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RADIATION CHEMICAL INVESTIGATIONS ON AQUEOUS SOLUTIONS OF $C_{60}(OH)_{18}$

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Abstract--The ultraviolet-visible absorption spectrum of $C_{60}(OH)_{18}$ in water showed an absorption band with $\lambda_{max} = 215$ nm and other characteristic absorption bands of C_{60} are not observed. The singlet-singlet and triplet-triplet absorption bands are not observed in the 400 - 900 nm region. It has low reactivity with e^-_{aq} and formed an absorption band with $\lambda_{max} = 580$ nm. The hydroxyl radicals react with a bimolecular rate constant of 2.4×10^9 $dm^3\ mol^{-1}\ s^{-1}$ and showed an absorption band at 540 nm.

INTRODUCTION

The successful laboratory synthesis of C_{60} in ultra high purity has generated tremendous interest in the preparation of new derivatives [1-7]. C_{60} has also been solubilized in water by incorporation into host-guest complex with γ-cyclodextrin, micellar systems, bilayer membranes and calixarenes [8-14]. Water soluble derivatives have attracted attention due to their possible use in biological applications [15-17]. Fullerenol, $C_{60}(OH)_{18}$, is highly soluble in water and for its possible use in biological applications, it is important to understand its photophysical and chemical behaviour. With this objective, radiation and photochemical investigations on aqueous solutions of $C_{60}(OH)_{18}$ have been carried out and the results are reported in this manuscript.

EXPERIMENTAL

The procedure for the preparation of $C_{60}(OH)_{18}$ has been described in reference [5]. All other chemicals used were of analytical grade purity. The solutions were prepared in deionized "nanopure" water and freshly prepared solutions were used in each experiment. Optical absorption studies were carried out with a Hitachi 330 spectrophotometer.

Pulse radiolysis studies have been carried out with high energy electron pulses (7 MeV, 50 ns), generated from a linear electron accelerator [18]. The dose delivered per pulse has been determined by employing $(SCN)_2^{\bullet-}$ dosimeter using Gε = 21520 $dm^3mol^{-1}s^{-1}$ for 100 eV of absorbed dose (the G value is the number of radicals formed for 100 eV of absorbed energy and ε is the molar absorptivity of $(SCN)_2^{\bullet-}$ at 500 nm [19]. As far as possible, the dose delivered was kept to a minimum to avoid decomposition of the solute. The dose per pulse was 15 Gy.

Picosecond laser photolysis experiments were carried out with a pulsed, mode-locked Nd:YAG laser (Continuum, model 501-C-10), generating pulses of 35 ps [20].

Radiolysis of N_2 saturated neutral aqueous solution leads to the formation of three highly reactive species (e^-_{aq}, $^\bullet H$, $^\bullet OH$) in addition to the formation of less reactive molecular products (H_2, H_2O_2)

$$H_2O \rightarrow {}^\bullet H,\ {}^\bullet OH,\ e^-_{aq},\ H_2,\ H_2O_2,\ H^+_{aq} \qquad \textbf{(1)}$$

The reaction of $^\bullet OH$ radicals was carried out in N_2O saturated solutions where e^-_{aq} are quantitatively converted to $^\bullet OH$ radicals (pH = 3-10).

$$N_2O + e^-_{aq} \rightarrow {}^\bullet OH + OH^- + N_2 \qquad \textbf{(2)}$$

The reaction of e^-_{aq} at neutral pH was carried out in N_2 saturated solutions and $^\bullet OH$ radicals were scavenged by t-butanol (0.2 mol dm^{-3}).

$$(CH_3)_3COH + {}^\bullet OH \rightarrow {}^\bullet CH_2(CH_3)_2COH + H_2O \qquad \textbf{(3)}$$

RESULTS AND DISCUSSION

Optical Absorption Studies

Figure 1a shows the ground state optical absorption spectrum of an aqueous solution of $C_{60}(OH)_{18}$, (2.9 ± 0.3) x 10^{-5} mol dm^{-3}, which exhibits an absorption band with λ_{max} = 215 nm ($\varepsilon_{215} = 6.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}). Small shoulders in the region of 230 - 280 nm [$\varepsilon_{260} = (5.2 \pm 0.6) \times 10^4$ dm^3 mol^{-1} cm^{-1}] and 300 - 360 nm ($\varepsilon_{330} = 2.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}) are also observed. C_{60} in cyclohexane has sharp absorption bands with λ_{max} at 213, 260, 330 nm and the molar absorptivity is very high (ε_{260} = 17.5 x

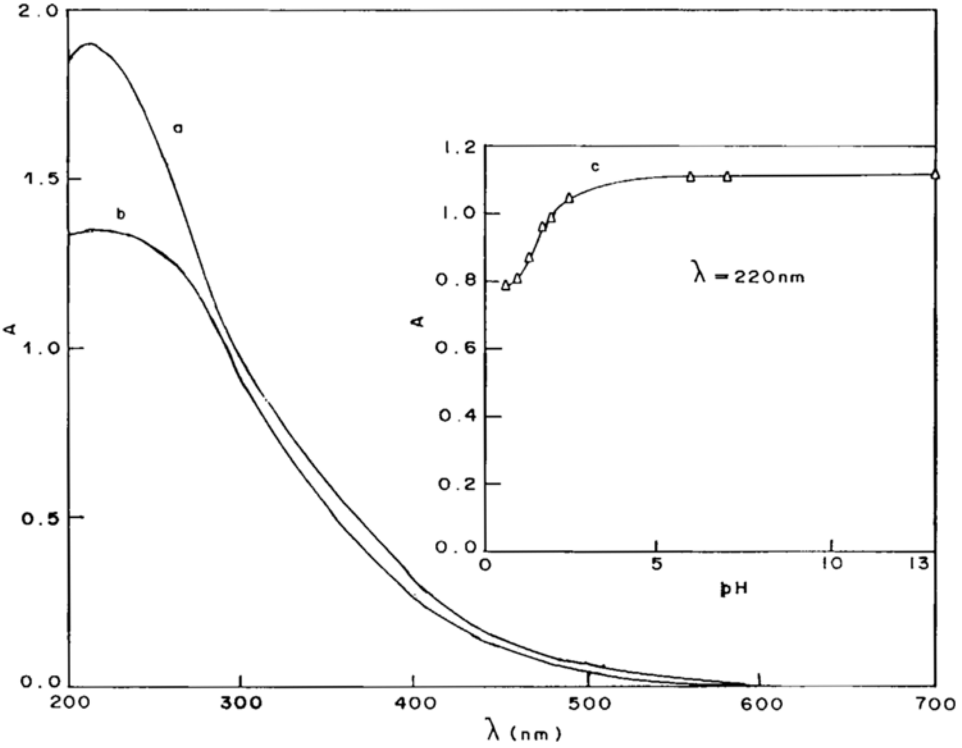

Figure 1. Ground state optical absorption spectrum of an aqueous solution of $C_{60}(OH)_{18}$, (2.9×10^{-5} mol dm^{-3}) at a- pH = 6.0 and b- 1.0. c- Variation of absorbance (220 nm) of aqueous solution of $C_{60}(OH)_{18}$, 1.7×10^{-5} mol dm^{-3} as a function of pH.

10^4 dm^3 mol^{-1} cm^{-1}). The molar absorptivity of C_{60} and its various derivatives is given in Table 1.

C_{60} in benzene has a broad absorption band in the region of 440 - 680 nm with very low extinction coefficient ($\varepsilon < 750$ dm^3 mol^{-1} cm^{-1}) [21]. This absorption

Table 1

Comparison of molar absorptivity of C_{60} with different derivatives.

Sample	λ (nm)	ε (dm^3 mol^{-1} cm^{-1})
$C_{60}(OH)_{18}$	260	$(5.2 \pm 0.6) \times 10^4$
$C_{60}Cl_{12}$	255	$(3.2 \pm 0.9) \times 10^4$ [a]
$C_{60}Cl_6$	255	$(7.6 \pm 1.2) \times 10^4$ [a]
C_{60}	260	17.5×10^4 [b]

[a] Ref. [22].
[b] Ref. [23].

band could be seen for higher concentrations of C_{60} (Figure 2a). This broad absorption was not observed in the aqueous solution of $C_{60}(OH)_{18}$ (Figure 2b) and benzene solution of $C_{60}Cl_6$ (Figure 2c). From these results and also those reported in the literature [22], it appears that the presence of functional groups in C_{60} lowers the molar absorptivity, broadens the absorption bands, and characteristic peaks of C_{60} disappear in $C_{60}(OH)_{18}$.

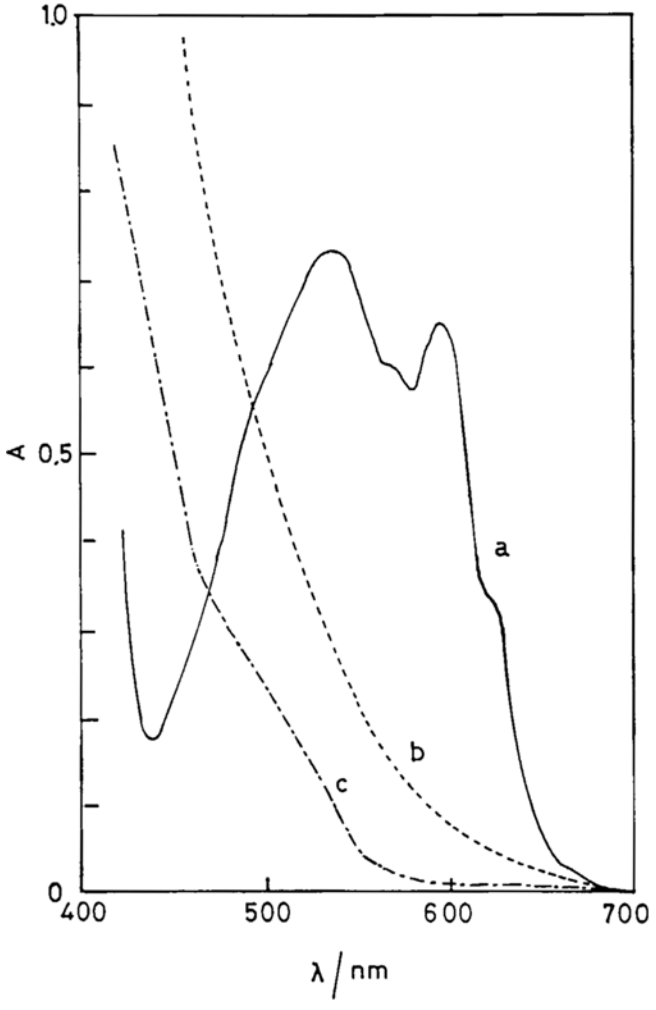

Figure 2. Ground state optical absorption spectrum of a- C_{60} in benzene (1.3×10^{-3} mol dm^{-3}); b- $C_{60}(OH)_{18}$ in water (6.5×10^{-4} mol dm^{-3}) and c- $C_{60}Cl_6$ in benzene ($5{,}5 \times 10^{-4}$ mol dm^{-3}).

The absorption spectrum of an aqueous solution of $C_{60}(OH)_{18}$ remains independent of pH in the range of 6 - 13. At lower pH, the absorption decreases. The variation in the absorbance at 220 nm as a function of pH is shown in Figure 1c and exhibits a pK of 1.7. This should be due to acid-base equilibria (Scheme 4). The spectrum at pH = 1 (Figure 1b), should be due to its neutral form (A) and in the neutral and alkaline pH (Figure 1a), it should be due to its anionic form (B).

$$\underset{A}{C_{60}(OH)_{18}} \rightleftharpoons \underset{B}{C_{60}(OH)_{17}O^{-}} + H^{+} \qquad \textbf{(4)}$$

Highly alkaline (pH > 13) and acidic (pH < 1) solution of $C_{60}(OH)_{18}$ are not stable and on prolonged standing, precipitates appeared.

Formation of Charge Transfer Complex

The aqueous solution of γ-CD-C_{60} had shown increased absorption on addition of electron rich amines such as DABCO, hexamine, and is assigned to the formation of charge transfer complex [24]. C_{60} in benzene has also shown the formation of charge transfer complex with amines such as diphenylamine, triphenylamine, triethylamine [20]. The aqueous solution of $C_{60}(OH)_{18}$ does not show any change in its absorption spectrum on addition of 1 mol dm^{-3} DABCO. This suggests that $C_{60}(OH)_{18}$ is unable to form the charge transfer complex with electron rich amines. The double bonds present in C_{60} now contain $^{\bullet}$OH groups and it must have lost its electron deficient character; and this explains the reason for not observing the charge transfer complex between $C_{60}(OH)_{18}$ and amines. These results are in conformity with optical absorption studies, which showed that the peculiar character of C_{60} is lost in $C_{60}(OH)_{18}$.

Formation of Excited States

C_{60} in benzene shows the formation of singlet (λ_{max} = 513, 885 nm) and triplet (λ_{max} = 745 nm) excited states both on direct excitation and by energy transfer from known triplets (biphenyl) [25]. Picosecond laser flash photolysis (λ_{ex} = 355 nm) of aqueous solution of γ-CD-C_{60} did not show any absorption in 400 - 900 nm region, immediately after the pulse and suggests that the singlet of C_{60} in the γ-CD-C_{60} complex absorbs at $\lambda < 400$ nm or its lifetime is extremely small and decays during the laser pulse itself (35 ps). However, the triplets were formed (λ_{max} = 745 nm) [26]. Picosecond laser flash photolysis of aqueous solution of $C_{60}(OH)_{18}$ did not show any absorption between 400 - 900 nm region from 0 ps to 6 ns, showing that both singlet and triplets if formed do not absorb in 400 - 900 nm region. Alternatively, the extinction coefficient value must be quite low to detect these species.

Another way to generate the triplet excited states is by pulse radiolysis of the solute in benzene. But $C_{60}(OH)_{18}$ is insoluble in benzene and therefore its triplet excited states could not be studied in benzene. $C_{60}(OH)_{18}$ has limited solubility in methanol and saturated solution of $C_{60}(OH)_{18}$ in benzene:methanol (70:30) could dissolve a very small amount of $C_{60}(OH)_{18}$ (1.6×10^{-5} mol dm^{-3}). Pulse radiolysis of a N_2 saturated solution of $C_{60}(OH)_{18}$ (1.6×10^{-5} mol dm^{-3}) in benzene:methanol (70:30) showed very little absorption in 350 - 700 nm region ($\Delta A \leq 0.002$). This could be due to low extinction coefficient coupled with low concentration of the triplets formed under these conditions.

Evidence for the formation of triplet excited states could be obtained qualitatively on energy transfer from a suitable donor to $C_{60}(OH)_{18}$. The energy of ^{3}(p-terphenyl)* is quite high and could be used for energy transfer studies. The transient absorption band (λ_{max} = 460 nm) of ^{3}(p-terphenyl)*, formed on pulse radiolysis of N_2 saturated solution of p-terphenyl (4×10^{-3} mol dm^{-3}) in benzene:methanol (70:30) became faster on addition of $C_{60}(OH)_{18}$ (1.6×10^{-5} mol dm^{-3}). The bimolecular rate constant was determined to be 1.1×10^9 dm^3 mol^{-1} s^{-1}. The decay could not be monitored for various concentrations of $C_{60}(OH)_{18}$ due to solubility limitations. Time-resolved studies did not show the formation of any new band in presence of $C_{60}(OH)_{18}$. These results are only qualitative in nature as the quenching of ^{3}(p-terphenyl)* may also be possible by the ground state of $C_{60}(OH)_{18}$.

The position of singlet and triplet absorption bands of C_{60} and its derivative are shown in Table 2. It is clear that the position of singlet and triplet excited states of derivatives of C_{60} show considerable blue shift.

Table 2

Position of singlet and triplet excited states of C_{60} and its derivatives.

Sample	Singlet (nm)	Triplet (nm)
C_{60}	513, 885	745[b]
γ-CD-C_{60}	---[a]	745[c]
$C_{60}Cl_{12}$	---[a]	380, 440-540[d]
$C_{60}Cl_6$	---[a]	370, 440-530[d]
$C_{60}(OH)_{18}$	---[a]	---[a]

[a] Not observed in 400 - 900 nm region.
[b] Ref. [25].
[c] Ref. [26].
[d] Ref. [22].

Pulse Radiolysis Studies

Reaction of e^-_{aq}. The rate constant for the reaction of e^-_{aq} with $C_{60}(OH)_{18}$ was studied by monitoring the decay of e^-_{aq} for various concentrations of the solute. Figure 3a and 3b shows that the decay of e^-_{aq} becomes faster in presence of $C_{60}(OH)_{18}$. The bimolecular rate constant, determined from the slope of the linear plot of pseudo first order (k_{obs}) with solute concentration (0 - 1.5 x 10^{-3}) mol dm^{-3} was 4.5 x 10^8 dm^3 mol^{-1} s^{-1}. The decay of e^-_{aq} in presence of $C_{60}(OH)_{18}$, showed significantly higher absorption at longer time scale (Figure 3b). The time-resolved studies showed formation of a broad band with λ_{max} = 580 nm (Figure 3c). The rate constant, determined from formation kinetics was 1 x 10^8 dm^3 mol^{-1} s^{-1}. The transients do not show any decay in 1 ms time scale (Figure 3d). The absorbance of the band (λ_{max} = 580 nm) remained independent of solute concentration (0.5 - 1.5) x 10^{-3} mol dm^{-3}, showing that electrons have completely reacted with the solute. Based on $G(e^-_{aq})$ = 2.7, the extinction coefficient of the transient band was determined to be 3.3 x 10^3 dm^3 mol^{-1} cm^{-1}. The band could be due to an electron adduct. The bimolecular rate constant for the reaction of e^-_{aq} with γ-CD-C_{60} and C_{60} is about 100 times higher than that with $C_{60}(OH)_{18}$ (Table 3). This could be due to the negative charge on the molecule and non-availability of π orbitals present in C_{60}. $COO^{\bullet-}$ is a strong one-electron reductant with reduction potential = -1.9 V. Pulse

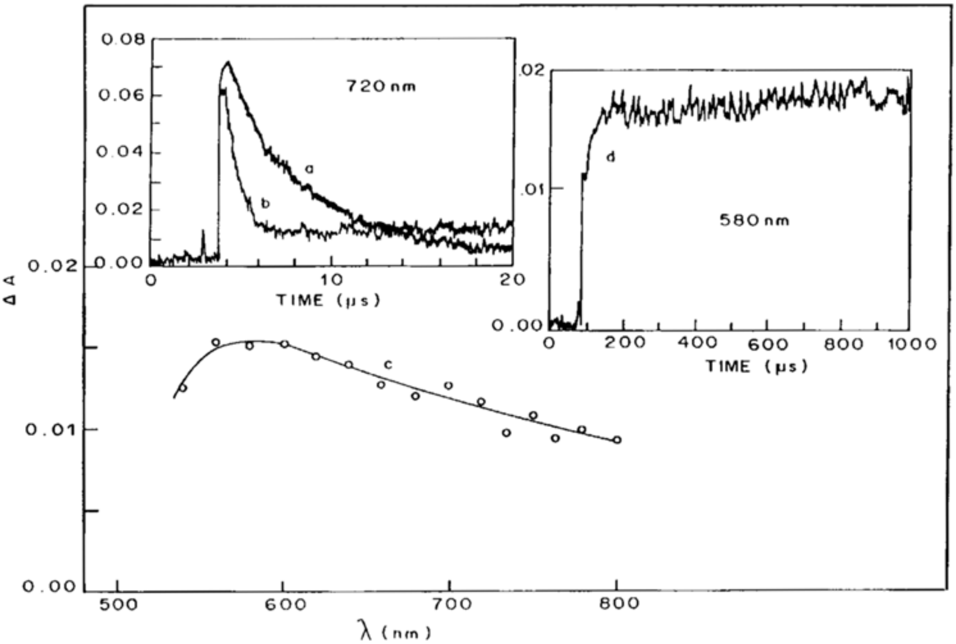

Figure 3. Absorption-time signal of e^-_{aq} (720 nm) a- in absence and b- in presence of $C_{60}(OH)_{18}$, 1.5 x 10^{-3}. c- Transient optical absorption spectrum obtained on pulse radiolysis (15 μs after the pulse) of N_2 saturated aqueous solution of $C_{60}(OH)_{18}$ (1.5 x 10^{-3} mol dm^{-3}, t-butanol = 0.2 mol dm^{-3}). d- Absorption-time signal at 580 nm.

Table 3

Characteristics of the transient species formed on pulse radiolysis of $C_{60}(OH)_{18}$ and other derivatives of C_{60}.

Reaction	λ_{max} (nm)	ε ($dm^3 mol^{-1} cm^{-1}$)	Formation Rate Constant ($dm^3 mol^{-1} s^{-1}$)
$C_{60}(OH)_{18} + e^-_{aq}$	580	3.3×10^3	4.5×10^8
γ-CD-$C_{60} + e_{aq}^-$	1080	---	$1.9 \times 10^{10\,a}$
$C_{60} + e^-_{aq}$	1080	---	$> 10^{10\,b}$
$C_{60}(OH)_{18} + {}^{\bullet}OH$	540	1.2×10^3	2.4×10^9
γ-CD-$C_{60} + {}^{\bullet}OH$	290	---	$1.0 \times 10^{10\,a}$

[a] Ref. [27].
[b] Ref. [28].

radiolysis studies (N_2O saturated, $HCOO^- = 4 \times 10^{-2}$ mol dm^{-3}, $C_{60}(OH)_{18} = 5 \times 10^{-4}$ mol dm^{-3}) showed a transient absorption band, which matched qualitatively with that formed on reaction with e^-_{aq}. Due to low absorption, its decay and formation kinetics could not be studied accurately.

Reaction of •OH Radicals. Pulse radiolysis of N_2O-saturated aqueous solution of $C_{60}(OH)_{18}$, (3.7×10^{-4} mol dm^{-3}), showed the formation of a broad absorption band with $\lambda_{max} = 540$ nm (Figure 4a). The absorption was not observed in presence of the •OH radical scavenger, t-butanol, showing that the band is due to reaction of •OH radicals with the solute. The bimolecular rate constant determined from the growth of 540 nm band was 2.4×10^9 dm^3 mol^{-1} s^{-1} (Figure 4b). The transient band formed on reaction of •OH radicals do not show appreciable decay even in 1 ms time scale (Figure 4c). The absorbance of the transient band (λ_{max} = 540 nm) remained independent of solute concentration (1.5×10^{-3} - 6.5×10^{-4} mol dm^{-3}), showing that all the hydroxyl radicals have reacted with the solute and the concentration of hydroxyl radicals can be taken equal to the concentration of the transient species formed on reaction of •OH radicals with the solute. The molar absorptivity of 540 nm band is thus determined to be 1.2×10^3 dm^3 mol^{-1} cm^{-1}.

The rate constant for the reaction of •OH radicals with $C_{60}(OH)_{18}$, determined by competition kinetics using KSCN as a standard solute ($k_{\bullet OH+SCN^-} = 1.1 \times 10^{10}$ dm^3 mol^{-1} cm^{-1}), was 2.3×10^9 dm^3 mol^{-1} s^{-1}. The value is close to that determined by formation kinetic studies. Although the λ_{max} of the transient species formed from SCN^- and $C_{60}(OH)_{18}$ on reaction with •OH radicals are not very far off (480 and 540 nm), the relative large difference in the ε_{max} values (7580 and 1200 dm^3 mol^{-1} cm^{-1}) would lower the possibility of interference in the determination of the bimolecular rate constant value. These results suggest that all the •OH radicals are

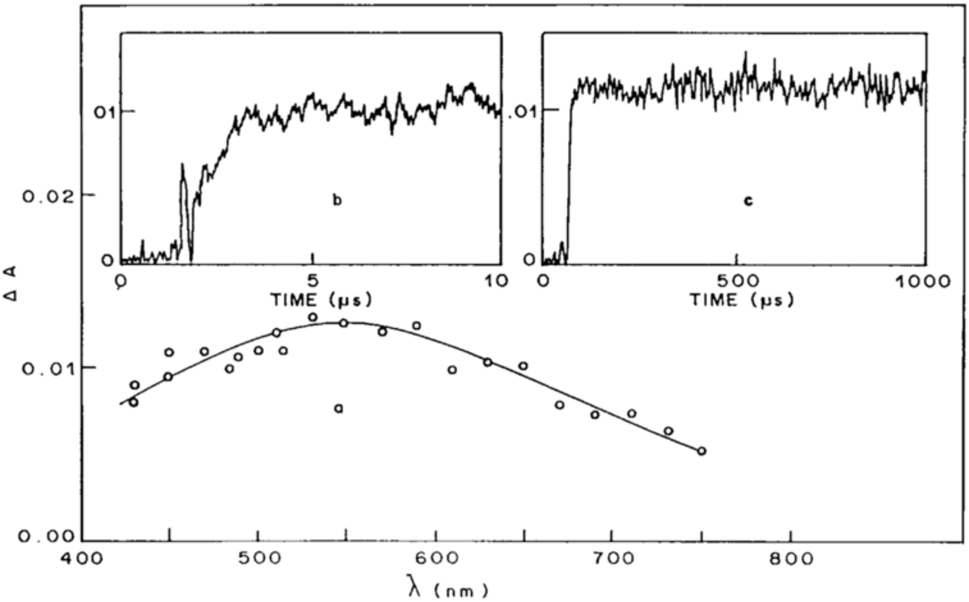

Figure 4. Transient optical absorption spectrum obtained on pulse radiolysis of N_2O saturated aqueous solution of $C_{60}(OH)_{18}$, (3.7×10^{-4} mol dm^{-3}, pH = 6.0). Absorption-time signal at 540 nm showing its b- growth and c- decay. Dose = 15 Gy per pulse.

essentially reacting with $C_{60}(OH)_{18}$ to form the transient band (λ_{max} = 540 nm).

The hydroxyl radicals are known to react by addition, abstraction and electron transfer mechanism. In order to distinguish between these possibilities, pulse radiolysis studies were carried out with specific one-electron oxidants such as $Cl_2^{\bullet-}$ (E^o = 2.1 V) and $SO_4^{\bullet-}$ (E^o = 2.4 V). The decay of these bands remained unaffected on addition of $C_{60}(OH)_{18}$ (4.5×10^{-4} mol dm^{-3}), showing that electron transfer is not possible from $C_{60}(OH)_{18}$ to the one-electron oxidants ($Cl_2^{\bullet-}$, $SO_4^{\bullet-}$). Therefore the absorption band observed on reaction of $^{\bullet}OH$ radicals with the solute (Figure 4a) is not due to its radical cation. It could be due to OH-adduct. The decay of the transient absorption band (λ = 540 nm) remained unaffected in N_2O saturated and aerated solutions of $C_{60}(OH)_{18}$ (Figure 5). The difference was in the initial absorbance which is due to lower $^{\bullet}OH$ radical yield in aerated solutions. These results also support the assignment of the transient band to OH-adduct. $C_{60}(OH)_{18}$ has been shown to act as a free radical scavenger [29], therefore, it is possible that the band is due to a species formed on scavenging of $^{\bullet}OH$ radicals by $C_{60}(OH)_{18}$.

The reaction of $^{\bullet}H$ and $O^{\bullet-}$ could be studied at pH = 1 and 13 respectively. But at these pHs, the solute was not stable and the reactions could not be investigated.

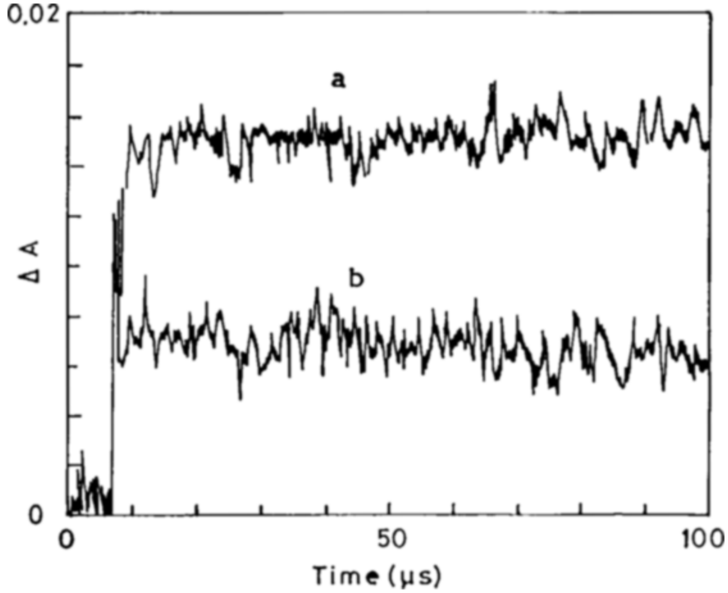

Figure 5. Absorption-time signal (λ = 540 nm) obtained on pulse radiolysis of aqueous solution of $C_{60}(OH)_{18}$ (1.5×10^{-3} mol dm^{-3}) in a- N_2O saturated and b- aerated conditions.

CONCLUSIONS

The characteristic absorption bands of C_{60} are not observed in $C_{60}(OH)_{18}$. The charge transfer absorption bands with electron rich amines such as DABCO, hexamine are not observed with $C_{60}(OH)_{18}$. Singlet and triplet excited states of $C_{60}(OH)_{18}$ in water do not show absorption bands in 400 - 900 nm region. The bimolecular rate constant for the reaction of e^-_{aq} is 3×10^8 dm^3 mol^{-1} s^{-1} and the transient species (λ_{max} = 580 nm) is assigned to electron adduct. The hydroxyl radicals react with a bimolecular rate constant of 2×10^9 dm^3 mol^{-1} s^{-1} and the transient species (λ_{max} = 540 nm) is assigned to OH-adduct.

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