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Excited-State Behavior and One-Electron Reduction of C_{60} in Aqueous γ-Cyclodextrin Solution

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Excited-state properties and one-electron reduction of C_{60} in aqueous γ-cyclodextrin (γ-CD) solutions have been studied by laser flash photolysis and pulse radiolysis techniques. The difference absorption spectrum of C_{60}^- anion radical in aqueous γ-CD solution has been characterized by reducing C_{60} with radiolytically produced radicals (e_{aq}^-, $(CH_3)_2\dot{C}OH$ or $MV^{\bullet+}$). The one-electron reduction potential of the ground-state C_{60} in aqueous γ-cyclodextrin solution ($E° = -0.25$ V vs NHE) has been measured by equilibrating fullerene solution with $MV^{2+}/MV^{\bullet+}$ couple. Inorganic anions, such as N_3^-, I^-, NO_2^-, ClO_2^- and SCN^-, quench the excited triplet C_{60} and participate in the electron-transfer process.

Introduction

Following the discovery and characterization of C_{60} and other fullerenes,[1,2] an entire field of fullerene chemistry has been established.[3-15] One of the primary interests of these investigations lies in understanding the chemical reactivity of fullerenes including their reactions with free radicals[12,13] and electron-transfer processes both in the ground and excited states.[14-21] The poor solubility of fullerene has often been a restrictive factor in choosing a medium for studying its chemical reactivity. For this reason, most of the photophysical and photochemical study of C_{60} and C_{70} has been carried out in a few organic solvents such as benzene, toluene, and benzonitrile. Efforts have also been made to study the excited-state behavior of fullerenes in polymer films[17b] and on oxide surfaces.[17c] A recently published procedure[22] of embedding C_{60} clusters into a water-soluble host molecule of γ-cyclodextrin (γ-CD) has evoked interest in investigating reactions of C_{60} in aqueous solutions.

In their work, Andersson and his co-workers have characterized a 2:1 host:guest complex between γ-cyclodextrin and C_{60} and identified triplet absorption of C_{60}.[22] However, no major effort has been made so far to investigate electron-transfer reactions of C_{60} in water. Such a polar medium also facilitates excited-state quenching by the common inorganic anions such as halides. We present here experimental results of laser flash photolysis and pulse radiolysis of C_{60} in aqueous medium.

Experimental Section

The sample of C_{60} (99.9% purity) was obtained from SES Research and γ-cyclodextrin from Aldrich. All other chemicals were analytical reagents, with the exception of $NaClO_2$ (80% purity, Aldrich). All chemicals were used as supplied. For preparation of aqueous C_{60}/γ-CD, Millipore water was used. The preparation of C_{60}/γ-CD was according to ref 22: the suspension of solid C_{60} in aqueous γ-CD (5–8 mmol dm^{-3}) refluxed for 24 h at 100 °C with intense stirring. After filtration, the C_{60} in aqueous solution was identified by its characteristic absorption spectrum. The concentration of C_{60} was in the range 5–10 μmol dm^{-3}. In our experiments, the concentration of γ-CD was 5 mmol dm^{-3}.

Nanosecond laser flash photolysis was performed with 337.1-nm laser pulses from a Molectron UV-400 nitrogen laser (pulse width 8 ns, 1–2 mJ/pulse). The excitation dose was maintained around 1.5×10^{-6} einsteins dm^{-3}, using anthracene triplet as the actinometry reference. The experimental details can be found elsewhere.[23] For picosecond measurements, laser pulses at 355 nm from a mode-locked, Q-switched Continuum YG-501 DP Nd:YAG laser system (pulse width ~ 18 ps, 2–3 mJ/pulse) were used.

Pulse radiolysis experiments were performed with the ARCO linear accelerator at the Notre Dame Radiation Laboratory with a dose in the range 2–5 Gy/pulse.[24]

Steady-state radiolysis was carried out at 20 ± 1 °C with a ^{60}Co source (dose rate 7 Gy/min).

Results and Discussion

Singlet and Triplet Excited States of C_{60} in Aqueous γ-Cyclodextrin Solution. The photophysical properties of C_{60} in organic solvents such as benzene, toluene, and hexane are well-known,[25] and the absorption spectra of singlet and triplet excited states have been reported. The half-life for intersystem crossing from singlet to triplet C_{60} varies from 1.2 to 1.6 ns depending upon the solvent employed. The absorption spectra recorded at different time intervals after laser pulse (pulse width 18 ps) excitation of C_{60}/γ-CD in aqueous solution are presented in Figure 1. The transient absorption recorded immediately after the laser pulse excitation ($\lambda_{max} \sim 920$ nm) corresponds to the excited singlet state of C_{60}. The spectra recorded in Figure 1 show concurrent disappearance of $^1C_{60}^*$ and formation of $^3C_{60}^*$. The lifetime for the formation of $^3C_{60}/\gamma$-CD was found to be 1.1 ns as monitored from the decay of singlet absorption at 920 nm and the growth of triplet absorption at 740 nm (Figure 1, inserts).

The triplet excited state of C_{60} can also be probed with nanosecond laser flash photolysis. The absorption maximum of $^3C_{60}/\gamma$-CD in water is at 750 nm (Figure 2), slightly red-shifted compared to that of $^3C_{60}$ in hexane. It has been reported[22] that $^3C_{60}/\gamma$-CD has a prolonged lifetime because a large part of C_{60} surface is covered by γ-CD, thus reducing the triplet–triplet annihilation process. Our result is in agreement with the reported lifetime of $^3C_{60}/\gamma$-CD in aqueous solution and was a factor of ~2 higher than that of $^3C_{60}$ in benzene.

Enhanced Intersystem Crossing Induced by External Heavy Atom Effect. It has been shown by Linschitz and his co-workers[29] that the intersystem crossing efficiency can be enhanced by the presence of CH_3I. In the frozen matrix at 77 K, they were able to suppress the fluorescence of C_{60} and promote the phosphorescence emission. Thus, it is interesting to see what effect anions such as I^- may have on the intersystem crossing efficiency. The triplet formation was monitored from the transients at 740 nm in the absence and presence of I^-. The formation of triplet is considerably faster in the presence of 2×10^{-3} mol dm^{-3} KI (trace b in Figure 3). At higher KI concentration (0.5 mol dm^{-3}, trace c in Figure 3), the triplet formation is completed within the laser pulse (~18 ps), and excited-state quenching by I^- dominates the absorption–time profile. CH_3I produces similar enhancement of the intersystem crossing efficiency. The faster rate of triplet excited-state formation is clearly evident from trace d in Figure 3.

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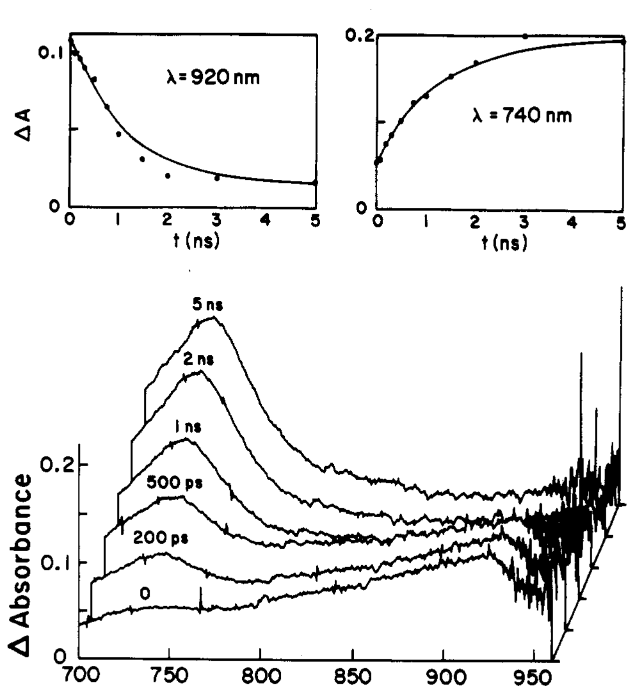

Figure 1. Time-resolved differences absorption spectra of singlet and triplet excited states of C_{60}/γ-CD in aqueous solution. Spectra were recorded following 355-nm laser pulse (pulse width 18 ps) excitation of 1×10^{-5} mol dm^{-3} C_{60} and 8×10^{-3} mol dm^{-3} γ-CD. Inserts show the decay of singlet (920 nm) and the formation of triplet (740 nm) excited states.

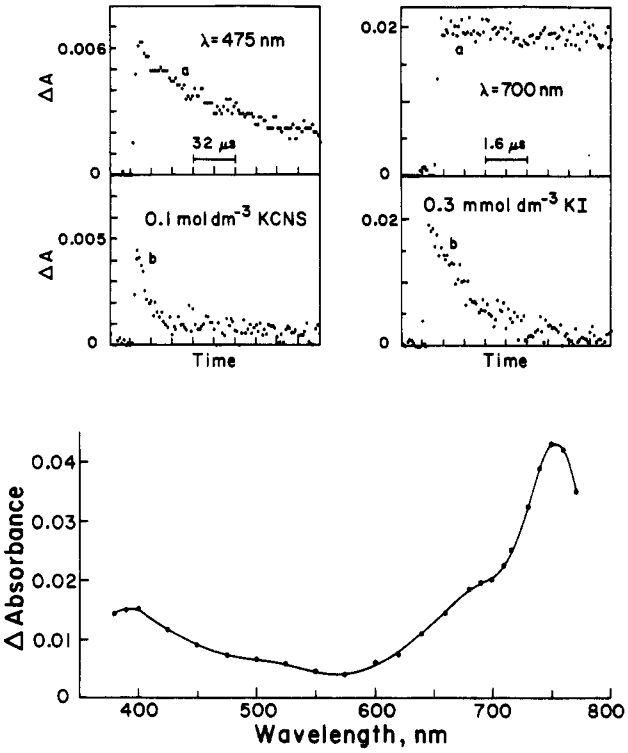

Figure 2. Difference absorption spectrum of triplet $^3C_{60}/\gamma$-CD in aqueous solution recorded after 337.1-nm nanosecond laser pulse excitation of 6×10^{-6} mol dm^{-3} C_{60} and 5×10^{-3} mol dm^{-3} γ-CD. Inserts show the time profiles of triplet signals (a) in the absence and (b) in the presence of anions.

Similar to earlier observations with CH_3I,[29] the external heavy atom effect induced by I^- is quite significant on the $S_1 \rightarrow T_1$ transition. While CH_3I has relatively little effect on the $T_1 \rightarrow S_0$ transition, I^- reduces the triplet lifetime by participating in the quenching of the triplet excited state.

Quenching of $^3C_{60}^*$ with Inorganic Anions. Earlier photochemical studies[15-18] have shown that efficient electron-transfer quenching of triplet C_{60} can be carried out with various amines, hydrocarbons, and stable nitroxyl radicals. We have now found that inorganic anions can also act as quenchers for the triplet C_{60} in aqueous solutions. The phenomenon of $^3C_{60}^*$ quenching by SCN^- and I^- ions is displayed in Figure 2. The first-order rate constants, k_{obs}, for the decay of triplet excited state were measured in the presence of varying concentration of anions in the nanosecond laser flash photolysis experiments. The bimolecular quenching rate constants, k_q, were obtained from the plot based on eq 1

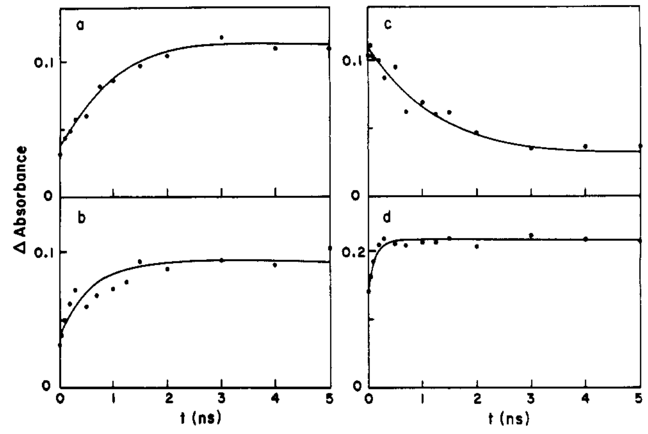

Figure 3. Time profiles of triplet signals recorded at 740 nm following the 355-nm picosecond laser pulse excitation of 6×10^{-6} mol dm^{-3} C_{60} and 5×10^{-3} mol dm^{-3} γ-CD in aqueous solution (a) in the absence of any additives, (b) in the presence of 2×10^{-3} mol dm^{-3} KI, and (c) in the presence of 0.5 mol dm^{-3} KI. Profile d shows the signal recorded in a benzene solution of C_{60} (1×10^{-4} mol dm^{-3}) containing 25% of CH_3I.

TABLE I: Quenching Rate Constants of Triplet C_{60}^*/γ-CD by Inorganic Anions in Aqueous Solution

quencher X^-	redox potential $E^\circ(X^\bullet/X^-)$ vs NHE,[26,27] V	ΔG, kcal mol$^-$	k_q, mol^{-1} dm^3 s^{-1}
ClO_2^-	0.936	-9.31	1.5×10^8
NO_2^-	1.03	-7.15	2.0×10^7
I^-	1.33	-0.23	2.3×10^9
N_3^-	1.35	0.23	1.5×10^8
SCN^-	1.62	6.46	5.4×10^5

$$k_{obs} = k_d + k_q[Q] \qquad (1)$$

where [Q] is the concentration of quencher and k_d is the rate of triplet decay in the absence of anions. Under present experimental conditions, the value of k_d was 1.2×10^4 s^{-1}. This value is slightly higher than the intrinsic decay rate constant reported for $^3C_{60}^*$.[25] As noted earlier,[25c] the values of k_d are dependent on the concentration of ground-state C_{60} and the initial concentration of $^3C_{60}^*$. Both ground-state quenching and T–T annihilation processes decrease the triplet lifetime significantly. All the measurements were done at neutral or slightly basic pH, and solutions were deaerated with nitrogen. The summarized results for quenching rate constants are presented in Table I.

Of the possible quenching mechanisms, the energy transfer from the fullerene triplet to the anions is ruled out on energetic grounds.[28] The quenching within the collision complex, reaction 2, and electron-transfer process, reaction 3, are other possibilities.

$$^3C_{60}/\gamma\text{-CD} + X^- \rightleftarrows [^3C_{60}/\gamma\text{-CD}\cdots X^-] \rightarrow C_{60}/\gamma\text{-CD} + X^- \qquad (2)$$

$$^3C_{60}/\gamma\text{-CD} + X^- \rightleftarrows [^3C_{60}/\gamma\text{-CD}\cdots X^-] \rightleftarrows [C_{60}^-/\gamma\text{-CD}\cdots X^\bullet] \rightarrow C_{60}^-/\gamma\text{-CD} + X^\bullet \qquad (3)$$

where $X^- = SCN^-$, I^-, N_3^-, NO_2^-, and ClO_2^-. The presence of anions did not affect the shape or the yield of triplet absorption as measured at the end of the 6-ns laser pulse, but the increased rate of formation of C_{60} triplet observed in the presence of heavy iodide ions suggests the influence of I^- in enhancing intersystem crossing in the collision complex. Thus in the case of I^-, reaction 2 is likely to contribute in the overall quenching mechanism.

The quantum yield for electron transfer (reaction 3) in all examined cases was low, ≤0.1, as determined from the absorption spectra of oxidation products, $X_2^{\bullet-}$, of anions. For example, the absorption spectrum of $(SCN)_2^{\bullet-}$ with a maximum at 475 nm was clearly identified. Radical ion $(SCN)_2^{\bullet-}$ is formed in the presence of excess thiocyanate.

$$SCN^{\bullet} + SCN^{-} \rightarrow (SCN)_2^{\bullet-} \qquad (4)$$

The bleaching signal at 335 nm which was observed after completion of reaction 3 confirmed the reduction of C_{60}. Unfortunately, due to limitations of our nanosecond laser flash photolysis apparatus, we were not able to observe transient absorption at wavelengths longer than 900 nm where C_{60}^- is reported to absorb.[14,15,30] Also, the absorption in the visible region (400 nm) is masked by the absorption of $(SCN)_2^{\bullet-}$.

The free energy for electron transfer, ΔG, in Table I was calculated from eq 5

$$\Delta G = 23.06[E^0(X/X^-) - E^0((C_{60}^-/\gamma\text{-CD})/(C_{60}/\gamma\text{-CD})) - \Delta E_{0,0} - e_0^2/a\epsilon] \qquad (5)$$

where $E^0(X/X^-)$ is the redox potential of the quenching donor. The value of $E^0((C_{60}^-/\gamma\text{-CD})/(C_{60}/\gamma\text{-CD})) = 0.25$ V vs NHE was determined in reaction with methylviologen (see next section for the procedure of determining E^0). The energy gained in bringing two radical ions to the encounter distance, $e_0^2/a\epsilon$, was calculated according to ref 15a, taking into account the dielectric constant of water and $\Delta E_{0,0} = 1.56$ eV.[25a]

Steady-State Radiolysis Experiments. Reaction with Methylviologen Cation Radical. In order to examine one-electron reduction of C_{60}/γ-CD in the ground state and to determine the redox potential of fullerene in aqueous solution, we have used methylviologen (MV^{2+}) as a redox partner. In this system, the cation radical $MV^{\bullet+}$ is generated by radiolytic processes. $MV^{\bullet+}$ is stable in an inert atmosphere and exhibits well-defined absorption.[31] Since this radical can equilibrate quickly with another redox couple, it has been used to determine the redox potentials of several redox couples and flat-band potentials of semiconductor colloids.[32] The radiolytic processes by which the cation radical $MV^{\bullet+}$ is formed in an aqueous solution are well-known.[33] In the presence of propan-2-ol, the following reactions occur upon radiolysis of nitrogen-saturated aqueous solutions:

$$H_2O \rightsquigarrow e_{aq}^-, H^{\bullet}, OH^{\bullet}, H_2, H_2O_2, H_3O^+, OH^- \qquad (6)$$

$$OH^{\bullet}/H^{\bullet} + (CH_3)_2CHOH \rightarrow H_2O/H_2 + (CH_3)_2\dot{C}OH \qquad (7)$$

The reduced methylviologen is produced in the reaction of hydrated electrons or 2-hydroxy-2-propyl radicals with MV^{2+}.[33]

$$e_{aq}^- + MV^{2+} \rightarrow MV^{\bullet+} + H_2O \qquad (8)$$

$$(CH_3)_2\dot{C}OH + MV^{2+} \rightarrow (CH_3)_2CO + MV^{\bullet+} \qquad (9)$$

After γ-radiolysis of a nitrogen-saturated aqueous solution of MV^{2+} (1×10^{-3} mol dm^{-3}), γ-CD (5×10^{-3} mol dm^{-3}), and propan-2-ol (0.5 mol dm^{-3}) cation radical, $MV^{\bullet+}$, is formed.[34] The value $G(MV^{\bullet+}) = 6.0$ molecules/(100 eV) was determined using the values for extinction coefficients of 4.21×10^4 and 1.37×10^4 M^{-1} cm^{-1} at 396 and 605 nm, respectively.[31] When C_{60}/γ-CD was present in the solution (6×10^{-6} mol dm^{-3}), a decrease of $MV^{\bullet+}$ absorption was observed. This is due to the reaction between cation radical $MV^{\bullet+}$ and C_{60} (reaction 10), as the concentration of the latter is too low to compete directly for hydrated electrons or $(CH_3)_2\dot{C}OH$ radicals.

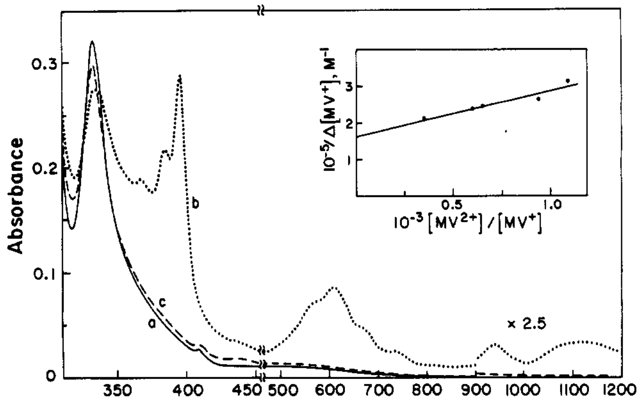

Figure 4. Absorption spectra of aqueous solution containing 6×10^{-6} mol dm^{-3} C_{60}, 5×10^{-3} mol dm^{-3} γ-CD, 1×10^{-3} mol dm^{-3} MV^{2+}, and 0.5 mol dm^{-3} propan-2-ol: (a) before irradiation; (b) after irradiation in nitrogen atmosphere, dose 14 Gy; and (c) irradiated solution exposed to air. Insert: Reciprocal concentration of reduced C_{60} as a function of initial concentration of methylviologen (as represented by eq 13), dose 7 Gy.

$$MV^{\bullet+} + C_{60}/\gamma\text{-CD} \rightleftarrows MV^{2+} + C_{60}^-/\gamma\text{-CD} \qquad (10)$$

The decrease of 332-nm absorption together with the appearance of new maxima at 950 and 1100 nm confirmed the formation of the C_{60}^- anion radical (Figure 4). The anion of C_{60} was stable and disappeared upon exposure to air (oxygen). The recovery of fullerene absorption is expected as reactions 11 and 12 result in the oxidation of C_{60}^- and $MV^{\bullet+}$.

$$C_{60}^-/\gamma\text{-CD} + O_2 \rightleftarrows C_{60}/\gamma\text{-CD} + O_2^- \qquad (11)$$

$$MV^{\bullet+} + O_2 \rightarrow MV^{2+} + O_2^- \qquad (12)$$

The equilibrium constant for reaction 10 was determined by measuring the absorbance of $MV^{\bullet+}$ after irradiation of the solutions containing propan-2-ol (0.5 mol dm^{-3}), C_{60}/γ-CD (6×10^{-6} mol dm^{-3} of fullerene), and different concentrations of MV^{2+}. The equilibrium constant can be calculated from eq 13

$$K = \frac{[MV^{2+}]}{[MV^{\bullet+}]} \frac{\Delta[MV^{\bullet+}]}{[C_{60}/\gamma\text{-CD}] - \Delta[MV^{\bullet+}]} \qquad (13)$$

where $[MV^{\bullet+}]$ is the equilibrium concentration of cation radical and $\Delta[MV^{\bullet+}] = [MV^{\bullet+}]_0 - [MV^{\bullet+}]$ is the concentration of $MV^{\bullet+}$ lost during the reduction of C_{60}. The concentration of $MV^{\bullet+}$ monitored in the absence and presence of fullerene corresponds to $[MV^{\bullet+}]_0$ and $[MV^{\bullet+}]$, respectively. The value of K derived from these measurements (Figure 4, insert) was 1.3×10^3. Using this value of K, we calculated the difference in redox potential between $MV^{2+}/MV^{\bullet+}$ and $(C_{60}/\gamma\text{-CD})/(C_{60}^-/\gamma\text{-CD})$ couples as 185 mV. Thus, the one-electron redox potential of C_{60}/γ-CD in aqueous solution is −0.25 V vs NHE. This value of the redox potential of C_{60} in aqueous γ-CD solutions is 70 mV more negative than the value reported in acetonitrile.[19] It is worth noting that the redox potential of methylviologen in aqueous solution, −0.44 V, is not affected by the presence of γ-CD as confirmed from the cyclic voltammetry measurements.

Pulse Radiolysis Experiments. UV–Visible Difference Absorption Spectrum of C_{60}^-. There seems to be some discrepancy regarding the absorption of C_{60}^- anions in the visible region.[15a,18,21,35] In order to characterize the difference absorption spectrum of C_{60}^- in the ultraviolet–visible region, we have performed pulse radiolysis measurements of C_{60}/γ-CD in aqueous solution. Figure 5 shows the difference absorption spectrum obtained 260 μs after pulse radiolysis of an aqueous solution

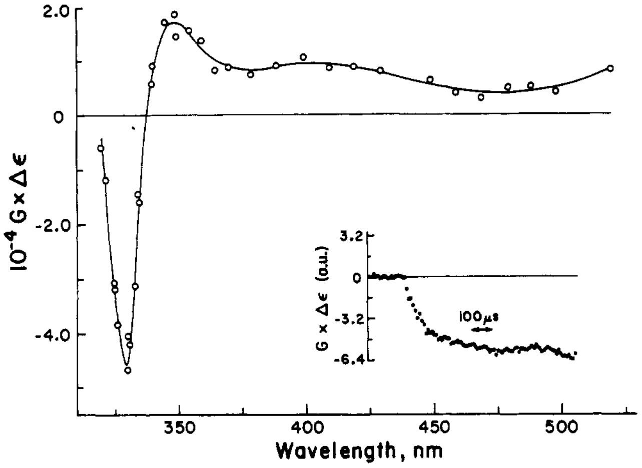

Figure 5. Difference absorption spectrum of C_{60}^-/γ-CD recorded 260 μs after pulse radiolysis of aqueous solution of 1.2×10^{-5} mol dm^{-3} C_{60}, 8×10^{-3} mol dm^{-3} γ-CD, and 0.1 mol dm^{-3} propan-2-ol saturated with nitrogen. Dose 2.3 Gy/pulse. Insert: Digitized traces of signal at 330 nm.

containing 1.2×10^{-5} mol dm^{-3} C_{60}/γ-CD and 0.1 mol dm^{-3} propan-2-ol, saturated with N_2. The reducing radicals, e_{aq}^- ($E° = -2.9$ V) and $(CH_3)_2\dot{C}OH$ ($E° = -1.23$ V), produced as a result of reactions 6 and 7 participated in the reduction of C_{60} (reactions 14 and 15).

$$e_{aq}^- + C_{60}/\gamma\text{-CD} \rightarrow C_{60}^-/\gamma\text{-CD} + H_2O \qquad (14)$$

$$(CH_3)_2\dot{C}OH + C_{60}/\gamma\text{-CD} \rightarrow C_{60}^-/\gamma\text{-CD} + (CH_3)_2CO \quad (15)$$

The difference absorption spectrum shown in Figure 5 exhibits a broad absorption in the region 350–520 nm and a bleaching at 340 nm. Although weak, these spectral characteristics confirm the absorption of fullerene anion in the visible region.[18,21] The rate of formation of fullerene anion was found to be 1.8×10^4 s^{-1}. In the presence of acetone (0.2 mol cm^{-3}), the rate of C_{60}^- formation decreased to 8×10^3 s^{-1}, while the difference absorption spectrum was unchanged. Acetone is an efficient scavenger for hydrated electrons and a source of $(CH_3)_2\dot{C}OH$ radicals. The rates of reactions with $(CH_3)_2\dot{C}OH$ radicals are known to be slower than corresponding reactions with hydrated electrons.

Conclusion

The singlet and triplet excited-state characteristics of C_{60} in aqueous γ-cyclodextrin solution are very similar to those observed in organic solvents. The $^3C_{60}/\gamma$-CD can be readily quenched by inorganic anions leading to the reduction of fullerene. The quenching rate constants vary from 10^5 mol^{-1} dm^3 s^{-1} for SCN$^-$ to 10^9 mol^{-1} dm^3 s^{-1} for I$^-$ ions. The heavy atom effect induced by iodide ions resulted in enhanced intersystem crossing in the collision complex. Radiolytically produced radicals, e_{aq}^-, $(CH_3)_2\dot{C}OH$, and $MV^{\bullet+}$, are capable of reducing C_{60} in aqueous γ-CD solution. The one-electron reduction potential of C_{60}/γ-CD was determined to be −0.25 V vs NHE. The anion radical of fullerene is stable in an inert atmosphere and exhibits broad absorption in visible region of spectrum.

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