ESR Spectroscopy of the C_{60} Cation Produced by Photoinduced Electron Transfer

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Abstract: In this study the existence of the C_{60} cation produced by photochemically induced electron transfer in the presence of different sensitising molecules is proved for the first time by using ESR spectroscopy. It is demonstrated for triphenylpyryliumtetrafluoroborate (TPP) by this spectroscopic method that the electron transfer from C_{60} to TPP occurs without an application of a cosensitiser. Furthermore it is shown that the addition of alcohols causes a new radical in the system C_{60}/TPP. The stationary concentration of the C_{60} cation diminishes even in the presence of a cosensitiser to such a low concentration that it is not detectable by ESR spectrosopy. The spectroscopic study of the sensitiser/C_{60} system is also extended to the reaction products.

Keywords: charge transfer · EPR spectroscopy · fullerenes · photochemistry · radical ions

Introduction

The formation of the fullerene cation was shown for the first time by Foote et al.[1] who were studying the photochemical excitation of *N*-methylacridiniumhexafluorophosphate in the presence of C_{60} by NIR spectroscopy. This behaviour was discussed on the basis of a photo-induced electron transfer (PET)[2] given in the scheme of Figure 1. The spectroscopic characterisation of such fullerene cations is a very important activity in current fullerene research,[3] not only as the synthesis of dihydrofullerenes is expected to involve an H abstraction by C_{60}^{+} in the reaction mechanism that is initiated by an oxidative PET,[4] but also as the role of this species in fullerite, the solid phase of fullerenes, has been discussed on the basis of ESR results.[5]

The electronegativity of fullerenes has been extensively studied by cyclovoltammetry, ex and in situ ESR and UV-visible spectroscopy.[6, 7] On the other hand, the oxidation of fullerenes, especially in electrochemical studies, has rarely been described. Echegoyen,[8] Heinze[9] and Dubois[10] have found an anodic reaction of C_{60} at certain states of the electrode surface and strong interactions with the solvent. In one case[8] the electrode reaction is even be claimed to be reversible.

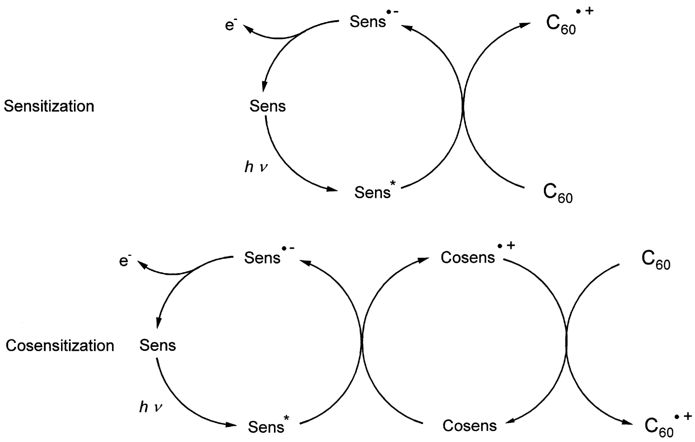

Figure 1. General mechanism of the photo-sensitised formation of the C_{60} cation. Sens = sensitiser (e.g., NMA or TPP); Cosens = cosensitiser (biphenyl); TPP can be applied without a cosensitiser.

In the reactions described in the literature, both the solvent and a surface layer at the electrode seem to contribute to the anodic reaction of C_{60}. In this context it was shown that a long-term electrochemical pre-treatment of the glassy carbon electrode is needed[8] to detect the above-mentioned anodic reaction, while the same reaction was not found with other electrode materials.[11] Furthermore, the spectroscopic proof of the existence of C_{60} cation under electrochemical conditions has been missing up till now.

On the other hand the existence of C_{60}^{+} has been proved both under γ irradiation in glasses at 77 K[12] and in the

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electron transfer to photo-excited states of aromatic compounds[1, 13] by NIR spectroscopy by means of the cation absorption band at 980 nm.

Very recently Fukuzumi et al.[14] described the formation of C_{60}^+ in zeolite Y at high temperatures. The C_{60} cations were stabilised in the zeolite cage and, therefore, still existed even at room temperature. Such encapsulated cations give an ESR signal with a *g* value of 2.0025 and a line width of 10 G.

The formation of a fullerene cation in an homogeneous redox reaction in solution has been proved by ESR spectroscopy in the case of C_{76}.[15] In this case Reed et al. have shown that the first oxidation potential is low enough to give no reaction with the solvent in the case of *o*-dichlorobenzene.

Furthermore it is possible to stabilise the cation by a carbanion. We point out that in reference [15] the proof of this paramagnetic cation is done by ESR spectroscopy and not by comparison with the NIR absorption of the fullerene in other oxidising systems. In the case of this C_{76} cation, the most intensive absorption band is found at 780 nm and not at 980 nm. Therefore it is important to realise that ESR spectroscopy is the only secure method to prove without doubt the existence of a paramagnetic fullerene cation.

In this paper it is shown for the first time, through in situ ESR spectrocopy, that the photochemical exitation with suitable PET sensitisers in the presence of C_{60} causes the formation of C_{60} cation in organic solvents. This cation further reacts with H donors like alcohols.

Results and Discussion

To understand the influence of the electronic properties of the sensitiser in the electron transfer, the redox properties of *N*-methylacridiniumhexafluorophosphate (NMA) and triphenylpyryliumtetrafluoroborate (TPP) were studied by cyclic voltammetry and the electron transfer of these compounds compared with that of C_{60}. Both substances show differences in their redox behaviour (Figure 2). While TPP gives a reversible electron transfer at −0.48 V, NMA shows only a reduction peak at the potential of −0.54 V that is totally irreversible. An anodic peak of minor significance is evidently caused by a reaction product and not due to very slow electron transfer.

Abstract in German: *In dieser Studie wird erstmals der ESR-spektroskopische Nachweis des C_{60}-Kations für verschiedene photochemische Sensibilisatorsysteme erbracht. Insbesondere wird für Triphenylpyryliumtetrafluoroborat (TPP) erstmals spektroskopisch demonstriert, daß ein Elektronentransfer vom C_{60} auf das TPP ohne einen Cosensibilisator erfolgt. Es wird außerdem gezeigt, daß bei Zusatz von Alkoholen zum Sensibilisatorsystem TPP mit C_{60} ein neues Radikal nachweisbar ist, während die stationäre Konzentration des C_{60}-Kations sich selbst in Anwesenheit eines Cosensibilisators derart erniedrigt, daß die spektroskopische Erfassung nicht mehr möglich ist. Die ESR-spektroskopischen Messungen an sensibilisierten Fullerenen werden im Hinblick auf die Charakterisierung der Reaktionsprodukte weitergeführt.*

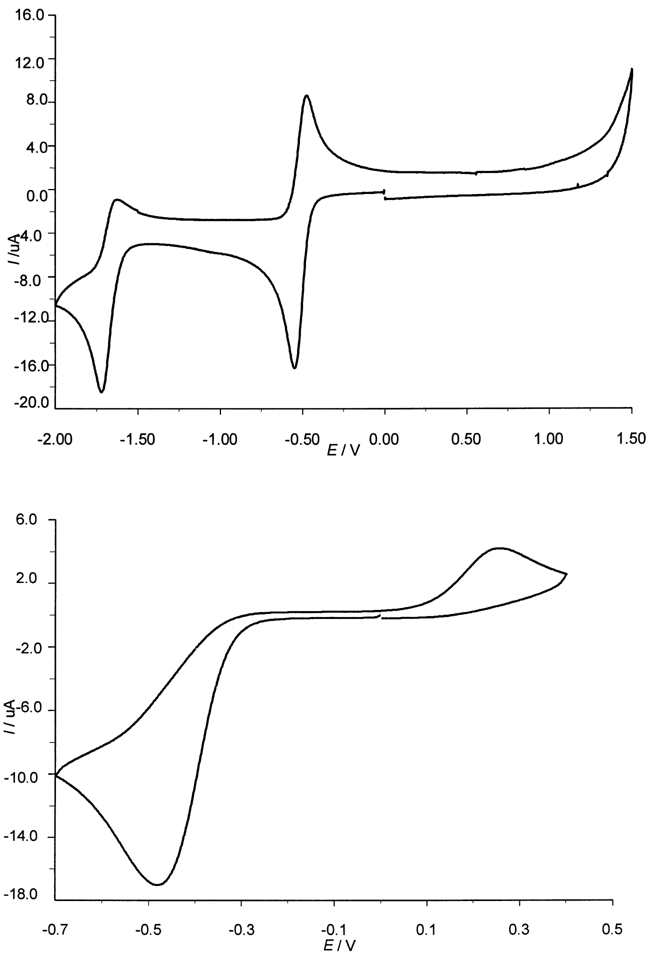

Figure 2. Cyclic voltammogram of TPP (top) and NMA (bottom) at a glassy carbon electrode in *o*-dichlorobenzene, supporting electrolyte: 0.1 M tetrabutylammoniumtetrafluoroborate, temperature 25 °C, scan rate 100 mV s^{-1}.

If the reduction of these sensitisers is studied in the presence of C_{60}, a cyclic voltammogram of NMA in solution gives evidence of reaction products with C_{60}. On the other hand the cyclic voltammogram of a solution of C_{60} and TPP is a superposition of the redox reactions of both substances; a chemical reaction product of C_{60} was not detected. The fast electron transfer of TPP evidently generates the neutral TPP radical, which seems to be unreactive with the C_{60} anion that is produced simultaneously.

Therefore, it was to be expected that both substances will differ in their electron transfer upon photochemical excitation, which was followed by ESR spectroscopy. For this purpose a solution of C_{60} and the sensitiser[3] was irradiated in a flow-through system in which the streaming solution was treated with light pulses of a wavelength of 436 nm. The duration of the pulses was varied between 200 ms and 10 s. The ESR spectroscopic measurements were done in the following manner: the ESR signal was recorded during the irradiation and accumulated up to 500 times. As shown in Figure 3, an ESR signal with a linewidth of 0.8 G and a *g* value of 2.0021 is found in the case of TPP as a photosensitiser. This

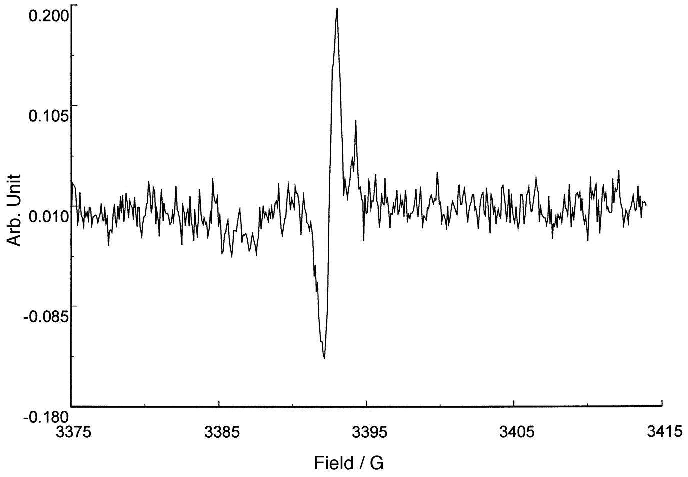

Figure 3. ESR spectrum of a solution of C_{60}/TPP in *o*-dichlorobenzene under irradiation at a wavelength of 436 nm in flowing solution.

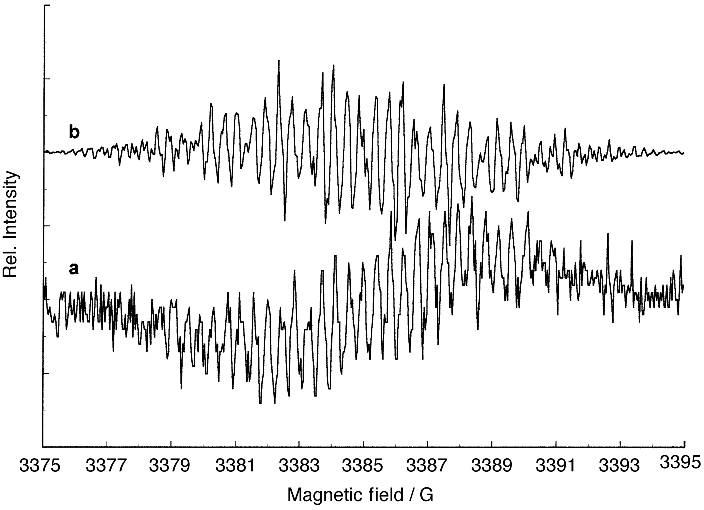

Figure 4. a) ESR spectrum of a C_{60}/TPP solution in *o*-dichlorobenzene under irradiation at a wavelength of 436 nm after the addition of methylalcohol. b) Simulated ESR spectrum of a TPP radical in solution.

signal is attributed to the existence of $C_{60}{}^{+}$ as it is formed only in the presence of C_{60}. The sensitiser TPP itself gives an ESR signal that consists of a single line of width 7.5 G. This is in contrast to the single line of the $C_{60}{}^{+}$ radical in fuming sulfuric acid,[16] for which a linewidth of 0.2 G and a *g* factor of 2.0030 were found for this paramagnetic fullerene structure. The deviation of the ESR results in the photochemical measurements from those in fuming sulfuric acid, in which chemical reactions can occur, is explained by the fact, that the *g* factor is similar to that of cation radicals of larger π systems.[17] The increase in the linewidth seems to be due to the interaction of the radical cation with the electron-rich conjugated system TPP in a solvent like *o*-dichlorobenzene.

The existence of the $C_{60}{}^{+}$ radical upon the application of TPP as a sensitiser clearly demonstrates that the electron transfer from C_{60} to TPP occurs without a cosensitiser, unlike most of the other sensitiser systems. This is demonstrated for NMA as a sensitiser for which the results are analogous to TPP except that biphenyl is added as a cosensitiser. Although the redox behaviour of NMA is different from TPP the electron transfer occurs; however, for this sensitser a cosensitiser is needed. Nevertheless no influence of the cosensitiser on the ESR signal is found under irradiation. In solutions containing C_{60} the ESR signal of $C_{60}{}^{+}$ is also clearly observed in this system.

Addition of a proton donator like methylalcohol to the solution changes the ESR signal of $C_{60}{}^{+}$ radical cation in solution completely. The single line of the C_{60} cation is diminished and finally disappears altogether. In the case of TPP, a new radical is formed, the ESR spectrum of which consists of a large number of hyperfine lines. This large number contradicts the paramagnetic structure of a reaction product of $C_{60}{}^{+}$ with alcohol. This spectrum (Figure 4a) is similar to that of an aromatic radical. As shown by simulation of the ESR spectrum of TPP (Figure 4b), the experimental spectrum is comparable with that of the TPP radical cation. Therefore it can be concluded that the $C_{60}{}^{+}$ radical is transferred to a non-radical structure in the presence of an alcohol. It seems to be possible that the $C_{60}{}^{+}$ radical undergoes a nucleophilic attack by methanol followed by H abstraction. Thus the radical cation disappears and its signal is no longer visible in the ESR spectrum.

Time-dependent ESR measurements (Figure 5) of a C_{60} solution in the presence of TPP as a sensitiser have shown that $C_{60}{}^{+}$ is formed upon the millisecond timescale. As shown in Figure 5 a stationary concentration of $C_{60}{}^{+}$ is reached after 13 ms. For the decay of $C_{60}{}^{+}$ a half-life of about 22 ms is estimated. This value is much larger than that one given in reference [1], in which a lifetime of 9 μs was found that is concentration dependent.[18] Recent results of laser flash spectroscopic studies gave lifetimes of 5.6 μs (NMA) and 4.9 μs (TPP).[13] The reasons for these differences have not yet been clarified.

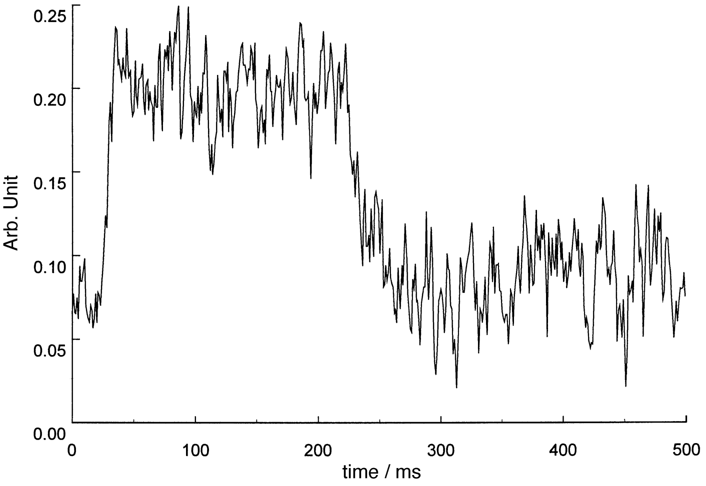

Figure 5. Time dependence of the ESR signal in a solution of C_{60}, NMA and biphenyl in *o*-dichlorobenzene under irradiation by 200 ms pulses at a wavelength of 436 nm.

Conclusion

In this study the existence of C$_{60}$ cation produced by photochemically induced electron transfer in the presence of different sensitising molecules is proved for the first time. For triphenylpyryliumtetrafluoroborate (TPP) it is demonstrated by ESR spectroscopy that the electron transfer from C$_{60}$ to TPP occurs without an application of a cosensitiser.

Furthermore, we have shown that the addition of alcohols causes a new radical in the C$_{60}$/TPP system. The stationary concentration of the C$_{60}$ cation diminishes even in the presence of a cosensitiser to such a low concentration that it is not detectable by ESR spectrosopy. The spectroscopic study of the sensitiser/C$_{60}$ system has been extended to the reaction products.

Experimental Section

C$_{60}$ (Hoechst AG) and triphenylpyryliumtetrafluoroborate (TPP) (Fluka) were used in highest purity. The latter was purified by precipitation from acetone solution. *N*-methylacridiuniumhexafluorophosphate (NMA) was prepared from sodiumhexafluorophosphate according to a literature procedure.[19]

The electrochemical studies were done with a potentiostat PAR 273 driven by the software PARC M 270 version 3.0 in a traditional voltammetric cell, installed in a glovebox to ensure inert conditions. *o*-Dichlorobenzene was used as a solvent; as working electrodes both platinum and glassy carbon electrodes were used and as counter electrode a platinum sheet was used. The reference electrode was a silver/silverchloride electrode in the same electrolyte solution. Tetrabutylammoniumtetrafluoroborate was used as a supporting electrolyte.

The in situ ESR measurements were done in a flow-through system with an UV-irradiation unit BUV 1 (ZWG Berlin) equipped with a mercury high-pressure lamp HBO 200 (Berliner Glühlampenwerk). The irradiation was made both continuously and in a pulsed-mode by using a shutter for pulse times in the range of 20 ms to 10 s (the interrupt between two pulses could be varied in the same interval). Generally the application of filters was possible. In this study a wavelength of 436 nm was used. Furthermore a cell as a heat filter was used to avoid negative influences of heat irradiation. The synchronisation of the irradiation and the interrupt times with the ESR measurement were achieved by using the computer of the ESR spectrometer to control the triggering.

In this study the electron spin resonance spectrometer ERS 221 (ZWG Berlin) was operated as an X-band continuous wave spectrometer by using the 100 kHz field modulation and a microwave power of 0.1 – 15 mW. The spectrometer had a separate rapid scan unit RSE 1, and pulses with a duration up to 100 ms scan^{-1} were employed. The analogue signals were converted with the AD/DA converter DT 2812A plug in card (Data Translation), the maximum frequency of which was variable up to 100 kHz at a resolution of twelve bits. The data treatment was carried out with the Signalys, PC-View and Turbo Lap software. All in situ ESR measurements were done at room temperature.

The ESR cell made of quartz glass was similar to a flow-through cell used for the electrochemical studies.[20] For the in situ measurements of the photochemical reactions of fullerenes, the solution was kept under inert conditions by a permanent purging with nitrogen in the stock solution. The solution was transferred through the cell by a Watson-Marlowe 101 R/U pump.

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