interesting absorption bands appear in the NIR portion of the spectrum: a peak at 1075 nm and four other maxima at 1058, 1031, 991 and 933 nm.

A similar spectrum also was observed by dissolving C\textsubscript{60} in n-butylamine, as shown in Figure 2. Initially there is a broad and weak absorption maximum at 974 nm and a shoulder at about 640 nm, as is already observed in Figure 1. Then the C\textsubscript{60} spectrum in n-butylamine (Figure 2) evolves toward the formation of a series of bands at 1058, 1028, 991 and 932 nm, which is practically the same as observed in Figure 1. In a later stage the spectrum of C\textsubscript{60} in n-butylamine evolves by showing an absorption band at 1076 nm, a weak band at 1058 nm and then the bands at 1020, 992 and 932 nm (Figure 2).

It is evident from these data that the absorption bands in the NIR are independent from the nature of the aliphatic primary amine adopted. To further confirm this interpretation, C\textsubscript{60} was also dissolved in 1,3-diaminepropane (DAP), and once again the spectrum in the

Figure 1. Electronic absorption spectrum of C\textsubscript{60} in n-propylamine (color figure available online).
NIR appears completely analogous to that observed in \( n \)-propylamine and \( n \)-butylamine. In fact, Figure 3 shows the canonical bands at 1058, 1032, 994 and 935 nm. The spectrum of Figure 3 shows also a shoulder at about 600 nm and a similar band appears in \( n \)-butylamine at about 580–610 nm and in \( n \)-propylamine at 600–633 nm. Previous investigators (17) have reported the radical anion spectrum of \( C_{60} \) in 1-amino-3-propanol as constituted by four absorption peaks at 930, 994, 1030 and 1076 nm, completely in line with our results. Furthermore, Gol’dshleger et al. (17) and Lobach et al. (18) have confirmed the presence of the monoanion radical of \( C_{60} \) in 1-amino-3-propanol by recording the ESR spectrum, and similar results were obtained previously by Wudl, Hirsch et al. (11–16) by measuring the ESR spectrum of \( C_{60} \) in primary aliphatic amines and other amines.

Since the following bands can be assigned to \( C_{60}^{-} \): 1075 nm (7,17,18), 1058 nm (5,6), 991 nm (5,6), the other bands at about 1020–1030 nm and at 933 nm could be tentatively assigned to the fullerene dianion \( C_{60}^{2-} \) (17,18), which is diamagnetic and its presence cannot be confirmed by ESR. In conclusion, the interaction of \( C_{60} \) with primary aliphatic amines can be described as follows:
There is an initial formation of a charge-transfer complex between the amine which acts as a donor and the C\textsubscript{60} molecule acting as electron acceptor. This initial stage of interaction could be suggested by the weak and broad band at 974 nm observed in the spectra of Figures 1 and 2 immediately after the fullerene starts to be mixed with the amine. The charge-transfer complex formation is followed by a true electron transfer from the amine lone pair to the fullerene cage thanks to the high electron affinity of C\textsubscript{60} (2.7 eV) so that the fullerene radical anion C\textsubscript{60}•\textsuperscript{−} is formed as reported more clearly in Scheme 1. The radical anion C\textsubscript{60}•\textsuperscript{−} is rather stable but reacts slowly with the amine by radical recombination, giving a zwitterion which finally is converted to the fullerene-amine adduct as detailed in Scheme 1. The adduct can then be easily isolated normally as a brown insoluble in water and in common solvents compound. The amine-fullerene adduct is commonly described as an adduct resulting from multiple amine addition to a single fullerene cage (12,13).

As reported in the experimental section, primary aromatic amines do not react with C\textsubscript{60} in the same circumstances of the primary aliphatic amines and do not produce adducts. In fact both aniline and 4-ethylaniline were separated from the unreacted C\textsubscript{60} after prolonged stirring at room temperature. The interaction between C\textsubscript{60} and aromatic amines is limited only to a simple charge-transfer complex interaction without the formation of a true radical anion as in the case of primary amines (20,21). Consequently, no adducts between aromatic amines and C\textsubscript{60} can be isolated. This different behavior between primary aliphatic amines and aromatic amines can be ascribed to their different basicity and hence to a different nucleophilicity (22). In fact, the pK\textsubscript{a} of primary aliphatic amines is about 10.64 while it is only 4.62 for aniline (22). Thus, aniline is a much weaker base than aliphatic amines because the unshared electron pair in the nitrogen atom are delocalized in the benzene nucleus (22). Therefore, the interaction between aniline (and its derivatives) and C\textsubscript{60} is simply limited to a weak charge-transfer interaction.

### 3.2. Spectra of C\textsubscript{60} in Secondary and Tertiary Amines

Secondary aliphatic amines are characterized by the same degree of basicity of primary amine or a slight higher value. For instance, for diethylamine a pK\textsubscript{a} = 10.93 is reported against a pK\textsubscript{a} = 10.67 of ethylamine (22). Therefore, the same reactivity with C\textsubscript{60} is expected as in the case of primary amines. Different types of secondary amines were added to C\textsubscript{60}, and a number of adducts were reported (12–16,23). However, the selection of dioctylamine as secondary amine was quite unfortunate since it does not react with C\textsubscript{60} to yield either a radical anion or adduct. In fact, Figure 4 shows only the formation of weak charge-transfer complex interaction between the secondary amine used and the substrate as suggested by the broad and weak band at 910 nm, which recalls the broad and weak band at 974 nm observed in Figures 1 and 2 in the case of primary amines interaction with C\textsubscript{60}. The other bands at 330, 404 and 595 nm are the usual C\textsubscript{60} absorption bands. Probably steric reasons and the mild condition adopted have hindered the addition of dioctylamine to fullerene.

Tertiary aliphatic amines have a pK\textsubscript{a} comparable to that of the secondary amines. For instance triethylamine shows a pK\textsubscript{a} = 10.88 (22). However, in this case the formation of the adduct C\textsubscript{60} amine is hindered by the lack of proton to be transferred from the amine to the fullerene cage (19). Therefore, only a charge transfer interaction between the tertiary amine and the fullerene is expected to occur. However, as shown in Figure 5, no interaction at all was detected by electronic absorption spectroscopy. The unique electronic
Scheme 1. Steps to the formation of fullerene-amine adduct.
transitions observed in Figure 5 at about 401 nm and at 592 nm are those due to pure $C_{60}$. Completely analogous results were gained when N,N,N',N'-tetramethylethylenediamine (TMEDA) was used as tertiary amine with $C_{60}$. The electronic absorption spectrum did not show any new band, which could give a hint of interaction.

### 3.3. Radical Anion Spectra of $C_{70}$ in Various Amines

The behavior of $C_{70}$ in primary amines was studied in 1,3-diaminepropane. Figure 6 shows a broad electronic absorption band with a shoulder at 748 nm, a broad maximum at 814 nm and another shoulder at 894 nm. Similar absorption bands were observed by Lobach et al. (18) in their aminolysis studies of $C_{70}$ in 1-amino-3-propanol. They assigned the mentioned absorption bands as due to both $C_{70}^{-}$ and to $C_{70}^{2-}$. Instead, the NIR absorption band due
Figure 4. Electronic absorption spectrum of C₆₀ in dioctylamine (color figure available online).

Figure 5. Electronic absorption spectrum of C₆₀ in triethylamine (color figure available online).

exclusively to C₇₀⁻⁻ was observed at 1370 nm and the band due to C₇₀²⁻ at 1170 nm, based also on previous studies on the radical anion of C₇₀ generated by γ irradiation (24,25). Both these transitions are beyond the spectra window accessible to our spectrometer. The band at 1078 nm observed in Figure 6 was also detected by Lobach et al. (18) in their study in 1-amino-3-propanol and assigned to C₆₀⁻⁻ impurity always present in C₇₀ samples. Figure 7 shows the electronic absorption spectrum of C₇₀ in the secondary amine dioctylamine (DOA). Certainly an interaction between C₇₀ and DOA occurs otherwise we cannot justify the broad and rather weak absorption maximum observed at 820 nm, approximately the same wavelength showing the interaction between C₇₀ and 1,3-diaminepropane reported in Figure 4. A similar broad band located at about 910 nm was observed in the interaction between C₆₀ and DOA (see Figure 4). Thus, the behavior of C₇₀ and C₆₀ with DOA appears similar: charge-transfer interaction but no adduct formation at least in the mild conditions adopted in the present work.

As tertiary amine use was made of N,N,N',N'-tetramethylethylene diamine (TMEDA). In the case of C₆₀ in TMEDA no interaction with that amine was detected. Instead C₇₀ shows the development of a weak and broad absorption band at 808 nm which grew in intensity with time shifting to 860 nm (Figure 8). After prolonged contact of C₇₀ with
Figure 6. Electronic absorption spectrum of C$_{70}$ in 1,3-diaminepropane.

Figure 7. Electronic absorption spectrum of C$_{70}$ in dioctylamine (color figure available online).

TMEDA, the charge-transfer band occurs at 820–840 nm (Figure 9). The other absorption bands shown in Figure 8, at 378 and 467 nm, are due to neutral C$_{70}$. It was possible to isolate also an adduct between C$_{70}$ and TMEDA whose FT-IR spectrum is shown in Figure 10.

The different response of C$_{60}$ and C$_{70}$ in their aminolysis behavior with TMEDA confirm that C$_{70}$ appears slightly more reactive with amines than C$_{60}$. C$_{70}$ dissolves most frequently more readily in neat amines than C$_{60}$, and the resulting solutions tend to darken more readily with C$_{70}$. With tertiary amines, C$_{60}$ has not given any interaction in the conditions adopted in the present work; C$_{70}$ has shown a weak but evident interaction which lead also to an adduct formation.

3.4. FT-IR Spectra of Some Fullerene-amine Adducts

In some cases the fullerene-amine adducts were isolated and collected for the FT-IR spectroscopical analysis. Figure 10 shows the spectra of the adducts C$_{60}$($n$-butylamine)$_n$, C$_{60}$($n$-propylamine)$_n$ and C$_{70}$(TMEDA)$_n$. The spectra of the C$_{60}$ adducts also show the infrared absorption bands of the unreacted C$_{60}$, which was recovered together with the
adducts. The infrared spectra reported in Figure 10 are in reasonable agreement with those described by Wudl and others (13).

4. Conclusions

The radical anion of $C_{60}^{-}$ can be generated quite easily by dissolving $C_{60}$ in primary aliphatic amines, and the resulting electronic absorption spectrum in the NIR appears as a multiplet where there is the contribution of the dianion specie $C_{60}^{2−}$. Similarly, the radical anion spectrum of $C_{70}^{-}$ can be generated in primary aliphatic amines. The interaction of $C_{60}$ and $C_{70}$ fullerene with primary amines is so strong that the amines undergo a nucleophilic addition to the fullerene cage producing fullerene-amine adducts as reported in Scheme 1 (12–16,23).

Aromatic primary amines due to their low basicity in comparison to the aliphatic amines are not reactive at all with $C_{60}$ fullerene. Secondary aliphatic amines are expected to be reactive as the primary one with fullerenes. However, dioctylamine used in the present study shows only a weak charge-transfer interaction with either the $C_{60}$ or $C_{70}$ molecule.
Tertiary amines are not reactive at all with C$_{60}$ fullerene. Both triethylamine and TMEDA do not show even a weak charge-transfer band in the electronic spectra when in contact with C$_{60}$. Instead C$_{70}$ shows a weak charge-transfer interaction with TMEDA.

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