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# Reactions of photoexcited $C_{60}$ with weak organic acids. Novel method for the derivatization of fullerenes

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## Abstract

Pyrex-filtered irradiation of  $C_{60}$  solutions in liquid diphenylmethane in the absence of oxygen is shown to result in  $Ph_2CH\cdot$  radicals, which further react with the electron-deficient  $C_{60}$  to give  $Ph_2CH-C_{60}H_n$  ( $n = 1, 3, 5$ ). The fullerene ground state to  $^3C_{60}$  transition is suggested to be accompanied by the increase of the fullerene solvation affecting thus the acidity of methylene hydrogens in  $Ph_2CH_2$  as well as the feasibility of their dissociation. Also, photolysis of  $C_{60}$  solutions in weakly acidic phenylacetylene is shown to lead to the addition of a varying number of phenylethynyl groups to the fullerene core. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Feasibility of multiple radical additions to fullerene in the presence of free radical species has been demonstrated in several studies in liquids [1–4] as well as in the gas phase [5]. A characteristic feature of such reactions is the addition of an unusually large number of functional groups to the fullerene core. For example, either 15 benzyl groups, or at least 34 methyl groups, could be covalently attached to fullerene during irradiation of di-*tert*-butylperoxide in toluene, depending on the reaction temperature [6]. However, such reactions often lead to the addition of radicals formed from the irradiated or-

ganic molecule (target molecule) as well as from the initiator of the radical reactions. A similar problem was encountered during the phenylation of  $C_{60}$  in the presence of a Grignard reagent (i.e.,  $PhMgBr$ ) and methyl iodide [7,8]. The latter usually leads to ring-opening reactions and gives four different fullerene isomers (diphenyl fulleroids and methanofullerenes) [9,10]. The fact that diphenylmethyl radicals can indeed be generated from DPM and photoexcited BP molecules comes from a recent study reported by Saitow et al. [11]. These authors observed exciton-assisted hydrogen abstraction from diphenylmethane doped in benzophenone crystal (however, no such studies have yet been reported in solution). Diphenylmethyl radicals formed upon UV irradiation of the crystal were stable in the solid state for more than two weeks. Surprisingly, we find that the presence of benzophenone in liquid diphenylmethane is

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not really necessary, since  $C_{60}$  itself assists photodecomposition of the latter molecule.

## 2. Experimental

0.5 mM solution of  $C_{60}$  in pure diphenylmethane was placed in a quartz cuvette containing a 5 cm long tube open on one end. The end of the tube was tightly closed with numerous layers of Parafilm (American Can). Two syringes were introduced into the cuvette in order to allow inlet and outlet of argon. Longer of the syringes was drawn directly into the solution. Before the photolysis, fullerene solution was purged intensively with the inert gas for  $\sim 5$  min. Intense purging of the solution was also maintained during the irradiation of the solution in order to allow solution mixing and to remove traces of oxygen. The absence of oxygen in the system was checked using UV–visible and NIR spectroscopy in the following way. Triethylamine was added to the fullerene solution in diphenylmethane and this mixture was irradiated for several minutes using a medium-pressure mercury lamp. Absorbance of  $C_{60}$  monoanion at 1075 nm formed upon such photolysis did not decrease more than 10% within 1 h after turning the mercury lamp off, indicating the absence of oxygen or impurities in the solvent which would react further with fullerene anions.

Samples containing products of fullerene photolysis were purified by means of analytical HPLC (Cosmosil column, toluene:acetonitrile (9:1) was used as the mobile phase; flow rate: 0.8 ml/min; detection wavelength: 340 nm). Diphenylmethane was removed from the sample by distillation under reduced pressure at 100°C and the reaction products were dissolved in toluene prior to HPLC separation. Efficiency of fullerene to  $Ph_2CH-C_{60}-H$  conversion, upon 15 min of photolysis, was  $\sim 60\%$ . Each fraction obtained during the photolysis was analysed by MS techniques (MAT 95 Finnigan). An exact measurement of molecular mass was done using positive mode field desorption mass spectrometry (FD MS) on carbon whiskers using fluorinated alkanes as an internal standard. Computer simulation based on the carbon isotope pattern supported the compound composition. Negative mode chemical ionisation mass spectrometry (CIMS) was done for comparison.

While electric field desorption of  $Ph_2CH-C_{60}-H$  from carbon whiskers occurs at  $\sim 6$  keV and does not require methane gas, CIMS has the advantage of higher sensitivity, but the sample has to be heated to at least 500°C (temperatures up to 1500°C were used in this study) in order to get fullerene derivatives into the gas phase. The addition of alkyl groups from methane plasma to  $Ph_2CH-C_{60}-H$  as well as to  $C_{60}$  could not be avoided in this case.

Cyclic voltammetry was carried out with a PAR 273 potentiostat interfaced to a microcomputer. The working electrode was mechanically polished Pt wire (1 mm in diameter) melted in glass. The counter electrode (Pt sheet  $\sim 4$  cm<sup>2</sup>) was separated from the cathodic compartment using the glass tube with a ceramic frit. All the electrochemical experiments were done at room temperature in DPM containing 20% v/v acetonitrile and 0.1 M tetrabutylammonium hexafluorophosphate ( $TBA^+PF_6^-$ ). All the electrode potentials are reported against the  $Ag/Ag^+$  reference electrode (in acetonitrile containing 0.01 M  $AgClO_4$  and 0.09 M  $TBA^+PF_6^-$ ).

<sup>1</sup>H NMR studies were done for HPLC purified DPM- $C_{60}$  (photolysis of  $C_{60}$  in DPM for 20 min) recorded in  $CS_2$  and containing deuterated acetone using 200 and 90 MHz NMR instruments (Bruker, Germany).

## 3. Results and discussion

Fig. 1 shows that  $C_{60}$  dissolved in pure diphenylmethane gives rather weak, orbitally forbidden singlet–singlet transitions in the visible range of the electronic spectrum, as observed for  $C_{60}$  dissolved in other aromatic solvents [12,13]. However, Pyrex-filtered irradiation (medium-pressure Hg lamp, times shorter than 15 min) of 0.5 mM  $C_{60}$  solution in DPM was accompanied by pronounced changes in the visible range of the spectrum with the appearance of new bands at 705, 480 and 435 nm, respectively (Fig. 1a). Isobestic points at 620.3 and 580.6 nm suggest the presence of two absorbing species in solution. The typical chestnut brown colour of the photolysis product and 435 and 705 nm bands indicate that the monoadduct  $H-C_{60}-R$  was formed upon photolysis of  $C_{60}$  in DPM [14]. Apparently, photoexcitation of  $C_{60}$  with energies exceeding 1.56

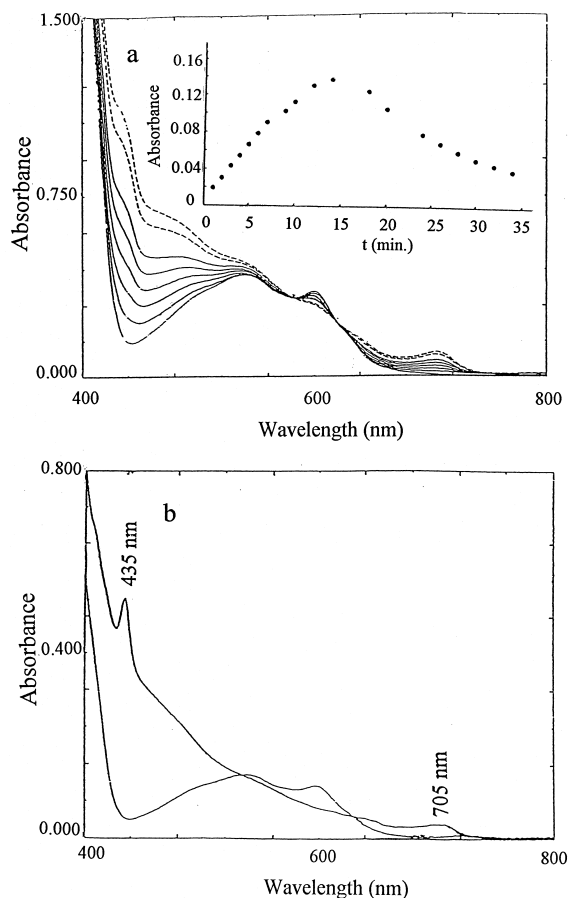


Fig. 1. (a) UV-Vis spectra recorded during the irradiation of  $C_{60}$  in diphenylmethane (DPM) for 0, 2, 4, 6, 8, 10, 13 and 15 min, respectively. Inset shows absorbance changes measured at 705 nm plotted against time during the photolysis of  $C_{60}$  in DPM (Pyrex filter). (b) UV-Vis spectra for  $C_{60}$  and  $Ph_2CH-C_{60}-H$  derivative recorded upon their HPLC separation.

eV (36 kcal/mol), as used in the present study, results in formation of the long-lived triplet  $^3C_{60}$  state which is a powerful electron acceptor, with a reduction potential near 1.14 V vs. SCE [15,16]. It has been demonstrated in several studies that  $^3C_{60}$  can be quenched by electron donors such as amines, pyrene, pyridine [17] or dimethylsulphoxide [18], resulting in the corresponding cation and  $C_{60}$  radical anion. Since diphenylmethane does not contain a lone pair of electrons, electron transfer from DPM to  $^3C_{60}$  is not likely to occur. Indeed, ESR experiments did not show any sign of DPM photodecomposition in the absence of fullerene (Pyrex-filtered Hg lamp,

no oxygen present). However, the strong interactions of photoexcited fullerene with aromatic rings of weakly acidic diphenylmethane molecules affect acidity of methylene group hydrogens and, therefore, makes the C–H bond scission more facile. The resulting  $Ph_2CH^\cdot$  and  $H^\cdot$  radicals then readily add to fullerene yielding  $Ph_2CH-C_{60}-H$  derivative. The latter molecule gave characteristic bands at 435 and 705 nm in the UV–visible spectrum, which can also be seen from its quantitative HPLC separation from  $C_{60}$  (Fig. 1b).

Irradiation of  $C_{60}$  solution in DPM for longer times than 15 min resulted in the disappearance of isobestic points at 620 and 580 nm and caused a continuous decrease in the absorbance at 705 nm (as shown in the inset of Fig. 1a). On the other hand, the intensity of bands at 435 and 480 nm grew continuously with the photolysis time. This might indicate that further additions of radicals to  $C_{60}$  have occurred (see below).

Positive mode field desorption mass spectrometric measurements (Fig. 2a) confirmed the presence of the  $C_{60}$  derivative having a molecular mass of 888.154, suggesting the compound composition  $C_{73}H_{12}$ , corresponding to the formula  $Ph_2CH-C_{60}-H$ . Irradiation of  $C_{60}$  in DPM for longer times than 15 min resulted in a more extensive hydrogenation of the fullerene derivative (Fig. 2b), and MS measurements have also confirmed the presence of  $Ph_2CH-C_{60}H_3$  in the photolysed solution. This directly confirms that reactive reaction intermediates are indeed radical species. Apparently, such additional hydrogenation of the  $C_{60}$  monoadduct is responsible for the disappearance of isobestic points in the visible range of the spectrum at longer irradiation times than 15 min. Note that following 1 h photolysis, the 886 mass unit signal (weaker in intensity than that for  $Ph_2CH-C_{60}-H$ ) appears for the first time in the FD MS spectra. The latter signal is likely to belong to diphenyl fulleroid  $Ph_2C_{61}$  (cyclopropane bridge-containing fullerene), a structure previously described by Suzuki et al. [9]. Interestingly, even on prolonged photolysis (i.e., exceeding 1 h), exclusively a single biphenyl addition occurred to the fullerene core. As one would expect, diphenylmethane adduct appeared to be very unstable under chemical ionization (CI) MS conditions. Since the 886 mass unit signal did not occur in FD MS spectra

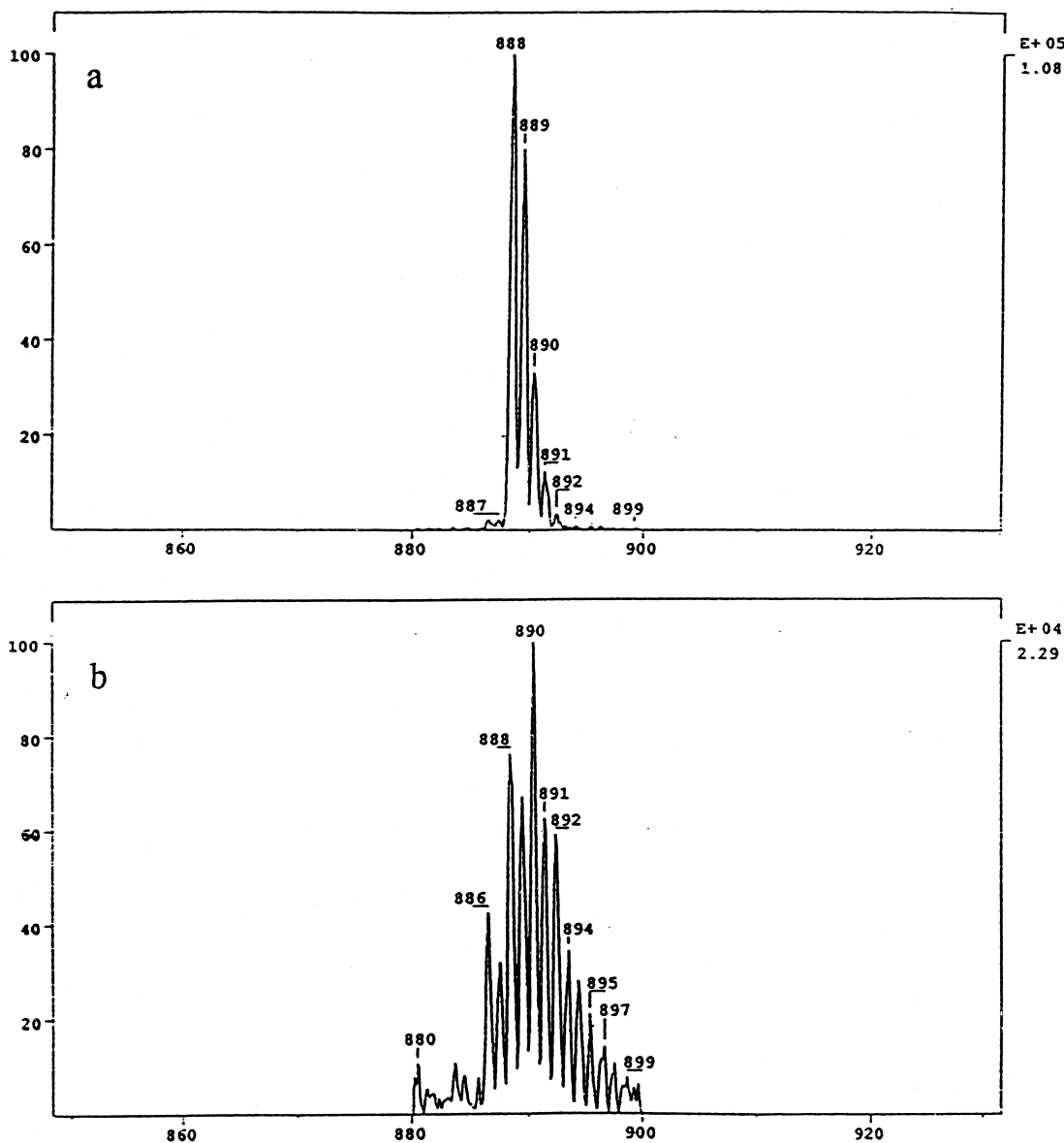


Fig. 2. (a) Field desorption mass spectra (positive mode) for the sample of  $\text{Ph}_2\text{CH}-\text{C}_{60}-\text{H}$  obtained after 15 min of  $\text{C}_{60}$  irradiation in DPM, (b) and that for derivatives formed upon 1 h of Pyrex-filtered irradiation of  $\text{C}_{60}$  in DPM.

during the short photolysis, it is concluded that hydrogen removal from the methine bridge in  $\text{Ph}_2\text{CH}-\text{C}_{60}-\text{H}$  followed by the cyclopropanation step occurred only in the methane plasma under CI conditions.

Cyclic voltammograms (Fig. 3A, curve a) recorded during the  $\text{C}_{60}$  reduction to mono-, di- and trianion

in diphenylmethane showed no sign of chemical reactivity between the fullerene anions and diphenylmethane (in the range of electrode potentials from 0 to  $-2.0$  V vs.  $\text{Ag}/\text{Ag}^+$  electrode). However, irradiation of the electrochemical cell containing 0.38 mM  $\text{C}_{60}$  in DPM (Hg lamp, argon purged solutions) for 20 min resulted in fullerene derivatization (Fig. 3A,

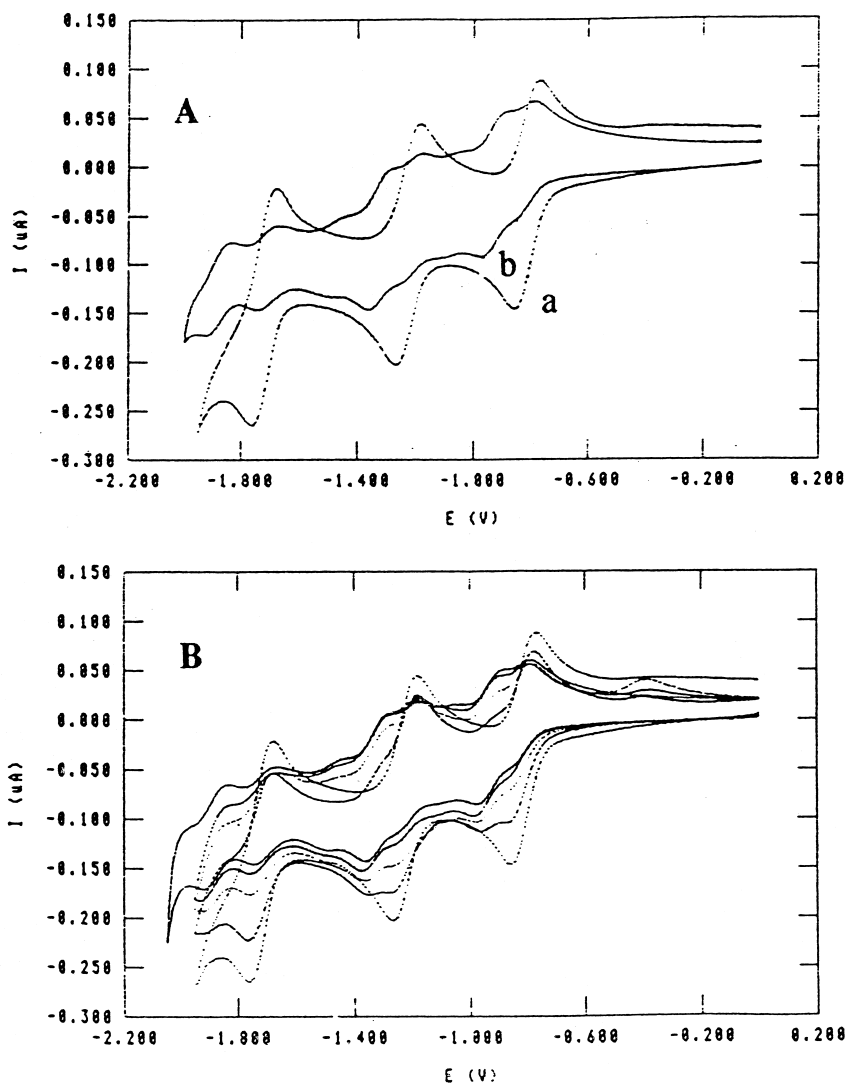


Fig. 3. (A) (a) Cyclic voltammograms (CVs) for the reduction of  $C_{60}$  on Pt electrode in DPM containing 0.1 M  $TBA^+PF_6^-$  and 20% v/v acetonitrile at a scan rate of 100 mV/s. (b) CV recorded after the irradiation of 0.38 mM  $C_{60}$  in DPM for 20 min in the absence of oxygen. (B) CVs recorded in a course of irradiation of  $C_{60}$  in DPM (Pyrex filter): 0, 5, 10, 15 and 20 min of irradiation. Scan rate: 100 mV/s.

curve b). The newly formed reaction products of such photoelectrolysis were found to be reducible at  $\sim 100$  mV more negative electrode potential than  $C_{60}$  molecules in DPM. Redox reactions of new formed derivative, namely,  $Ph_2CH-C_{60}-H$ , were found to be electrochemically reversible at scan rates not exceeding 1 V/s. Progressive decrease in the cathodic currents during the  $C_{60}$  reduction to mono-,

di- and trianions in DPM, under the concomitant irradiation of the solution for a period of 20 min, is shown in Fig. 3B. Under such conditions,  $\sim 60\%$  of fullerene converted into  $Ph_2CH-C_{60}-H$ , as confirmed by HPLC. The formal redox potential for the  $Ph_2CH-C_{60}-H$  then appears to be quite close to that for the diphenyl fulleroid,  $Ph_2C_{61}$  (note: formal redox potential for  $C_{60}^{0/-}$  couple in DPM/acetonitrile

(9:1) mixture is close to that in toluene:acetonitrile (9:1) mixture containing 0.1 M  $\text{TBA}^+\text{PF}_6^-$  (being only 16 mV more negative for the latter system).

Infrared spectra for biphenyls linked to the fullerene core via cyclopropane, and via a methine bridge are expected to differ from each other because of differing symmetries of both molecules and due to the presence of hydrogen(s) on the fullerene core in the former case but not in the latter. As expected, the FTIR spectrum (not shown) of samples of  $\text{C}_{60}$  in DPM irradiated for 15 min showed high-intensity stretching modes around  $2920\text{ cm}^{-1}$ , typical for hydrogenated fullerene and a weak C–H stretching mode for the methine bridge. Bands between  $1300$  and  $1500\text{ cm}^{-1}$  (deformations of aromatic C–H groups) and strong signals in the  $700\text{--}750\text{ cm}^{-1}$  region (out-of-plane vibrations of aromatic hydrogens) were also detected. Bands at  $2850$  and  $2825\text{ cm}^{-1}$ , typical for  $\text{C}_{60}\text{H}_2$  [19] or  $2912$ ,  $2847$  and  $2827\text{ cm}^{-1}$  characteristic of  $\text{C}_{60}\text{H}_{36}$  [20] were absent in the IR spectrum of diphenyl fulleroid [9].

We have attempted to separate  $\text{Ph}_2\text{CH}-\text{C}_{60}-\text{H}$  from the solvent following the photolysis of  $\text{C}_{60}$  in diphenylmethane ( $\sim 20$  min) for the  $^1\text{H}$  NMR experiment. However, in order to distil the solvent out (b.p. =  $264^\circ\text{C}$ ), solutions had to be heated to relatively high temperatures ( $\sim 100^\circ\text{C}$  under the reduced pressure). Under such conditions, some decomposition of fullerene derivative and/or their further chemical reactions could have occurred in a process. Fig. 4 shows  $^1\text{H}$  NMR spectra for such a mixture of reaction products recorded in the region from  $4.0$  to  $8.5$  ppm. In the region of aromatic protons, only the signal at  $\sim 8.18$  ppm is compatible with the chemical shift of *ortho* protons of phenyl rings that are bent toward the surface of the  $\text{C}_{60}$  [9,21–23]. The aromatic signals occurring in the  $6.85\text{--}7.75$  ppm region are difficult to assign without additional  $^{13}\text{C}$  NMR experiments. They might be, at least in part, due to the rotation of phenyl rings in  $\text{Ph}_2\text{CH}-\text{C}_{60}-\text{H}$ , and also due to aromatic proton signals of more than one kind of phenyl ring [24]. The signals at  $6.03$ ,  $6.17$  and  $4.92$  ppm should correspond to protons that are directly bound to the  $\text{C}_{60}$  moiety. Note that all the signals are singlets. They may be due to a proton near the  $\text{C}_{60}$ –methine bond, or due to pairs of nearby protons that are chemically equivalent since no coupling structures are observable: ( $\text{C}_{60}\text{H}_2$   $\delta = 5.94$

ppm [19],  $\text{C}_{60}\text{H}_4$ ,  $\delta = 5.06\text{--}5.50$  ppm [25], or  $\delta = 4.6\text{--}5.4$  ppm [26], and  $\text{C}_{60}\text{H}_{18}$ ,  $\delta = 3.42\text{--}5.43$  ppm [27]). The signals at  $4.18$  (dd,  $J \approx 6\text{ Hz}$ ,  $J \approx 2\text{ Hz}$ ) and  $4.23$  ppm (t,  $J \approx 7\text{ Hz}$ ) cannot be assigned to protons directly connected to the  $\text{C}_{60}$ . The coupling usually measured in hydrogenated  $\text{C}_{60}$  is  $> 9\text{ Hz}$  in all cases reported in the literature [19,25–27]. The transition of protons on the methylene group in diphenylmethane (solvent) is usually observed at  $\sim 4.0$  ppm. If one of the three signals in the range from  $4.1$  to  $4.4$  ppm be due to an additional hydrogen on the  $\text{C}_{60}$ , it is only possible if it sits symmetrically with respect to other addends (the only way to appear as a singlet). Interesting in this respect is that hydrogen trotting on the fullerene core has been detected in the case of the morpholine adduct of  $\text{C}_{60}$  [28].

Our preliminary experiments on the irradiation of  $\text{C}_{60}$  (irradiation time was 1 h) in phenylacetylene (PA), followed by CIMS analysis of reaction products, revealed that up to 11 phenylethynyl radicals add to  $\text{C}_{60}$  under similar conditions as utilized in the case of fullerene photolysis in DPM (Fig. 5). We assume, that in each case, the acidic C–H bond in PA gets labilized due to a strong interaction of photoexcited fullerene with the delocalized system of  $\pi$ -electron over the phenyl ring. Here, two possibilities can be considered. First, C–H bond scission, as discussed above, would lead to a direct  $\text{C}\equiv\text{C}$  bond introduction onto the  $\text{C}_{60}$  core and one hydrogen atom on an adjacent carbon on the fullerene. A second alternative would rely on cycloaddition of PA to  $\text{C}_{60}$ . The corresponding derivative formed under such conditions would have a similar molecular mass as in the previous case but the structure would contain a double bond connected to fullerene via two single bonds (with no hydrogen directly on the fullerene core). FTIR experiments performed on products formed upon fullerene photolysis in phenylacetylene and deuterated phenylacetylene suggest the presence of H or D atoms on the fullerene core and, therefore, the first possibility seems to be more plausible. The identification of asymmetric and symmetric stretches typical for the  $\text{C}\equiv\text{C}$  bond around  $1600\text{ cm}^{-1}$  is not straightforward in this case since these bands are often quite weak.

As manifested in the present work, photolysis of fullerene solutions in DPM allows one to attach

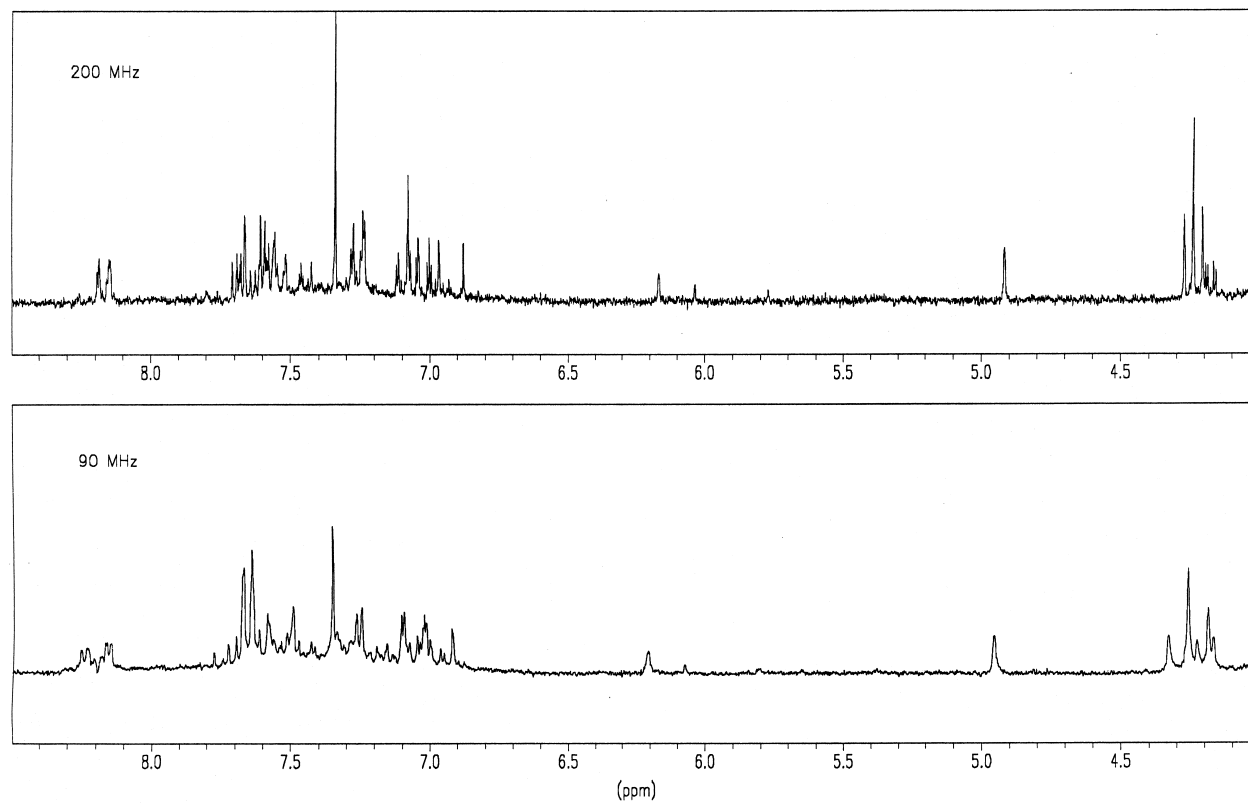


Fig. 4.  $^1\text{H}$  NMR spectra obtained for the  $\text{Ph}_2\text{CH}-\text{C}_{60}-\text{H}$  derivative dissolved in  $\text{CS}_2$ .



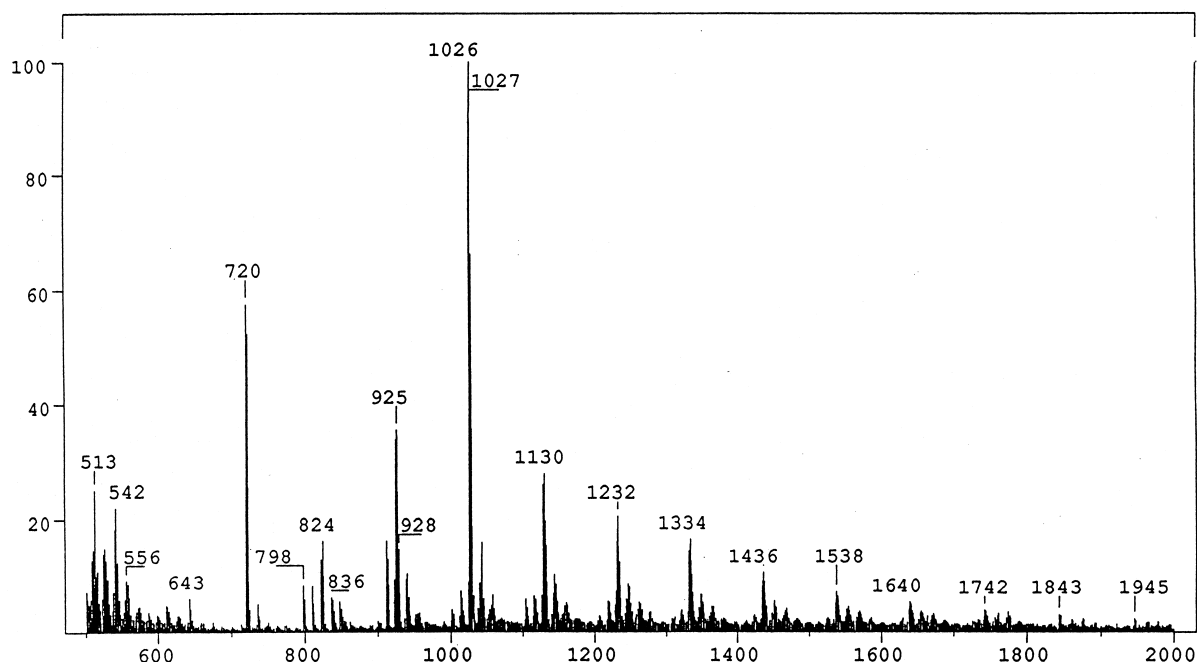


Fig. 5. Negative mode chemical ionization MS of products formed during the photolysis of 0.5 mM  $C_{60}$  in phenylacetylene in quartz upon continuous illumination of the solution using a mercury lamp for 1 h.

biphenyl group to  $C_{60}$  via the methine bridge. It is interesting, in this respect, that our efforts to introduce the  $Ph_2CH-$  group during the electrochemical reduction of  $Ph_2CH-Cl$  on a mercury cathode, as well as during the irradiation of such solutions in the presence of  $C_{60}$ , have failed. In fact, benzylated fullerene in the former case and diphenyl fulleroid in the latter case were synthesized [29]. Reactions of photoexcited  $C_{60}$  molecules with weak aromatic acids open up new attractive routes to fullerene derivatization, and might be applicable to other organic acids as well. This method especially is valuable since it does not require any promoters of radical reactions which are often involved in further chemical side reactions with fullerene. Furthermore, reactive radicals to be added to fullerene are generated from the solvent itself so that purification of reaction products might in some cases be simplified. In general, such reactions follow pseudo-first-order kinetics since solvent will always be in a large excess in respect to fullerene (which is limited by the solubility of  $C_{60}$  in such media). Because of that, one would expect multiple addition of radicals to  $C_{60}$  as is the case of

phenylacetylene reported here or phenyl radicals reported previously [30]. The fact that photolysis of  $C_{60}$  in diphenylmethane solutions leads to the addition of a single  $Ph_2CH-$  group to  $C_{60}$  is rather surprising, and might simply be due to the more effective competition of hydrogen radicals than  $Ph_2CH\cdot$  radicals for the fullerene.

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