Photochemical reduction of water-soluble fullerene $C_{60}(C_4H_{10}N^+)$ in titanium dioxide suspensions (EPR-study): a comparison with radiolytically-induced reduction

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Abstract

N-methylfulleropyrrolidinium $(C_{60}(C_4H_{10}N^+)/I^-)$ was found to be efficiently reduced in photoexcited TiO_2 suspensions in a toluene/acetonitrile/2-propanol (10:10:1 v/v) solvent mixture. The formation of the π-radical anion, $(C_{60}^{\cdot-})(C_4H_{10}N^+)$, was monitored by in situ EPR spectroscopy. Despite the fullerene's functionalization, the reduction process proceeds analogously to that reported earlier for pristine C_{60}. In aqueous solutions, the behaviour of $C_{60}(C_4H_{10}N^+)/I^-$ towards reduction is, however, very complex. Although the N-methylfulleropyrrolidinium is sufficiently water-soluble, no reduction could be observed in irradiated aqueous TiO_2 suspension. This is attributed to the formation of fullerene clusters in aqueous solutions which seems to prevent transfer of an electron. Addition of a surfactant, such as lauryl sulfate, successfully inhibited fullerene clustering and, in turn after prolonged irradiation $(C_{60}^{\cdot-})(C_4H_{10}N^+)$ was observed in low yields. Using γ-cyclodextrin (γ-CD) encapsulated fullerene, $C_{60}(C_4H_{10}N^+)/\gamma$-CD, instead of the surfactant capped fullerene, the fullerene's π-anion-radical was formed immediately. These observations underline the dominant role of cluster formation with respect to reduction and other processes, in general, of water-soluble monofunctionalized fullerene derivatives. A considerably lower activity was also noticed for the reduction of $\{C_{60}(C_4H_{10}N^+)\}$-clusters by $(CH_3)_2\dot{C}(OH)$ radicals relative to the analogous reduction of $C_{60}(C_4H_{10}N^+)/\gamma$-CD. This emerged from competitive experiments with applying 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap in aqueous TiO_2 suspensions, containing 2-propanol.   © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the initial phase of fullerene research the majority of studies were concerned with the most abundant member and perfect spherical (I_h) carbon allotrope of the fullerene family, namely, C_{60} and, to somewhat smaller extent, its higher analogues C_{70}, C_{76}, C_{78}, C_{84}, etc. [1–4]. More recently considerable attention focused also on the modification of the fullerene core by means of functionalization. [5–7]. In view of potential applications, the accessibility of suitably functionalized fullerenes stimulated an intense interest, particularly in the fields of biology and medicine [8–14]. However, these envisaged applications necessitate enhancement of the water-solubility of the hydrophobic, and therefore water-insoluble, fullerene core. Hydrophylization of C_{60} was successfully demonstrated by (i) carboxylation [15,16], (ii) introduction of a quartery ammonium cation in form of a

pyrrolidinium group [17], (iii) encapsulation of fullerenes in a water-soluble γ-cyclodextrin host [18–22], and (iv) via capping the fullerene surface with adequate surfactants [23].

The solubility of large hydrophobic molecules, such as C_{60} and its higher analogues, in aqueous media is closely coupled with aggregation phenomena and their dynamics. Various structures have been suggested ranging from smaller associates and large clusters [17], for pristine C_{60} and some monofunctionalized fullerene derivatives, to non-aggregated but well solvated individual molecules in the case of polyfunctionalized fullerenes. The respective structural arrangements are expected to exert substantial impact on the solute's (fullerene) property and chemical reactivity.

The low redox potential of its first reduction step, comparable to quinones and methylviologene, renders the fullerenes excellent acceptors in electron transfer reactions. This has extensively been investigated, for example, in homogenous organic solutions [24–38]. Water-soluble fullerene systems,

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such as γ-cyclodextrin encapsulated (C_{60}/γ-CD) and ($C_{60}C(COO^-)_2/\gamma$-CD) were found to be readily reduced upon application of radiolytic [15,36], photochemical, and electrochemical techniques [20–22,39], affording the formation of the π-radical anion, $C_{60}^{\cdot-}/\gamma$-CD and ($C_{60}^{\cdot-}$)C(COO$^-$)$_2/\gamma$-CD. The characterization of the singly reduced state has been based on EPR [39] and transient near-IR absorption (NIR) spectroscopy [15,36]. In contrast, the reduction of $C_{60}C(COO^-)_2$ without a supramolecular host was largely hindered in aqueous solutions because of the formation of fullerene clusters in this environment. A scenario was suggested in which the cluster, consisting of the hydrophobic fullerenes, is surrounded by a layer of negatively charged carboxylic groups [15].

Although the ground-state properties of the pyrrolidinium derivative $C_{60}(C_4H_{10}N^+)$ unequivocally prompt to clustering, hydrated electrons and $(CH_3)_2^{\cdot}COH$ radicals rapidly reduce the fullerene core [17]. More importantly, the rate of electron transfer, relative to monofunctionalized fullerene derivatives and also to pristine C_{60} (all encapsulated as monomers in γ-CD), is enhanced, indicating remarkable electron acceptor properties of this particular fullerene derivative. Motivated by this observation we now extended our earlier studies to the photochemically induced reduction of $C_{60}(C_4H_{10}N^+)$ and $C_{60}(C_4H_{10}N^+)/\gamma$-CD aqueous TiO$_2$ suspensions in water and mixture of organic solvents with 2-propanol. In these systems, supra-band gap irradiation of TiO$_2$ particles with UV light leads to the concomitant generation of conduction band electrons and valence band holes [35,38]. According to our previous investigations [38–41], we expected that photogenerated electrons would readily reduce the pyrrolidinium derivative yielding the corresponding fullerene π-radical anion. In addition, the photogenerated holes are effectively scavenged by 2-propanol and, as a consequence of this reaction, strongly reducing $(CH_3)_2^{\cdot}COH$ radicals are produced [42,43]. The latter are known to contribute to a rapid fullerene reduction [17,36] and should, therefore, do so also in our present system.

2. Experimental details

The quartery ammonium N-methylfulleropyrrolidinium salt $C_{60}(C_4H_{10}N^+)/I^-$ and its γ-CD encapsulated form, $C_{60}(C_4H_{10}N^+)/\gamma$-CD, were prepared according to the procedures described in Refs. [44,45]. The following organic solvents: acetonitrile, toluene, 2-propanol and tetrahydrofuran (analytical grade) were purchased from Fluka. Lauryl sulfate and 5,5-dimethyl-1-pyrroline-N-oxide (spin trap agent) were obtained from Aldrich. Degussa kindly gifted the TiO$_2$ P25 (high surface). The photochemical reductions of the fullerene derivatives were performed in a TiO$_2$ suspension, which was prepared by ultrasonication of either a toluene/acetonitrile/2-propanol mixture (10:10:1 v/v) or an aqueous solution. All systems were thoroughly deoxygenated by bubbling with argon prior to irradiation. The aqueous

solutions of $C_{60}(C_4H_{10}N^+)/I^-$ were prepared from a THF suspension as recommended in Ref. [17], and the aqueous solutions of $C_{60}(C_4H_{10}N^+)/\gamma$-CD were centrifuged before reduction. The radical generation during the photochemical reductions was monitored by in situ EPR measurements in the TM cavity of a Bruker 200D EPR spectrometer coupled with an Aspect 2000 computer. Simulations of the recorded EPR spectra were performed with a Bruker standard program. A medium-pressure mercury lamp (Applied Photophysics, UK) served as the irradiation source in combination with a Pyrex filter to cut off the wavelength region below 300 nm. The spin concentrations of fullerene radicals were determined taken 4-hydroxy-TEMPO (4-hydroxy-2,2,6,6-tetramethyl-piperidine-N-oxyl) (Sigma) as the reference. The EPR spectra of the reference solutions, prepared in the organic solvents or in water, were recorded under strictly analogous conditions as the fullerenes' EPR spectra. However, generally, an exact quantitative evaluation of EPR spectra remains problematic [46]. Consequently, the experimental errors of the fullerenes' radical yields determined is relatively high of about 20%. Steady state irradiations were done in a Gammacell 220 ^{60}Co source with a dose rate of 1 Gy s^{-1}. Irradiation times were up to several minutes. Optical absorption spectra were recorded within several minutes before and after irradiation.

3. Results and discussion

Fig. 1a,b show the two sets of EPR spectra that were measured during the continuous irradiation of 0.1 mg/ml TiO$_2$ suspensions in a toluene/acetonitrile/2-propanol solvent mixture (10:10:1 v/v) at different $C_{60}(C_4H_{10}N^+)/I^-$ concentrations (0.2 mM in Fig. 1a and 0.06 mM in Fig. 1b). Under these experimental conditions no cluster formation is expected. Starting with the higher fullerene concentration (Fig. 1a), the EPR spectrum is clearly dominated by a singlet line A, which can be characterized by a g-value of $g_A = 2.0000$ and a peak-to-peak width of $pp_A = 0.095$ mT. Its intensity was found to increase as a function of progressing irradiation. In contrast stands the EPR behaviour of the TiO$_2$ suspension at lower fullerene concentrations (Fig. 1b). At the initial stage of the photochemical reduction a similar line A is observed which, upon continuation of the irradiation, converts to a radical species B, characterized by $g_B = 2.0005$, $pp_B = 0.042$ mT. Despite the positive charge of the pyrrolidinium group of $C_{60}(C_4H_{10}N^+)$, the measured EPR spectra are reminiscent of those reported previously for the photochemical or electrochemical reduction of pristine C_{60} [38] and some derivatives [39–41].

The assignment of narrow EPR lines called 'spikes' measured in reduction of C_{60} is a complex problem as it is strongly dependent on the experimental conditions and reduction methods (e.g., in situ generation in solution and measurement in EPR cavity or electrochemical reduction followed by the freezing of the solution and measurement of EPR spectra long time after generation at low temperatures [24–30,37–
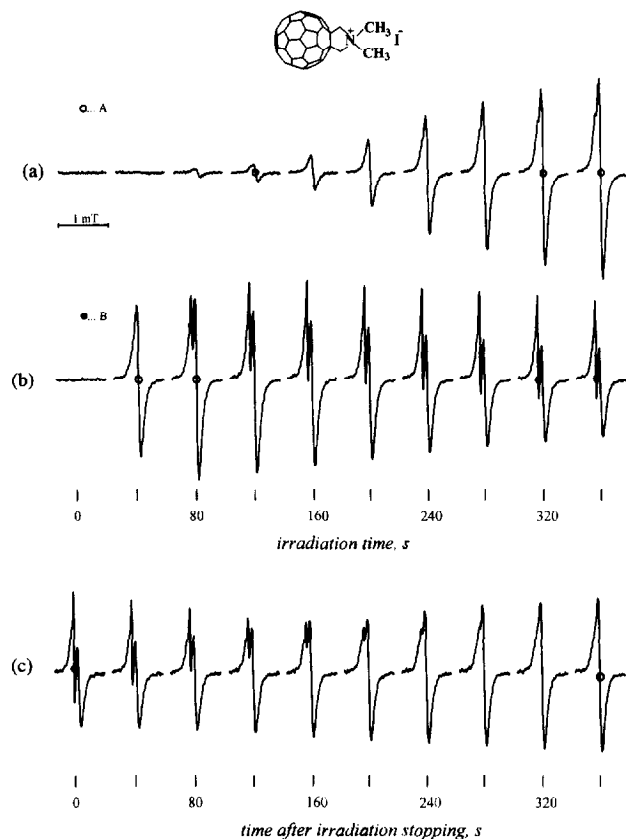
Fig. 1. EPR spectra of fullerene $C_{60}(C_4H_{10}N^+)/I^-$ measured in toluene/acetonitrile/2-propanol (10:10:1 v/v) TiO_2 suspensions ([TiO_2] = 0.1 mg/ml): (a) by a continuous irradiation of 0.2 mM $C_{60}(C_4H_{10}N^+)/I^-$; (b) by a continuous irradiation of 0.06 mM $C_{60}(C_4H_{10}N^+)/I^-$; (c) after stopping irradiation in system shown in (b).

41]). The puzzle of EPR spectra of C_{60} anions was reviewed by S.S. Eaton et al. [47] and recently a new contribution to this problem was published by Olsen et al. [48], where the attempt was made to clarify the conflicting reports on the broad and narrow EPR lines of C_{60}.

Based on systematic investigations in our earlier studies, we had assigned the singlet line A to the mono-anion of pristine C_{60} or of the respective fullerene derivative. More complex appeared the assignment of line B. Tentatively we had attributed this line to the di-anion or, alternatively, to an associate formed by the interaction of (C_{60}^{2-}) with the ground state fullerene educt (Eq. (1)).

$$(C_{60}^{2-}) + C_{60} \rightarrow [C_{60} \cdots C_{60}]^{2-} \tag{1}$$
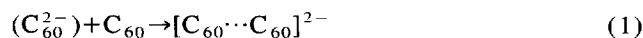
According to some recent investigations, the second alternative, implementing the formation of associates, seems to be the more probable rationale [49]. Since the EPR spectra and the kinetic behaviour of the species A and B in our present study are essentially identical, we therefore postulate the following assignment: the singlet line A represents the π-radical anion ($C_{60}^{\bullet-}$)($C_4H_{10}N^+$), while B relates to a transient aggregated species of the di-anion.

A further close relationship between the radical species A (π-radical anion) and B emerges from the EPR behaviour

shown in Fig. 1b,c. As already mentioned above, photoinduced electron transfer from TiO_2 suspensions initially leads to the formation of radical A, which converts into radical B upon progressing irradiation (Fig. 1b). Discontinuing the irradiation, however, results in a loss of line B and a simultaneous reappearance of line A (Fig. 1c). This, in analogy to the studies on C_{60} and some functionalized derivatives [40,41,49], may be due to dissociation of the aggregate, $[C_{60} \cdots C_{60}]^{2-}$, with concurrent regeneration of the π-radical anion. Equilibrium between the two forms, associated and disassociated, cannot be ruled out, as the spin concentration, resp. fullerene radical yield remains constant in the time, as will be later shown in Fig. 3A,c.

$$[C_{60} \cdots C_{60}]^{2-} \leftrightarrow 2(C_{60}^{\bullet-})$$
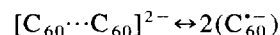
Preparation of an aqueous solutions containing $C_{60}(C_4H_{10}N^+)/I^-$ was achieved by evaporation of the THF component from a suspension. The ground state absorption spectrum gives rise to strong light scattering in the UV–VIS range, which is taken as support for a cluster structure of this fullerene derivative in aqueous solutions. This cluster formation could be prevented, however, if a surfactant was added to the THF solvent, or by encapsulation of $C_{60}(C_4H_{10}N^+)$ into the cavity of two γ-cyclodextrin hosts.

Radiolytic reduction of $\{C_{60}(C_4H_{10}N^+)\}$-clusters in aqueous media (containing 10 vol.% 2-propanol) showed a rapid reduction of the fullerene core by either hydrated electrons or $(CH_3)_2\dot{C}OH$ radicals [17]. Upon UV-illumination of aqueous TiO_2 suspensions, containing up to 0.3 mM $C_{60}(C_4H_{10}N^+)$, on the other hand, no EPR signal was observed (Fig. 2a). This may, however, only be an apparent discrepancy. In the radiolytic process the reduction of $\{C_{60}(C_4H_{10}N^+)\}$-clusters can directly be followed by pulse radiolysis using visible/NIR spectroscopy at a time resolution of less than a microsecond. In contrast, the photochemical experiments were based on continuous irradiation and EPR spectroscopy which is limited to a time resolution of seconds.

It should be noted, that a number of scavenging reactions for the photochemically generated conduction band electrons are associated with the heterogeneity of the semiconductor system which are absent in radiolytically irradiated aqueous solutions. In particular, surface traps or electron-hole recombination impact the lifetime of the reducing radical and, in turn, may prevent a meaningful and, more importantly, detectable signal of the diamagnetic radical anion. Furthermore, the reduction potential of the TiO_2 electrons differs quite significantly from that of radiolytically generated hydrated electrons (-0.2 V vs. − 2.7 V) and may, in fact, not be sufficient for a fullerene reduction at the TiO_2 interface. In summary, it appears that the low reduction efficiency can be associated with a cluster-specific phenomenon.

The lack of an EPR signal may thus simply imply a very low reduction yield but, alternatively, may also indicate a limited stability of $\{(C_{60}^{\bullet-})(C_4H_{10}N^+)\}$ formed under the given conditions. In order to assess the latter argument,
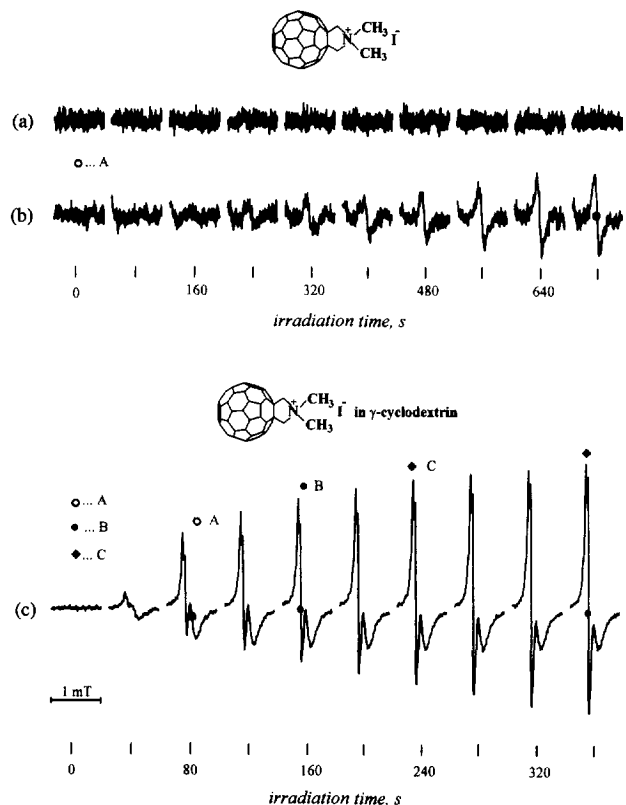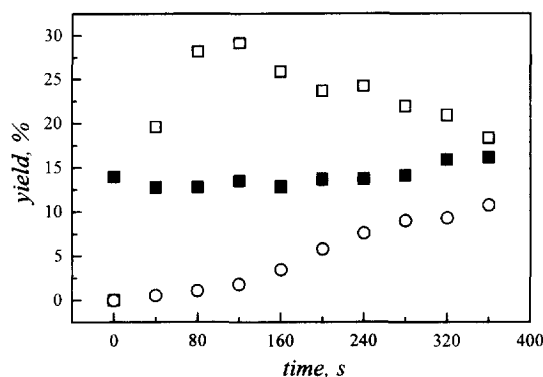
Fig. 2. EPR spectra observed upon continuous irradiation in aqueous TiO_2 suspensions: (a) 0.3 mM $C_{60}(C_4H_{10}N^+)/I^-$, ([TiO_2] = 1 mg/ml); (b) 0.3 mM $C_{60}(C_4H_{10}N^+)/I^-$ with lauryl sulfate ([lauryl sulfate] = 1 mM, [TiO_2] = 1 mg/ml); (c) 0.6 mM $C_{60}(C_4H_{10}N^+)/\gamma$-CD ([$TiO_2$] = 0.1 mg/ml).
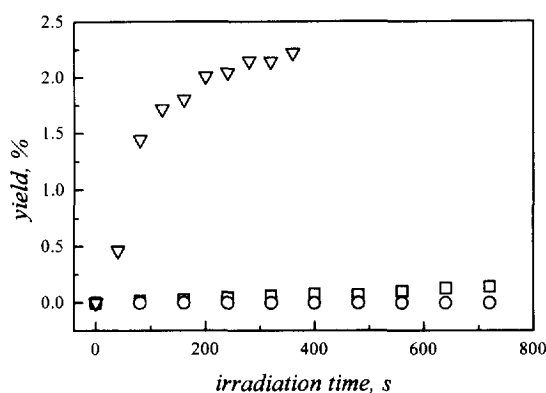

Fig. 3. Fullerene radical yield as a function of time: (A) In toluene/acetonitrile/2-propanol = 10:10:1. (a) ○ by a continuous irradiation of 0.2 mM $C_{60}(C_4H_{10}N^+)/I^-$; (b) □ by a continuous irradiation of 0.06 mM $C_{60}(C_4H_{10}N^+)/I^-$; (c) ■ after stopping irradiation in system shown in (b). (Data extracted from EPR spectra shown in Fig. 1a–c). (B) In water. (a) ○ 0.3 mM $C_{60}(C_4H_{10}N^+)/I^-$, ([TiO_2] = 1 mg/ml); (b) □ 0.3 mM $C_{60}(C_4H_{10}N^+)/I^-$ with lauryl sulfate ([lauryl sulfate] = 1 mM, [TiO_2] = 1 mg/ml); (c) ∇ 0.6 mM $C_{60}(C_4H_{10}N^+)/\gamma$-CD ([$TiO_2$] = 0.1 mg/ml). (Data extracted from EPR spectra shown in Fig. 2a–c).

steady-state γ-radiolytic reduction of the cluster solutions were carried out in either N_2 or N_2O purged aqueous solutions containing 10 vol.% 2-propanol. The spectra were recorded prior and after several intervals of irradiation. Regardless of the irradiation time, no stable fullerene reduction product could be detected in the NIR region (around 1000 nm). In fact, the absorption spectra revealed only an unspecified degradation of the fullerene's ground state absorption features. Since time-resolved pulse radiolysis unmistakably demonstrated formation of the fullerene π-radical anion, the current finding is clearly in support of the low stability of singly-reduced $\{C_{60}(C_4H_{10}N^+)\}$-clusters, at least on the minute time-scale.

The addition of lauryl sulfate to a THF solution of $C_{60}(C_4H_{10}N^+)$, prior to subsequent addition of water, inhibits cluster formation and, in turn, secures a monomeric fullerene dissolution. Fullerene reduction is still retarded at low TiO_2 concentrations, but upon increasing the semiconductor concentration (TiO_2) and prolonging the irradiation periods, a distinct EPR spectrum emerges (Fig. 2b). The characteristics of this signal, with $g_A = 2.0000$ and $pp_A = 0.095$ mT are in close resemblance to those of radical species A, which points towards the formation of π-radical anion of the fullerene. This is in agreement with the radiolytical fullerene reduction in aqueous surfactant solutions, where the life-time of

the hydrated electrons was also significantly shorter. In this case, the overall reduction efficiency was lowered by about a factor of 2.

A slightly different situation was encountered in the reduction of $C_{60}(C_4H_{10}N^+)$ which was embedded in the cavity between two γ-CD molecules. In this case, a very rapid and effective radical formation was detected in the aqueous TiO_2 suspensions (Fig. 2c). This confirms that the positively charged pyrrolidinium group can be regarded as an entrance channel that facilitates the electron transfer to the fullerene core [17]. Furthermore, an additional radical C ($g_C = 2.0009$ and $pp_C \cong 0.03$ mT) is formed besides radical species A and B (see Fig. 2c). A similar radical was described previously in the reduction of pristine C_{60} by alkali metals [50,51] or organometallic compounds [40,52], and was assigned to the free di-anion, ($C_{60}{}^{2-}$). The relative concentrations of radicals A, B, and C, evolving from the irradiation of $C_{60}(C_4H_{10}N^+)/\gamma$-CD in TiO_2 suspensions, depend strongly on the fullerene concentration, TiO_2 concentrations, and on the irradiation period.

Fig. 3 illustrates the fullerene radical yield measured in organic solvents (toluene/acetonitrile/2-propanol = 10:10:1) and in water, presented as a function of time extracted from EPR spectra of radicals shown in Figs. 1 and 2. The yields of fullerene radicals in the organic solvents can graduate up to 30% conversion upon irradiation (Fig. 3A,b). Similar conversions (10–20%) of C_{60}-orthoquinodimethane adducts to mono-anions were obtained by the photochemical reduction with triethylamine in DMSO monitored by EPR and NIR spectroscopy [53].

However, the reduction yield of fullerenes' radicals in the aquatic media is lower. Under the given experimental conditions, the reduction in water is fully hindered due to the $C_{60}(C_4H_{10}N^+)$ cluster formation, but it may proceed in the presence of surfactants or if the fullerene molecule is embedded in the γ-cyclodextrin cavity (Fig. 3B,c). Here the relatively low fullerene radical yield may be explained as the influence of the aquatic environment on the stability of radical anions formed.

The lower efficiency of $C_{60}(C_4H_{10}N^+)$ cluster reduction compared to $C_{60}(C_4H_{10}N^+)/\gamma$-CD stimulated us to perform a further investigation, namely, on the fate of the $(CH_3)_2{}^\cdot COH$ radicals in the two systems by employing a spin trap (DMPO) (Fig. 4a). Irradiation of a $C_{60}(C_4H_{10}N^+)$ solution in the presence of DMPO leads to a quantitative trapping of the photogenerated $(CH_3)_2{}^\cdot COH$ radicals according to Eq. (3). The resulting stable radical adduct, $^\cdot(DMPO-C(OH)(CH_3)_2)$, is characterized by a six-line EPR spectrum [42,54–58] with a bimolecular formation rate constant of 1.1×10^8 M^{-1} s^{-1} [55].

(3)
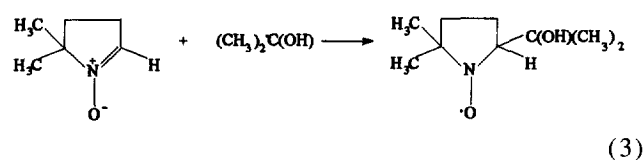
The experimental six-line EPR spectrum, as shown in Fig. 4a, was simulated using splitting constants of $a_N = 1.611$ mT and $a_H = 2.324$ mT. These simulation data are in good agreement with those splittings published for the $^\cdot(DMPO-C(OH)(CH_3)_2)$ adduct [42,54–58]. More importantly, the EPR signal of Fig. 4a lacks any evidence for the fullerene π-radical anion, expected to evolve from a direct reduction of $C_{60}(C_4H_{10}N^+)$ (Eq. (4)). This observation suggests that in this system, despite of the high fullerene concentration, addition of $(CH_3)_2{}^\cdot COH$ radicals to DMPO (Eq. (3)) dominates over the reduction of the fullerene core.

$$C_{60}(C_4H_{10}N^+) + (CH_3)_2C^\cdot OH$$

$$\rightarrow (C_{60}^{\cdot-})(C_4H_{10}N^+) + (CH_3)_2CO + H^+$$

(4)
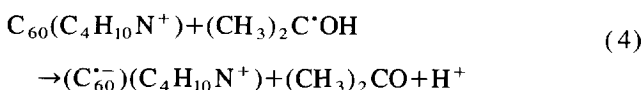
Spin trap experiments with the $C_{60}(C_4H_{10}N^+)/\gamma$-CD complex, on the other hand, led only during the initial stage of the irradiation to an EPR signal of the $^\cdot(DMPO-C(OH)(CH_3)_2)$ adduct, which, furthermore, was very small. With progressing irradiation the prevailing EPR spectrum
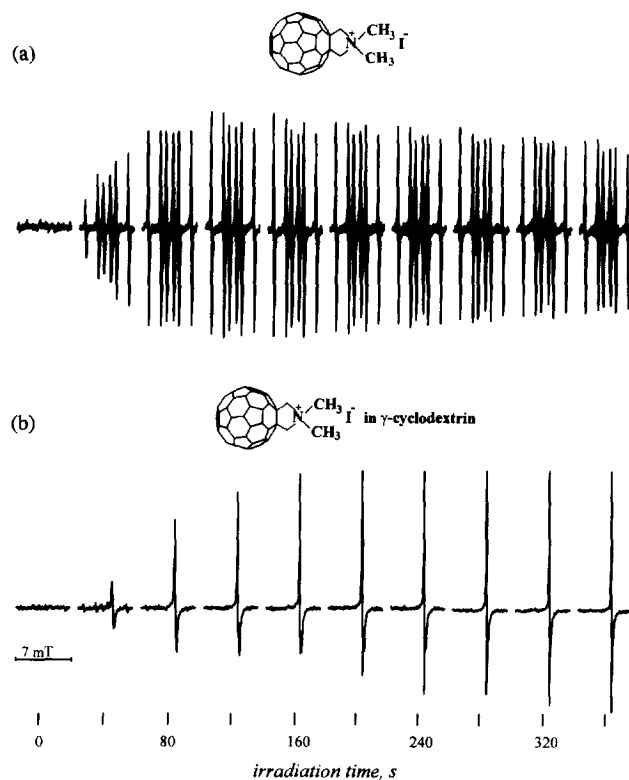

(a)

(b)

Fig. 4. EPR spectra measured upon continuous irradiation of aqueous TiO$_2$ suspensions containing 12.5 vol.% of 2-propanol and DMPO spin trap ([TiO$_2$] = 0.25 mg/ml, [DMPO] = 0.01 M): (a) 0.3 mM $C_{60}(C_4H_{10}N^+)/$ I$^-$; (b) 1.0 mM $C_{60}(C_4H_{10}N^+)/\gamma$-CD.

was that of $(C_{60}{}^{\cdot-})(C_4H_{10}N^+)/\gamma$-CD (Fig. 4b). It should be mentioned that, as a consequence of selecting a larger sweep width (in order to ensure the recording the spectra of the DMPO adducts) the resolution of the individual radicals A, B, and C is rather poor. The current observation leads to the conclusion that the fullerene core of the $C_{60}(C_4H_{10}N^+)/\gamma$-CD complex reacts faster with $(CH_3)_2{}^\cdot COH$ radicals than with the DMPO spin trap. This is well in line with the high bimolecular rate constant of 5.1×10^8 M^{-1} s^{-1}, which we reported for the reduction of $C_{60}(C_4H_{10}N^+)/\gamma$-CD with radiolytically generated $(CH_3)_2{}^\cdot COH$ radicals [17]. In summary, while $(CH_3)_2{}^\cdot COH$ radicals react effectively with monomeric solvated $C_{60}(C_4H_{10}N^+)/\gamma$-CD to yield the singly reduced fullerene core, the reduction is substantially retarded in the case of $\{C_{60}(C_4H_{10}N^+)\}$-clusters.

Acknowledgements

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