On the Radical Cation Spectra of Fullerenes and Fulleranes. Part 2: C$_{60}$H$_{36}$, C$_{70}$H$_{38}$, C$_{60}$H$_{18}$ and C$_{60}$H$_x$/C$_{70}$H$_y$ Mixture

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Available online: 14 May 2012

To cite this article: Franco Cataldo, Susana Iglesias-Groth & Arturo Manchado (2012): On the Radical Cation Spectra of Fullerenes and Fulleranes. Part 2: C$_{60}$H$_{36}$, C$_{70}$H$_{38}$, C$_{60}$H$_{18}$ and C$_{60}$H$_x$/C$_{70}$H$_y$ Mixture, Fullerenes, Nanotubes and Carbon Nanostructures, 20:8, 672-680

To link to this article: http://dx.doi.org/10.1080/1536383X.2011.552996
On the Radical Cation Spectra of Fullerenes and Fulleranes. Part 2: C₆₀H₃₆, C₇₀H₃₈, C₆₀H₁₈
and C₆₀Hₓ/C₇₀Hᵧ Mixture

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A series of fulleranes, namely C₆₀H₃₆, C₇₀H₃₈, C₆₀H₁₈ and a mixture of hydrogenated fullerenes composed by 77% C₆₀Hₓ and 22% C₇₀Hᵧ, were dissolved in oleum (fuming sulfuric acid) in order to record the radical cation spectra of these molecules. Surprisingly, it was found that the fulleranes spectra in oleum corresponded to the radical cation spectra of pristine C₆₀ and C₇₀ fullerenes. Therefore, it was concluded that the fulleranes in a high ionizing and oxidizing medium such as oleum are dehydrogenated and oxidized to C₆₀⁺⁺ and C₇₀⁺⁺. The prolonged contact with oleum leads to multiple sulfonation of the radical cations.

Keywords Fullerenes, hydrogenated fullerenes, oleum, fuming sulfuric, radical cation, spectroscopy

Introduction

The radical cation of polycyclic aromatic hydrocarbon and of the fullerene homologue series can be generated quite easily in laboratory by using oleum (fuming sulphuric acid) (1–3). The radical cation spectra are important, among other things, in the search and identification of organic molecules in space. For instance, ionized C₆₀⁺⁺ spectral features were searched in the diffuse interstellar bands (4), and the PAHs radical cations were actively investigated in the laboratory in order to have reference spectra for their identification in space (1,5–7).

In part 1 of this work (3), we have investigated the radical cation spectra of the homologous series of fullerenes from C₆₀ to C₈₄. The fullerenes were recently detected in space either in certain planetary nebulae (8,9) or even in the interstellar medium (10). Certainly, fullerenes are formed in hydrogen-poor carbon rich stars and then are ejected in the interstellar medium where laboratory studies have assessed a considerable resistance to high energy radiation of both C₆₀ and C₇₀ fullerenes (11). However, an important chemical property of the fullerenes regards their reactivity with hydrogen (12). When exposed

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to hydrogen, either atomic or molecular, the fullerenes undergo an hydrogenation reaction. Different degrees of hydrogenation can be achieved and the hydrogenated fullerenes are known as fulleranes (12). Thus, fullerenes once formed in carbon-rich and hydrogen depleted region of certain late-type stars already in the stage of protoplanetary and planetary nebulae are expelled in external hydrogen-rich regions where they are almost certainly hydrogenated (9). The next infrared search for fullerenes in space may focus also on hydrogenated fullerenes and we already know their infrared spectra (9,13–17). In contrast, we do not know the radical cation spectra of the fulleranes. As in the case of fullerenes (8), the fulleranes may display a neutral absorption spectrum if adsorbed on the amorphous carbon dust and can be ionized as radical cations if they are free molecules. This paper is dedicated to the attempt to record the radical cation spectra of a series of fulleranes.

**Experimental**

**Materials and Equipment**

Fulleranes $C_{60}H_{36}$ and $C_{70}H_{38}$ were synthesized as described previously (13–15). The fullerene $C_{60}H_{18}$ was synthesized from the action of hydrogen iodide on $C_{60}$ (17). A mixture of hydrogenated fullerenes was obtained from ABCR GmbH (Germany) and characterized in a previous study (16). Oleum (fuming sulphuric acid) with 30% free SO$_3$ was from Merck (Germany). Warning, though: oleum is an extremely corrosive and powerful oxidizing agent. The fumes released by oleum must not be inhaled. Wear suitable protective gloves and goggles and work always under an appropriate fume hood.

The electronic absorption spectra of the fulleranes in oleum were recorded on a Shimadzu UV2405 spectrometer in the range between 190 and 1100 nm (6.53–1.13 eV). Optical grade quartz UV cuvettes were used for recording the spectra.

**Electronic Absorption Spectra of Fulleranes in Oleum**

After a baseline correction (oleum vs oleum), the spectra of the fulleranes radical cations were recorded by dissolving in oleum (3.5 ml) about $<1$ mg of the fullerane under study; stirring with a glass stick was in most cases necessary to help the fullerane dissolution and homogenization. The electronic spectra were recorded immediately after the PAHs dissolution at room temperature (unless otherwise stated). Wherever possible, the evolution of the electronic absorption spectrum with time was followed and studied as discussed in the results and discussion section.

**Results and Discussion**

**Behavior of Fullerane $C_{60}H_{36}$ in Oleum**

The electronic absorption spectrum of $C_{60}H_{36}$ in hexane is characterized by a broad absorption band at 217 nm, recalling in its shape and absorption peak the interstellar light extinction curve (18). $C_{60}H_{36}$ in hexane does not show any other absorption feature in the visible and in the near infrared. Furthermore, $C_{60}H_{36}$ is not stable when exposed to air. Thus, as soon as synthesized and isolated (13,14), $C_{60}H_{36}$ ($<1$mg) was transferred into a quartz cuvette filled with oleum, and the electronic absorption spectrum was recorded immediately after the rapid dissolution of $C_{60}H_{36}$ as shown in Figure 1. The spectrum of $C_{60}H_{36}$ in oleum is characterized by a broad absorption band in the visible region with two
features at 710 and 815 nm and a smaller band in the near infrared region at 968 nm. These three electronic transitions occur, respectively, at 1.75 eV, 1.52 eV and at 1.28 eV. The last two transitions are very close to those observed on the fresh solution of C\textsubscript{60} in oleum: 1.50 and 1.33 eV (3). It is usually assumed that in strongly oxidizing solutions such as oleum, as in the present case, the formation of the radical cation of the oxidized molecule occurs in the early stages of dissolution because, on standing, further reactions occur, for example, the sulfonation of the substrate (3). Furthermore, in the case of C\textsubscript{60} in oleum, the sulfonation reaction occurs exclusively through the addition to the double bonds of the SO\textsubscript{3} or S\textsubscript{2}O\textsubscript{6} species present in oleum. Instead, in the case of fullerenes in general and C\textsubscript{60}H\textsubscript{36} in particular, parallel addition reactions to the residual double bonds and substitution reactions to the hydrogenated double bonds may occur simultaneously after prolonged dissolution in oleum. As already observed, the electronic transitions of C\textsubscript{60}H\textsubscript{36} in oleum at 1.52 eV and at 1.28 eV are very close to those already assigned to, respectively, C\textsubscript{60} charge transfer complex with oleum and to C\textsubscript{60}\textsuperscript{+} occurring at 1.50 and 1.33 eV (3). This fact implies that the hydrogenated fullerene C\textsubscript{60}H\textsubscript{36} resembles C\textsubscript{60} in its behavior in oleum; the additional new absorption band at 711 nm may be attributed to the interaction of the hydrogenated part of the fullerene molecule with oleum.

Figure 1 shows also the evolution of the electronic spectrum of C\textsubscript{60}H\textsubscript{36} in oleum with time. After 1 hour, the peak at 815 nm appears more intense, but substantially the spectrum is the same as at the beginning of the experiment, although the band originally located at 968 nm now appears shifted at 928 nm (hence there was a shift of this band from 1.28 eV to 1.34 eV, the transition is now even closer to that of C\textsubscript{60}\textsuperscript{+}). The spectrum taken after 3 hours shows a substantial decrease in the intensity of the absorption band in the visible without substantial changes in the position of the three bands which still occur at 713, 819 and 928 nm. The decrease in intensity is evidently due to further reactions (sulfonation) undergone by the fullerene. After 24h the band at 819 nm has completely disappeared and the band at about 928 nm is accompanied by another band at 1011 nm (1.23 eV). On standing 48 hours, the brown-green color of the solution faded and the absorption bands in the visible and near infrared portion of the spectrum appear now weak and still positioned at

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Electronic absorption spectra of fullerane C\textsubscript{60}H\textsubscript{36} dissolved in oleum. The absorption spectra were recorded after t = 0, 1h, 3h, 24h and 48h (from top to bottom) (color figure available online).
711, 924 and 1011 nm (Figure 1). After 48 hours of C_{60}H_{36} in oleum, Figure 1 shows also the electronic transitions occurring in the ultraviolet part of the spectrum and these can be found at 247, 297 and 371 nm. Since pure C_{60}H_{36} in inert solvents shows only one electronic transition at 217 nm (18) while C_{60} in the same inert solvents shows three main transitions, respectively, at 213, 257 and 319 nm, the three transitions of C_{60}H_{36} in oleum at 247, 297 and 371 nm observed in Figure 1 can be interpreted in terms of dehydrogenation of the fullerane back to the mother fullerene C_{60}. The energy of the UV transitions of C_{60} are 5.82, 4.82 and 3.89 eV; the three transitions are spaced approximately 1 eV. The UV transitions of C_{60}H_{36} in oleum occur at 5.02, 4.18 and 3.34 eV, regularly spaced by 0.84 eV. These considerations together with the observation of the known reversibility of the hydrogenation of C_{60} (18) and the observed UV transitions of C_{60} in oleum at 4.96 and 3.88 eV (3) suggest that C_{60}H_{36} is also subjected to a dehydrogenation reaction in oleum. Such a phenomenon was already observed by dissolving partially oxidized C_{60}H_{36} in concentrated sulphuric acid (13,15): a series of bands at 228, 269, 340 and 458 nm were observed.

It is worth mentioning here that with C_{60}H_{36} in the gas phase and under the action of electron impact, the radical cations of hydrofullerenes do not show extensive dehydrogenation but undergo the loss of hydrocarbon moieties through cage rupture or shrinkage. This seems to be in line with the proposed sequence of dehydrogenation followed by oxidation, rather than the other way around (19).

**Behavior of Fullerane C_{70}H_{38} in Oleum**

The chemical properties of C_{70}H_{38} are quite similar to those of C_{60}H_{36} (15,18). Figure 2 shows the electronic absorption spectra of C_{70}H_{38} as soon as it is dissolved in oleum and after 24 hours. Figure 3 reports a detail of the spectra of Figure 2 and also includes the electronic spectrum of C_{70}H_{38} after 15 minutes in oleum. The electronic absorption spectrum of C_{70}H_{38} in inert solvents is characterized by a broad transition at 214 nm (20). As soon as it is dissolved in oleum, C_{70}H_{38} displays a maximum in the UV at 242 nm, followed by a series of broad and relatively weak absorption bands at 344, 423, 558, 710 and 885 nm (Figure 1). After 15 minutes in oleum, a new band appears at 297 nm followed by a band at 328 nm probably due to a blue shift of the band originally found at 344 nm (Figure 2). At 15 minutes another transition can be found at 445 nm and then the band broadening of the transition at 710 nm and the weakening of the band at 885 nm. It is useful to recall that C_{70}^{++} transitions in oleum occur at 648–636 nm with a shoulder at 710 nm and transition at 791 nm in aged solutions. Thus, it appears reasonable to associate the transition of C_{70}H_{38} in oleum at 710 nm with that of the C_{70}^{++} in the same solvent. At 15 minutes the band at 710 nm in Figure 3 is so broad to include also another transition at about 640 nm. Such band can be observed more clearly in the aged spectrum of C_{70}H_{38} dissolved in oleum (Figures 2 and 3) and has the same energy and wavelength of that dominating the C_{70}^{++} spectrum in oleum (3). Thus, also in the case of C_{70}H_{38} in oleum, it has been found a correspondence of the electronic transitions of this molecule and those of the radical cation C_{70}^{++} in the same solvent. Even the electronic transition at shorter wavelength that at about 442 nm reported in Figures 2 and 3 has been observed in the C_{70}^{++} spectrum in oleum (3). It was already reported (15) that oxidized C_{70}H_{38} dissolved in concentrated sulphuric acid produces a complex spectrum with absorption bands at 210, 271, 310, 330, 340 and 460 nm. This spectrum was interpreted in terms of partial dehydrogenation of the fullerane back to its mother C_{70} (15). Evidently, this occurs also in oleum.
where C\textsubscript{70}H\textsubscript{38} is partially dehydrogenated and then oxidized to the radical cation C\textsubscript{70}\textsuperscript{+•} and where sulfonation reactions are likely to occur especially after prolonged contact with oleum.

**Behavior of Fullerane C\textsubscript{60}H\textsubscript{18} in Oleum**

C\textsubscript{60}H\textsubscript{18} is the most stable and well-known fullerene, and it is easily accessible through various synthetic routes (12). Recently a new and convenient synthesis of C\textsubscript{60}H\textsubscript{18} was reported reacting C\textsubscript{60} and hydrogen iodide (17). A sample of C\textsubscript{60}H\textsubscript{18} produced with such synthesis was used in the present work. The electronic absorption spectrum of C\textsubscript{60}H\textsubscript{18} in inert solvents is quite complex and is characterized by the following absorption maxima (21): 218, 237 and 255 nm (the latter band with two shoulders at 249 and 261 nm). An additional strong absorption maximum occurs at 340 nm with a shoulder at 326 nm.
Figure 4. Electronic absorption spectra of fullerene $C_{60}H_{18}$ dissolved in oleum. The absorption spectra were recorded after $t = 0$, 15 and 100 min (from bottom to top) (color figure available online).

(20). $C_{60}H_{18}$ dissolved in oleum displays two bands in the UV at 247 and 323 nm as shown in Figure 4. On standing, the band at 323 nm broadens, and a new feature appears as a shoulder at about 305 nm. In the visible part of the spectrum (see also Figure 5) it is possible to distinguish initially ($t = 0$) a couple of broad bands, respectively, at 510 and at 592 nm. After 15 minutes from the beginning of the experiment, the band at 510 nm appears shifted at 519 nm accompanied by the 592 nm band and by a new band at 830 nm. The latter band becomes more evident in the absorption curve recorded at 100 minutes and is accompanied by an additional weak and broad band at 910 nm. The radical cation bands of pure $C_{60}$ occur at 823 and 931 nm (3), and once again we find that the fulleranes tend to produce the radical cation spectrum of their pristine fullerene, $C_{60}^{+•}$ in this case. Expressed in terms of energy the near infrared absorption bands of $C_{60}H_{18}$ in oleum are respectively at 1.49 and 1.36 eV; these values are very close to the transitions of $C_{60}^{+•}$ synthesized in oleum: 1.51 and 1.33 eV (3). The concept of a dehydrogenation reaction in oleum is completely reasonable and does not exclude subsequent sulfonation reactions.

**Behavior of Hydrogenated Fulleranes Mixture $C_{60}H_x$ and $C_{70}H_y$ in Oleum**

A mixture of hydrogenated fullerenes (HMF) composed of 77% $C_{60}H_x$ and 22% $C_{70}H_y$ were characterized in a recent work (16). It was a complex mixture of fulleranes and hydrogenated products derived from the reductive decomposition of fullerenes. In the HMF mixture it was found the presence of fulleranes $C_{60}H_x$ and $C_{70}H_y$ with $x > 36$ and $y > 38$ (16). The crude mixture was dissolved in oleum and the electronic spectra recorded are shown in Figure 6. As soon as the HMF is dissolved in oleum, it displays a spectrum with two absorption peaks in the UV, namely at 248 and at 340 nm, followed by a long and featureless absorption tail until 1000 nm. On standing, further HMF dissolves in oleum as shown by the increase in the absorption bands in the UV (see Figure 6), and the initial featureless long tail absorption starts to show after 30–60 minutes at a series of broad absorption bands at 453, 631, 826 and 921 nm. Although less intense, these bands are still detectable after 24 hours from the beginning of the experiment.
In an inert solvent-like hexane, the HMF shows an absorption maximum in the range of 190-200 nm and a weak and broad peak at 230 nm (16). In contrast, when HMF is dissolved in concentrated sulphuric acid, it displays an absorption maximum at 210 nm followed by a strong absorption band at 348 nm and a broad peak at 408 nm (16). In oleum, the band at 210 nm appears shifted to 248 nm while the other strong band is located at 340 nm. Such spectrum resembles that of C$_{60}$H$_{18}$ in oleum (compare Figure 6 with Figure 5), and it should be recalled that pure C$_{60}$ has a strong peak at 330 nm in inert solvents.

Moving into the visible and near infrared regions of the absorption spectrum it can be observed that the absorption bands of HMF shown in Figure 6 at 453 and 631 nm can be compared with the bands at 442 and 630 nm of C$_{70}$H$_{38}$ in oleum (Figures 2 and 3) or with the C$_{70}^{+•}$ bands in oleum at 452 and 636 nm (3). The HMF bands at 826 and 921 nm shown
in Figure 6 should be compared with the absorption bands at 815 and 928 nm observed on C\textsubscript{60}H\textsubscript{36} dissolved in oleum (see Figure 1) and the C\textsubscript{60}\textsuperscript{+}\textsuperscript{*} bands in oleum at 824 and 931 nm (3). In this case, the HMF composed of 77% C\textsubscript{60}H\textsubscript{x} and 22% C\textsubscript{70}H\textsubscript{y} once dissolved in oleum displays the radical cation spectra of the respective mother molecules C\textsubscript{60}\textsuperscript{+}\textsuperscript{*} and C\textsubscript{70}\textsuperscript{+}\textsuperscript{*}.

Conclusions

All fulleranes studied in the present work are soluble in oleum (fuming sulfuric acid with 30% free SO\textsubscript{3}). C\textsubscript{60}H\textsubscript{36} and C\textsubscript{60}H\textsubscript{18} display the radical cation spectrum of C\textsubscript{60}\textsuperscript{+}\textsuperscript{*}. C\textsubscript{70}H\textsubscript{38} displays the radical cation spectrum of C\textsubscript{70}\textsuperscript{+}\textsuperscript{*}. The HMF, being a mixture of hydrogenated fulleranes, produces the electronic absorption spectrum of a mixture of C\textsubscript{60}\textsuperscript{+}\textsuperscript{*} and C\textsubscript{70}\textsuperscript{+}\textsuperscript{*}.

It can be concluded that in high ionizing and oxidizing media (e.g., oleum), fulleranes undergo a dehydrogenation reaction restoring the pristine fullerene from which they derived; such fullerene is in an oxidized state displaying a radical cation spectrum of C\textsubscript{60}\textsuperscript{+}\textsuperscript{*} and C\textsubscript{70}\textsuperscript{+}\textsuperscript{*}. The radical cation spectra are not stable and tend to fade with time and the electronic transition become weaker. Evidently the C\textsubscript{60}\textsuperscript{+}\textsuperscript{*} and C\textsubscript{70}\textsuperscript{+}\textsuperscript{*} species are consumed in further reactions, for example, in multiple sulfonation reactions.

Acknowledgment

The present research work has been supported by grant AYA2007-64748 Expe. NG-014-10 of the Spanish Ministerio de Ciencia e Innovacion.

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