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Single and double reduction of C_{60} in 2:1 γ -cyclodextrin/[60]fullerene inclusion complexes by cyclodextrin radicals

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Abstract

Spectroscopic and chemical properties of γ -CD \cdot radicals, resulting from the abstraction by $HO\cdot$ radicals of hydrogen atoms, have been investigated using pulse radiolysis. The reactions of γ -CD \cdot radicals with C_{60} in 2:1 γ -CD/ C_{60} inclusion complexes have been studied in aqueous solutions. It has been demonstrated that the γ -CD \cdot radicals are reducing species producing $C_{60}^{\bullet-}$ monoanion radicals, as well as doubly reduced C_{60}^{2-} , well characterized by their absorption spectra in the near IR. The oxidation potential of γ -CD \cdot radical is estimated to be more negative than –390 mV vs. NHE. The kinetics of the C_{60} reduction by γ -CD \cdot radicals have been determined and compared with kinetics by other reducing species including the solvated electron (e_{aq}^-) and $CO_2^{\bullet-}$ radicals. It was observed that the method of preparation of the 2:1 γ -CD/ C_{60} inclusion complexes modifies the C_{60} reduction mechanism.

Keywords: 2:1 γ -Cyclodextrin/[60]fullerene inclusion, complexes, pulse radiolysis, oxidized γ -cyclodextrin, fullerene reduction, reduction potentials, $C_{60}^{\bullet-}$, C_{60}^{2-} , 9,10-Anthraquinone-2-sulfonate ion

1. Introduction

Cyclodextrins (CD), water-soluble cyclic oligomers of glucose, have a hydrophobic cavity able to form inclusion complexes with hydrophobic molecules [1]. They are employed as drug carriers [2–6], studied in recognition processes [7,8] and for applications in nanodevice construction [9]. These CD are also an interesting matrix for spectroscopic studies since they are transparent throughout a part of the IR, and in the visible and near-UV spectral region. The internal diameters of the largest CD, the γ -CD which are constituted by 8 glucose units, allow the formation of 2:1 γ -CD/[60]fullerene inclusion complexes (γ -CD/ C_{60}) [10,11].

Previously, Priyadarsini et al. [12] performed pulse radiolysis studies of γ -CD/ C_{60} inclusion complexes prepared using methanol as solvent of C_{60} . These authors displayed the transient species resulting from reactions of these complexes with $HO\cdot$ radicals, in the spectral range 200–500 nm. From

the data obtained, they suggested two possible reactions: (i) addition of $HO\cdot$ to C_{60} double bonds, and (ii) abstraction of an H atom from γ -CD, leading to γ -CD \cdot radicals which subsequently adds to C_{60} , acting as a radical sponge. These authors also indicate that the radical product of this addition has a λ_{max} at 290 nm and that its formation kinetics matches a C_{60} bleaching at 330–335 nm.

Our investigation has a triple aim: (i) extension of the 200–500 nm spectral region, studied by Priyadarsini et al. [12], to the IR, a spectral region where absorption changes are a probe for identifying the presence of C_{60} anions, $C_{60}^{\bullet-}$ and C_{60}^{2-} , (ii) demonstration that γ -CD \cdot radicals can be reducing species, and discussion of the observed reactions using the analysis of Swallow [13] and Adams et al. [14] on products of glucose radiolysis in aqueous solutions, (iii) discussion of the reduction mechanism of C_{60} in inclusion complexes for two different preparation methods, using either methanol or toluene to solubilize C_{60} .

2. Experimental

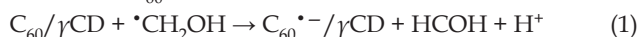
2.1. Materials

Chromatographically pure fullerene, C₆₀, was purchased from Syncom (Groningen, Holland), the 9,10-anthraquinone-2-sulfonate (AQS) from Lancaster Research Chemicals (UK), and the γ -cyclodextrin (γ -CD), as hydrate C₄₈H₈₀O₄₀ · xH₂O, from Acros (99% purity, Geel, Belgium). Ultrapure water from a Purite Neptune Analytical Process Flow model was used to make all aqueous solutions.

2.2. Preparation of the γ -CD/C₆₀ inclusion complexes

The method we used to make γ -CD/C₆₀ inclusion complexes was derived from the protocol of Yoshida et al. [15] and employs toluene to solubilize C₆₀. A mixture of two solutions consisting of C₆₀ (20 mg, 27.8 μ mol) in toluene (10 cm³) and γ -CD (67 mg, 52 μ mol) in water (10 cm³) was refluxed at 118 °C for 30 h under vigorous mechanical stirring. After cooling to room temperature, the aqueous layer containing precipitated γ -CD/C₆₀ complex was centrifuged. The precipitate was then dissolved in cold H₂O (10 cm³) and centrifuged at 10 °C (for 30 min at 4000g), in order to remove as much free γ -CD as possible. After filtration, the precipitate was dried under vacuum for 15 h. The final γ -CD/C₆₀ complexes were obtained as purple crystals. The quality of the complexes obtained was evaluated by the UV-visible spectra in water, which displayed the characteristic absorption bands of C₆₀ in organic solvents. It has to be noted that it is difficult to avoid self-association of γ -CD in aqueous solutions [3].

We have observed that organic solvents present in 2:1 γ -CD/C₆₀ inclusion complexes cannot be easily eliminated. For this reason, we have preferred the Yoshida to Priyadarsini preparation because residual methanol competing with γ -CD in the reaction with HO[•] radicals, might give [•]CH₂OH radicals, reducing agents (E (CH₂O, H⁺/[•]CH₂OH) = -920 mV [16]) able to reduce C₆₀ *via*



In the Yoshida preparation, the HO[•] radical may react with residual toluene mainly by addition to a double bond to form OH[•]CH₆CH₃ [17,18] which is not a reducing radical in contrast to [•]CH₂OH radicals generated in the case of the Priyadarsini preparation.

2.3. Spectrophotometry

Ground state absorption spectra were recorded on a Varian Cary spectrophotometer (bandwidth: 2 nm) using 10 mm quartz cuvette. The concentration of γ -CD/C₆₀ inclusion complexes in water was estimated by assuming for C₆₀, $\epsilon_G(330) \sim 50,000 \text{ M}^{-1} \text{ cm}^{-1}$, being similar to C₆₀ in a non-polar environment like cyclohexane, $\epsilon_G(330) = 49,500 \text{ M}^{-1} \text{ cm}^{-1}$ [19]. Yoshida et al. [15] obtained for γ -CD/C₆₀ $\epsilon_G(330) = 42,700 \text{ M}^{-1} \text{ cm}^{-1}$.

2.4. Pulse radiolysis set up

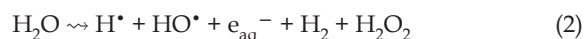
The pulse radiolysis experiments were carried out with a 12 MeV Radiation Dynamics Ltd. (UK) electron linear accelerator. We used single pulses of duration 0.22–2 μ s and with a peak current of about 30 mA. The accelerator is normally operated at 10 pulses per second but the single pulse mode is achieved by modifying the pulses to the electron gun [20]. The detection system consisted of a Xe arc lamp and pulsing unit, high radiance Kratos monochromator and quartz optics. The sample cell, constructed by Spectrosil quartz, had an optical path length of 25 mm [21]. Optical transmissions at various wavelengths selected with the monochromator (bandwidths 10–40

nm) were observed as a function of time before and after the radiation pulse using photoelectric detection. The output of the photomultiplier (EMI 9558Q) was displayed on a Tektronix TDS 380 digitizing oscilloscope. Data processing was performed on a Dan 486DX33 PC (UK) fitted with Pentium type processors, using software developed in house.

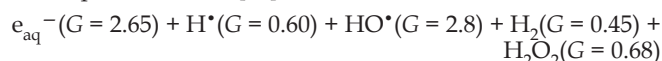
Absorbed doses, between 2 and 21 Gy, were determined from the transient (SCN)₂^{•-} formation in air-saturated 10⁻² M KSCN as described by Adams et al. [14], but using the updated G_e value of 2.59 × 10⁻⁴ m² J⁻¹ obtained by Buxton and Stuart [22], G being the radiation chemical yield of (SCN)₂^{•-} and ϵ its molar absorption coefficient at 475 nm. Saturation of such solutions with N₂O results in a doubling of the (SCN)₂^{•-} yield.

2.5. Generation of the primary radicals (e_{aq}⁻, H[•] and HO[•]) by pulse radiolysis

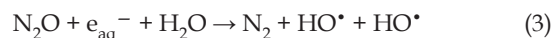
Within 10⁻⁹ s of high energy radiation deposition, the radiolysis products of water present at neutral pH are the reducing radicals: hydrated electron (e_{aq}⁻) and hydrogen atom H[•], the oxidizing radical HO[•], and the molecular products: hydrogen peroxide and molecular hydrogen:



The radiolysis yields (G) expressed in radical or molecules formed per 100 eV are [23]



For generating almost exclusively HO[•] radicals (~92%), aqueous solutions were saturated with N₂O which converts e_{aq}⁻ into hydroxyl radicals by dissociative electron attachment



In such conditions the remaining radicals (~8%) are reducing hydrogen radicals [24].

For generating almost exclusively hydrated electrons, e_{aq}⁻, HO[•] radicals are removed by *tert*-butanol to form [•]CH₂(CH₃)₂COH radicals which are normally very unreactive.

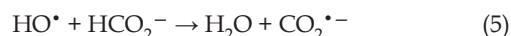
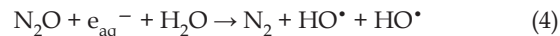
2.6. Generation of γ -CD[•] and CO₂^{•-} radicals

2.6.1. Generation of γ -CD[•] radicals

In irradiated water saturated with N₂O, primary hydrogen (H[•] and hydroxyl (HO[•] radicals may react with γ -CD to produce γ -CD[•] radicals. This reaction will be discussed in detail in Section 3.2.1.

2.6.2. Generation of CO₂^{•-} radicals

In irradiated water saturated with N₂O and in presence of a high concentration (0.1 M) of sodium formate, the HO[•] radicals produce CO₂^{•-} radicals, which are reducing species



The concentration of HO[•] and CO₂^{•-} radicals was estimated to be between 0.8 and 5 μ M.

3. Results and discussion

3.1. Ground state absorption spectra of γ -CD/C₆₀ inclusion complexes

The ground state absorption spectra of the γ -CD/C₆₀ inclusion complexes prepared by the Yoshida and Priyadarsini methods are reported in Figures 1a and 1b.

These spectra exhibit three intense peaks at 213, 260, 332, a weaker peak around 408 nm and a large band between 410 and 700 nm, which are spectral features related to (i) the allowed singlet-singlet transitions of the C_{60} molecule observed in the 210-, 260-, 330- and 404–408 nm regions in n-heptane, cyclohexane, 1-octanol solutions, both in energy and transition strength [25,26] and (ii) a set of weak forbidden transitions observed in the 410–700 nm observed in n-hexane, toluene, and micellar solutions [25,26].

The γ -CD/ C_{60} inclusion complexes remained stable for several days at room temperature, and for more than three months at 4 °C, as shown by their unmodified ground state absorption spectra. Several systems might coexist depending on the relative concentration of cyclodextrin and C_{60} , the type of preparation, the time and temperature of storage, and the presence or exclusion of air [10,27–29]. In agreement with previous studies, we confirmed that mainly two forms of complexes resulted between C_{60} and γ -CD: (i) one featuring the C_{60} included in the cavities of two γ -CD, the solution having a magenta color, typical of non-aggregated C_{60} , with the ground state absorption spectrum exhibiting a small, sharp and characteristic peak at 408 nm and (ii) a second form, partially consisting of non-inclusion complexes [30], where the C_{60} molecules are associated in clusters surrounded by several γ -CD [10,29], the solution being yellowish-brown, a typical color of C_{60} aggregates without the 408 nm peak in the absorption ground state spectrum. In all our investigations, we exclusively used the first type of complex.

3.2. Spectroscopic and chemical properties of γ -CD* radicals in γ -CD/ C_{60} inclusion complexes prepared via the Yoshida protocol

3.2.1. Generation and spectroscopic properties of γ -CD* radicals

The reaction of HO^\bullet radicals with γ -CD/ C_{60} inclusion complexes was investigated using complexes made *via* the Yoshida method.

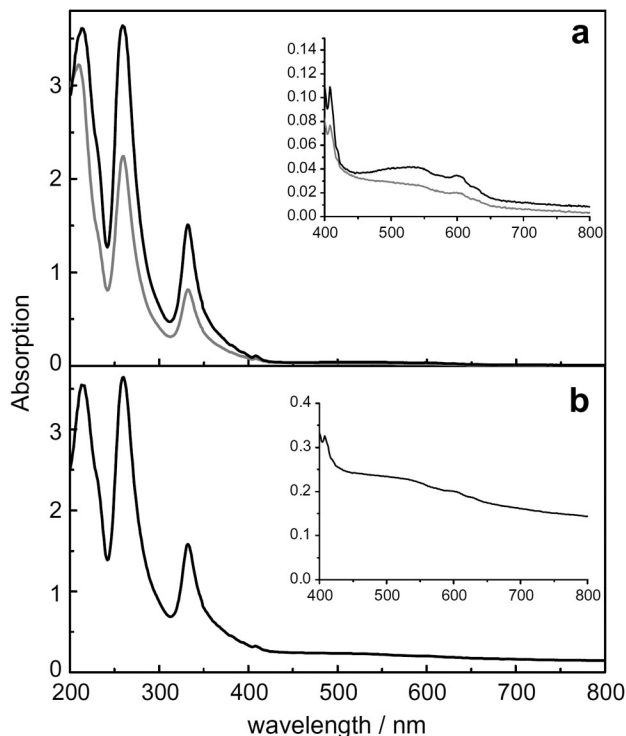
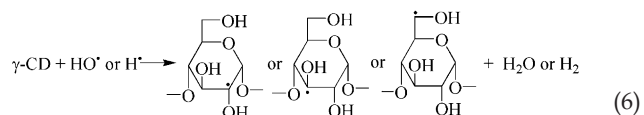


Figure 1. Absorption spectra of 2:1 γ -CD/ C_{60} inclusion complexes in aqueous solution prepared by (a) Yoshida method followed by one (gray) or two centrifugations (black), and (b) Priyadarsini method.

In irradiated water saturated with N_2O , H^\bullet and HO^\bullet radicals, generated by reactions (2) and (3), abstract H atoms which are α - to a hydroxyl group in γ -CD, as in the case of simple alcohols [31]. This abstraction gives three types of γ -CD* radicals by reaction (6). Below only one glucose monomer out of the 8 units constituting the γ -CD molecules is represented



These three γ -CD* radicals are those suggested by Swallow [13] for the reaction of HO^\bullet with glucose. The rate constants of reaction of glucose with H^\bullet and HO^\bullet are, respectively, $k = 6.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [32], and $k = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [32]. Thus, the reaction of γ -CD with HO^\bullet radicals is preponderant not only because of the faster rate constant but also because HO^\bullet radicals are ~ 10 times more concentrated than H^\bullet .

Reaction of HO^\bullet with γ -CD* ($3 \times 10^{-5} \text{ M}$) gives the transient spectrum shown in Figure 2, and occurs with a rate constant $k = 0.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which is lower than that reported in the literature ($k = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [33]. The average molar absorption coefficient $\epsilon_\lambda(\gamma\text{-CD})^*$ of the three γ -CD* radicals at wavelength λ was calculated by the Beer-Lambert expression below:

$$\epsilon_\lambda(\gamma\text{-CD})^* = \frac{\Delta A_\lambda}{[HO^\bullet]\ell} + \epsilon_\lambda(\gamma\text{-CD}) \quad (7)$$

where $\epsilon_\lambda(\gamma\text{-CD})$ is the molar absorption coefficient of the parent molecule, ΔA_λ is the maximum transient absorbance of the γ -CD* radical at wavelength λ , ℓ is the optical path in cm, and $[HO^\bullet]$ is the molar concentration of the hydroxyl radical.

We have measured at 320 nm the $\epsilon_\lambda(\gamma\text{-CD})$ in aqueous solutions for different γ -CD concentrations, considering that a sample of γ -CD hydrate contains 12.9% by weight of water molecules on average [1]. The values obtained for $\epsilon_{320}(\gamma\text{-CD})$ are: $360 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\gamma\text{-CD}] = 10^{-5} \text{ M}$, $60 \text{ M}^{-1} \text{ cm}^{-1}$ for $[\gamma\text{-CD}] = 10^{-4} \text{ M}$, and $20 \text{ M}^{-1} \text{ cm}^{-1}$ for a concentration of $[\gamma\text{-CD}] = 10^{-3} \text{ M}$. The decrease of the ϵ_λ value observed when γ -CD concentration increases, called hypochromism, is observed in dimers and in chromophore aggregates for stacked molecules of adenine, tyrosine, tryptophan, retinol, porphyrin, and anthracene. Quantum mechanical treatment of hypochromism theory has been described by Cantor and Schimmel [34]. Using for $\epsilon_{320}(\gamma\text{-CD})$ the value found for $[\gamma\text{-CD}] = 10^{-5} \text{ M}$, the molar absorption coefficient of the $(\gamma\text{-CD})^*$ radical at 320 nm

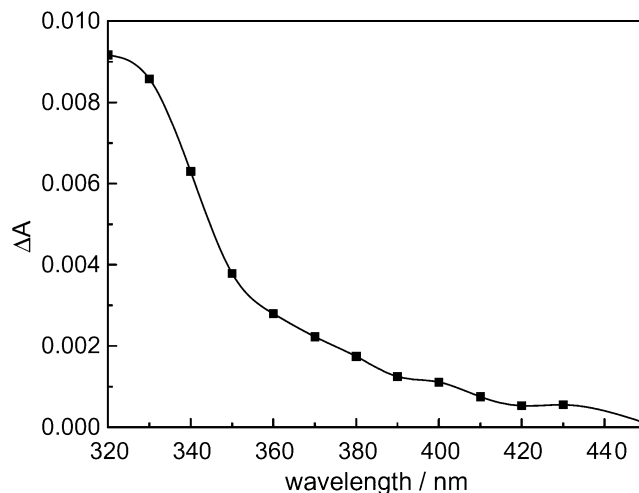


Figure 2. Differential spectrum obtained upon pulse radiolysis of a N_2O saturated aqueous solution containing $30 \mu\text{M}$ of γ -CD, $200 \mu\text{s}$ after pulse.

$\epsilon_{320}(\gamma\text{-CD})^{\bullet}$ was estimated to be approximately $\approx 760 \text{ M}^{-1} \text{ cm}^{-1} \pm 150 \text{ M}^{-1} \text{ cm}^{-1}$ with the assumption that every HO $^{\bullet}$ hydroxyl radical reacts with one γ -CD molecule.

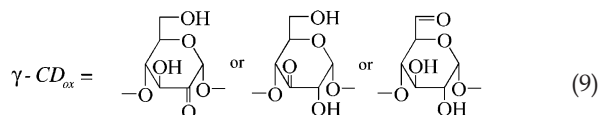
3.2.2. Reaction of γ -CD $^{\bullet}$ radicals acting as reducing agents of C₆₀

In irradiated N₂O saturated aqueous solution containing 14 μM of γ -CD/C₆₀ inclusion complexes prepared by the Yoshida method, we observed the transient difference spectra, at 9 and 439 μs after the electron pulse, shown in Figure 3. These spectra exhibit (a) large absorptions at $\sim 350 \text{ nm}$, (b) broad low absorptions in the region 350–700 nm, (c) two infrared bands with λ_{max} at 940 and 1080 nm (Figure 3) and (d) kinetic differences at 940 and 1080 nm suggesting the presence of two species, which will be discussed below in the kinetic analysis section.

The infrared peaks at 940 and 1080 nm are characteristic of the C₆₀ $^{\bullet-}$ anion in benzonitrile [35], dichloromethane [36], methyltetrahydrofuran [37], toluene [38,39], toluene/2-propanol/acetone (8:1:1) [38], 2-propanol [40], and toluene/CH₂Cl₂ mixtures [41]. They have also been observed for γ -CD/C₆₀ inclusion complexes reduced by e_{aq}^{-} [40]. The full width at half maximum (FWHM) at 1080 nm in our experimental conditions (40 nm monochromator bandwidth in the IR) is $\sim 100 \text{ nm}$, with a ratio of the absorbance maxima, ΔA at 1080 nm/ ΔA at 940 nm ~ 3 . It is interesting that the C₆₀ $^{\bullet-}$ absorption band profile at 1080 and 940 nm is not significantly modified by the γ -CD environment when compared to organic solvents. The γ -CD $^{\bullet}$ radical is transformed, after reduction of C₆₀, into a non-radical species $\gamma\text{-CD}_{\text{ox}}$ via:



where $\gamma\text{-CD}_{\text{ox}}$ is a non-radical species resulting from two consecutive oxidations of a glucose unit of γ -CD after (i) abstraction of an H atom by HO $^{\bullet}$ leading to the γ -CD $^{\bullet}$ radical *via* reaction (6), and (ii) transfer of an H atom from the γ -CD $^{\bullet}$ radical to C₆₀ followed by a deprotonation of C₆₀H (or electron transfer from γ -CD $^{\bullet}$ radical to C₆₀ followed by deprotonation). Reaction (8) leads to the three possible γ -CD oxidised products γ -CD (2-dehydro- α -D-glucose, 3-dehydro- α -D-glucose and 6-dehydro- α -D-glucose) shown below, where only one doubly oxidized glucose unit is represented:



The formation of these doubly oxidized glucose units is suggested by the observation of Phillips [42], that the final prod-

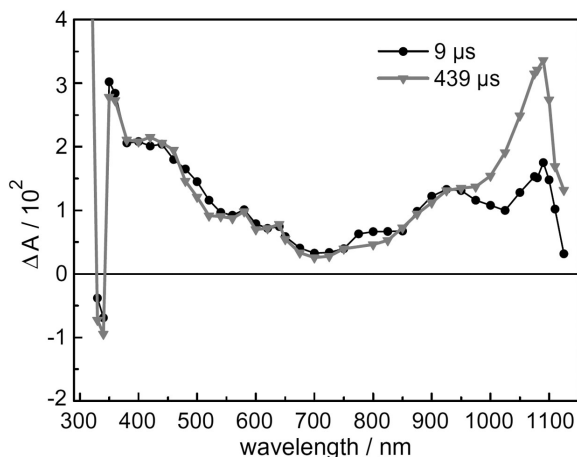


Figure 3. Differential spectrum obtained upon pulse radiolysis of a N₂O saturated aqueous solution containing 14 μM of γ -CD/C₆₀ inclusion complex prepared by Yoshida's method at a dose of 20 Gy.

ucts of reaction of hexoses with HO $^{\bullet}$, in the absence of O₂, are mainly glucosones.

The observation of reaction (8) allows us to assess that the oxidation potential of the γ -CD $^{\bullet}$ radical is more negative than -250 mV because γ -CD $^{\bullet}$ is capable of reducing the inclusion complex 2:1 γ -CD/C₆₀ which has a reduction potential

$$E_7(2:1\gamma\text{-CD}/\text{C}_{60}/2:1\gamma\text{-CD}/\text{C}_{60}^{\bullet-}) = -250 \text{ mV vs. NHE} [33].$$

The rate constant of formation of the C₆₀ anion is (i) $>10^{10} \text{ M}^{-1} \text{ s}^{-1}$ by solvated electrons in 2-propanol [38] and (ii) about $1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ by hydrated electrons in the 2:1 γ -CD/C₆₀ inclusion complex [12]. For the C₆₀ internal reduction by the γ -CD $^{\bullet}$ radical in the inclusion complex, we obtained a first order rate constant of $1 \times 10^4 \text{ s}^{-1}$.

3.2.3. Reaction of γ -CD $^{\bullet}$ radicals acting as reducing agents of AQS

In order to confirm that γ -CD $^{\bullet}$ radicals are reducing species, we replaced C₆₀ with another electron acceptor, 9,10-anthraquinone-2-sulfonate ion (AQS). We irradiated by pulse radiolysis an N₂O-saturated AQS aqueous solution in the presence and in the absence of γ -CD, and observed the differential spectra shown in Figure 4.

The spectrum of the species produced by HO $^{\bullet}$ radicals in the presence of γ -CD (10 mM) and AQS (10 μM) (Figure 4a) is identical to that observed upon reaction of hydrated electron e_{aq}^{-} with AQS (Figure 4b). This spectrum is that of AQS $^{\bullet-}$ anion previously characterized [16,43]. In the absence of γ -CD, the reaction of HO $^{\bullet}$ radicals with AQS gives a spectrum (Figure 4c) different from that of AQS $^{\bullet-}$. Therefore AQS reduction can be attributed to γ -CD $^{\bullet}$ radicals. It is possible to establish that the oxidation potential of the γ -CD $^{\bullet}$ radicals is more negative than the reduction potential of AQS, $E_7(\text{AQS}/\text{AQS}^{\bullet-}) = -390 \text{ mV vs. NHE} [44]$.

Reduction of AQS by the radical γ -CD $^{\bullet}$ occurs with a bimolecular rate constant of $\sim 6.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, lower than that by the hydrated electron, e_{aq}^{-} , for which the rate constant is $2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This is due to the difference between the one-electron oxidation potentials of the two reducing species: the γ -CD $^{\bullet}$ radical and the solvated electron.

3.2.4. Addition of γ -CD radicals to C₆₀

It can be considered that γ -CD $^{\bullet}$ radicals may also add to C₆₀ double bonds as demonstrated for alkyl [45,46], benzyl [45,47,48], methyl [47,49], phenyl [50], peroxy [51] radicals. Under our experimental conditions, it is difficult to assess the

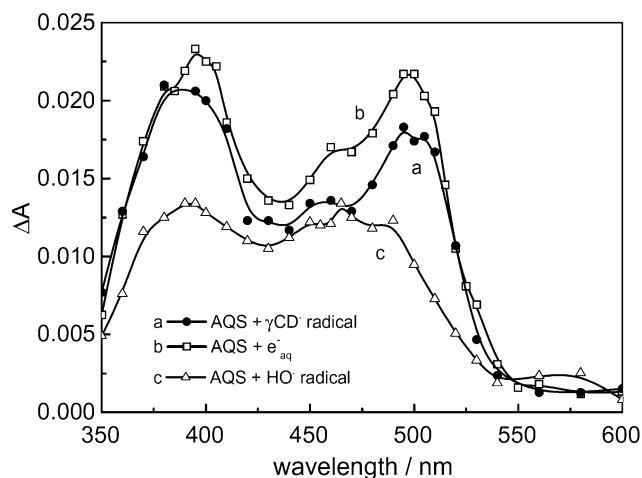


Figure 4. Differential spectra obtained upon pulse radiolysis of 10 μM AQS aqueous solutions (a) in presence of 10 mM γ -CD in a N₂O saturated solution (\bullet , delay from pulse: 400 μs); (b) in N₂ saturated solution with 1% *tert*-butanol (\square , delay from pulse: 50 μs); (c) in N₂O saturated solution (Δ , delay from pulse: 284 μs).

fraction of these γ -CD $_{-}$ radicals which would add to C_{60} and thus would not act as a reducing species.

3.2.5. Comparison with the pulse radiolysis results obtained by Priyadarsini et al. and Dimitrijević and Kamat

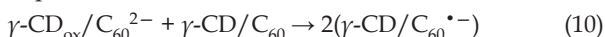
As mentioned in Section 1, Priyadarsini et al. [12] have previously studied the reaction of HO^{\bullet} radical with γ -CD/ C_{60} inclusion complexes, prepared using methanol as solvent. These authors investigated this system in the spectral region from 200 to 500 nm and did not include spectral observations in the IR, which here allowed us to discover that γ -CD $^{\bullet}$ radicals can act as reducing species for C_{60} as well as for AQS molecules. In the region between 300 and 500 nm, the spectral features which we have observed for a C_{60} reduction by γ -CD $^{\bullet}$ are rather similar to those observed by Dimitrijević and Kamat [33] for a C_{60} reduction by hydrated electrons and $(CH_3)_2^{\bullet}COH$ radicals.

3.3. Kinetic analysis of the reduction of C_{60} in γ -CD inclusion complexes by γ -CD $^{\bullet}$ radicals

At radiation doses below 12 Gy, reaction of γ -CD $^{\bullet}$ with C_{60} embedded in γ -CD leads to the concomitant formation of the two infrared absorption bands at 940 and 1080 nm (4×10^4 s $^{-1}$) due exclusively to the monoanion $C_{60}^{\bullet-}$.

At doses between 12 and 21 Gy, we observe between 9 and 439 μ s that the absorbance at 825 nm decreases, at 940 nm remains almost constant and at 1080 nm grows (Figure 3). The spectrum observed at 9 μ s can be interpreted as due to the presence of $C_{60}^{\bullet-}$ monoanion characterized by its 1075 nm band and of the doubly reduced C_{60}^{2-} , characterized by its absorption bands at 950 and 830 nm [52]. The spectrum observed at 439 μ s is that of the $C_{60}^{\bullet-}$ radical monoanion.

Figure 5 shows the absorption spectra of $C_{60}^{\bullet-}$ and of C_{60}^{2-} which superpose in the region 800–1050 nm. The doubly reduced C_{60}^{2-} present at 9 μ s disappears with time and generates monoanions $C_{60}^{\bullet-}$ via a reduction of neighboring inclusion complexes:



In Figure 3, absorbance around 825 nm, mainly due to C_{60}^{2-} , decreases and is accompanied by an absorbance growth of the band peaking at 1080 nm, due to $C_{60}^{\bullet-}$, while the absorbance around 940 nm remains almost constant. In this latter spectral region, the C_{60}^{2-} absorbance decay is compensated by a $C_{60}^{\bullet-}$ absorbance growth.

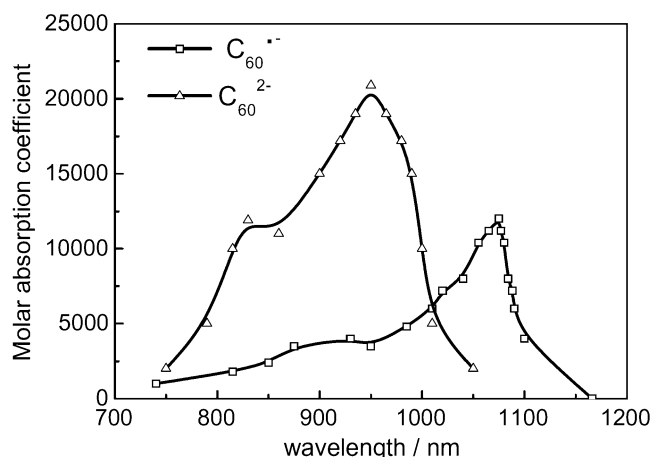


Figure 5. Graphical representation of the molar absorption coefficients vs. wavelength of $C_{60}^{\bullet-}$ anions (\square) and of C_{60}^{2-} anion (Δ), adapted from spectra given in Reference [52], with molar absorption coefficients at their maxima being $\epsilon_{1075} = 12,000$ M $^{-1}$ cm $^{-1}$ for $C_{60}^{\bullet-}$ and $\epsilon_{940} = 21,000$ M $^{-1}$ cm $^{-1}$ for C_{60}^{2-} .

3.4. Kinetic analysis of the reduction of C_{60} in γ -CD inclusion complexes by other species

Reactions of γ -CD/ C_{60} with reducing species e_{aq}^- and $CO_2^{\bullet-}$ were also examined and confirm the formation of $C_{60}^{\bullet-}$, accompanied by the doubly reduced C_{60}^{2-} , at doses higher than 12 Gy.

3.4.1. Reduction by the hydrated electron, e_{aq}^-

The transient absorption spectrum obtained after reaction of the hydrated electron, e_{aq}^- , with a solution of 26 μ M of γ -CD/ C_{60} complexes is similar to that shown in Figure 3 for reduction by γ -CD $^{\bullet}$ radicals. Similarly, at radiation doses higher than 12 Gy between 6 and 89 μ s a decay of absorbance at 830 nm concomitant with a growth at 1080 nm were observed, as well as an unchanged absorbance at 940 nm. These modifications are attributed once more to the transformation of C_{60}^{2-} into $C_{60}^{\bullet-}$, via reaction (10). The molar absorption coefficient of the $C_{60}^{\bullet-}$ at 1080 nm, calculated by equation (11)

$$\epsilon_{\lambda}(C_{60}^{\bullet-}) = \frac{\Delta A_{\lambda}}{[e_{aq}^-]l} \quad (11)$$

is $\epsilon_{1080} \geq 11,000$ M $^{-1}$ cm $^{-1}$, consistent with the values found for $C_{60}^{\bullet-}$ in dichloromethane (12,000 M $^{-1}$ cm $^{-1}$) [36] and CH_2Cl_2 /toluene (12,000 M $^{-1}$ cm $^{-1}$) [41] solutions.

3.4.2. Reduction by C_{60}^{2-} radicals

The transient absorption spectrum obtained after reaction of C_{60}^{2-} radicals with a solution of 60 μ M of γ -CD/ C_{60} complexes shown in Figure 6 is also similar to that observed for reduction by γ -CD $^{\bullet}$ radicals (Figure 3). At radiation doses lower than 12 Gy, growth at 950 and 1080 nm occurs with the rate constant $\sim 1.5 \times 10^4$ s $^{-1}$. For dose of 2 Gy, a molar absorption coefficient is estimated to be $\epsilon_{1080} = 12,225$ M $^{-1}$ cm $^{-1}$ and $\epsilon_{980} = 3700$ M $^{-1}$ cm $^{-1}$, values typical of C_{60} monoanion absorption in organic solvents. At higher radiation doses (12–21 Gy), for γ -CD/ C_{60} concentration varying between 7.5 and 75 μ M, and for pH varying between 5 and 9, C_{60} reduction invariably occurs in two steps: following a fast formation (1.5×10^4 s $^{-1}$), a further slow absorbance growth is observed at 1080 nm while the transient absorbance around 940 nm and 800 nm, due partially to C_{60}^{2-} , decays as shown in Figure 6. The experimental conditions of this reduction by $CO_2^{\bullet-}$ radicals shows more clearly the 940 nm band decay than in the case of the reduction by γ -CD $^{\bullet}$ radicals or by the hydrated electron e_{aq}^- .

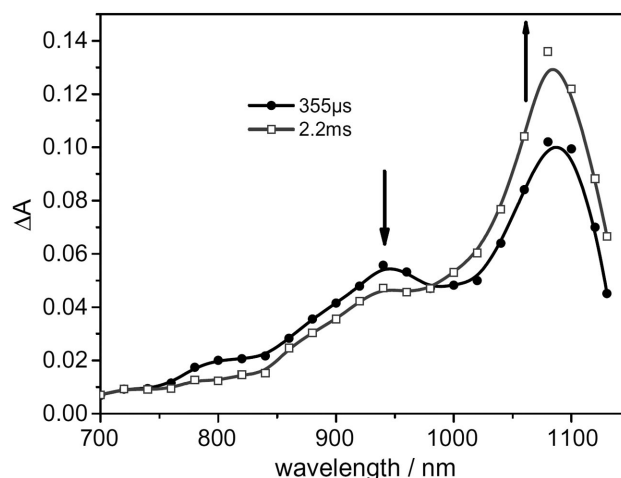


Figure 6. Differential spectra obtained upon pulse radiolysis of a N_2O saturated γ CD/ C_{60} water solution (60 μ M) in presence of 5 μ M of C_{60}^{2-} .

4. Conclusion

Our pulse radiolysis investigation on 2:1 γ -cyclodextrin/[60] fullerene inclusion complexes in aqueous solutions, establishes an important property of γ -CD[•] radicals, which are generated by HO[•] radicals abstracting hydrogen atoms of a glucose ring, component of the cyclodextrin: their ability to act as reducing species when reacting with C₆₀ in 2:1 γ -CD/C₆₀ inclusion complexes *via*

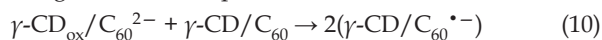


Reaction (8) allows us to estimate that the oxidation potential of γ -CD[•] radicals is more negative than -250 mV vs. NHE, because the γ -CD[•] radicals are capable of reducing the inclusion complex 2:1 γ -CD/C₆₀ which has a reduction potential

$$E(2:1\gamma\text{-CD}/\text{C}_{60}/2:1\gamma\text{-CD}/\text{C}_{60}^{\bullet-}) \sim -250 \text{ mV vs. NHE} \quad [33].$$

These γ -CD[•] radicals can also reduce another electron acceptor molecule, 9,10-anthraquinone-2-sulfonate ion (AQS). Thus, these γ -CD[•] radicals have an oxidation potential more negative than the reduction potential of AQS, E (AQS/AQS^{•-}) which is ~ -390 mV vs. NHE [44].

At radiation doses higher than 12 Gy, a doubly reduced fullerene, C₆₀²⁻, is observed. This doubly reduced fullerene, C₆₀²⁻, decays to give the C₆₀ monoanion *via* a reduction of neighboring inclusion complexes:



It can be emphasized that the γ -CD environment does not significantly modify the absorption spectrum and the molar absorption coefficient of the mono-anion of C₆₀ as compared to those previously determined in organic solvents, such as benzonitrile [35], dichloromethane [36], methyltetrahydrofuran [37], toluene [38,39] toluene/2-propanol/acetone (8:1:1) [38], 2-propanol [40], and toluene/CH₂Cl [41].

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