Triplet state and phenoxyl radical formation of 3, 4-methylenedioxy phenol: a combined laser flash photolysis and pulse radiolysis study

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ABSTRACT: Formations of triplet state, molecular cation radical, and phenoxyl radical of 3,4-methylenedioxy phenol (sesamol, SOH) in organic solvents have been investigated by laser photolysis as well as pulse radiolysis techniques. Photolysis of SOH in cyclohexane has been found to produce both triplet state ($\lambda_{max} \sim 480\,nm$) and phenoxyl radical (425–430 nm) of SOH by mono-photonic processes. However, radical cation ($\lambda_{max} = 450\,nm$) and phenoxyl radical of SOH have been observed on radiolysis in cyclohexane. Further, radiolysis of SOH in benzene has been found to produce phenoxyl radical only. Mechanism of phenoxyl radical formation by photo-excitation of SOH has been studied and triplet energy level of SOH is estimated to lie between 1.85 and 2.64 eV. Copyright © 2007 John Wiley & Sons, Ltd.
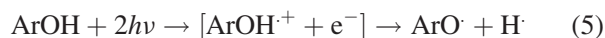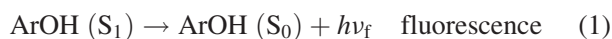
KEYWORDS: sesamol; radiolysis; photolysis; radical cation; triplet

INTRODUCTION

Photochemical reactions of phenyl derivatives, especially phenols, are of importance because of their widespread use and resemblance to aromatic amino acids. Photo-dissociation of alkylbenzenes is known to yield benzyl radical.[1] Extensive investigations on the formation of benzyl and its isovalent radicals have been reported earlier in the context of molecular structure and excited state dynamics.[2] Phenols, which are isovalent to alkylbenzenes, are extensively used as free radical scavengers and light quenchers. Porter *et al.*[3] first reported absorption spectra of phenoxyl radical produced on photolysis. Absorption spectra of phenoxyl radicals were further confirmed by pulse radiolysis[4] and photolysis of phenol, anisole, and their derivatives.[2,5,6] Carbonyl sensitized formation of phenoxyl radical in laser flash photolysis is also well known.[7]

Photo-excitation of phenols can lead to fluorescence, phosphorescence, photo-ionization, phenoxyl radical formation, etc. [Eqns (1–6)]. These processes depend on the reaction conditions like solvent, wavelength of excitation, intensity of excitation beam, etc.[8–17] In organic solvents, photolytic formation of phenoxyl radical[15,16] is assumed to originate from the first excited singlet state by direct O—H bond dissociation Eqn (4)] at low excitation energy and via the deprotonation of the intermediate phenol radical cation [Eqn (5)] at higher excitation energies ($>0.5\,mJ/pulse$) of laser pulses.

$$\text{ArOH (S}_1) \rightarrow \text{ArOH (S}_0) + h\nu_f \quad \text{fluorescence} \quad (1)$$

$$\rightarrow \text{ArOH (S}_0) \quad \text{Internal conversion} \quad (2)$$

$$\rightarrow \text{ArOH (T}_1) \quad \text{Intersystem crossing} \quad (3)$$

$$\rightarrow \text{ArO}^{\cdot} + \text{H}^{\cdot} \quad \text{dissociation} \quad (4)$$

$$\text{ArOH} + 2h\nu \rightarrow [\text{ArOH}^{\cdot+} + e^-] \rightarrow \text{ArO}^{\cdot} + \text{H}^{\cdot} \quad (5)$$

$$\text{ArOH}^{T} + \text{ArOH} \rightarrow \text{ArO}^{\cdot} + (\text{H} - \text{ArOH})^{\cdot} \quad (6)$$

Grabner *et al.*[14] have reported formation of phenoxyl radical from photo-excited S_1 state of phenols derivatives in organic solvents. Similarly, Hermann *et al.*[15] have also reported formation of phenoxyl radical ($\Phi < 10\%$) explicitly from photo-excited S_1 state of phenols and not from the triplet state by using 266 nm photons and low energy ($<0.5\,mJ/pulse$). The triplets of phenol and phenol derivatives are reported to have life times of a few microseconds; weak absorption in the visible range ($\sim$430 nm) and varying quantum yields depending on the substituent.[14,15,17] It has been also shown that ArO—H bond dissociation is a purely mono-photonic process in

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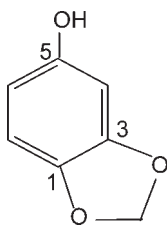
Scheme 1. Sesamol (SOH)

organic solvents.[14] Earlier, Kajii and Obi[2] have also shown that photo-dissociation of phenol does not take place through multiphoton process but in a mono-photonic process by pre- and/or direct-dissociation.

In the present paper, kinetics and mechanism of formation of transients of 3,4-methylenedioxy phenol, sesamol, produced on photolysis and radiolysis in organic solvents have been reported (Scheme 1). Sesamol (SOH) is a constituent of sesame seed oil, which imparts antioxidant activity and thermal stability to the oil. The study is of importance due to its proposed use as a photo-protector.[18,19]

EXPERIMENTAL

Laser flash photolysis

The laser flash photolysis setup (7 ns, 266 nm excitation) at Interdisciplinary Group, Time Resolved Spectroscopy, University of Leipzig, Leipzig, was used and is described elsewhere.[15]

Fluorescence studies

Ground-state absorption measurements were made with a Shimadzu UV-160A UV–visible spectrophotometer. Steady state fluorescence experiments were carried out with a Hitachi F-4010 fluorescence spectrophotometer fitted with a Hamamatsu R-928 photomultiplier tube. Fluorescence lifetime measurements were performed with a time domain fluorescence spectrometer (model 199, Edinburgh Instruments, UK) which uses a gated hydrogen discharge lamp as the excitation source (repetition rate of 30 kHz and FWHM ~ 1 ns) and EG&G ORTEC single-photon-counting data acquisition system, interfaced with a LSI-11/23 (Plessey, UK) computer. The observed fluorescence decay function $F(t)$ is a convolution of the true fluorescence decay function $G(t) = \sum_i B_i \exp(-t/\tau_i)$ and the instrument response function $I(t)$ and was analyzed by using an appropriate re-convolution program employing a non-linear iterative least squares fitting method. Here B_i is the pre-exponential factor and τ_i the fluorescence lifetime for the ith component.

Electron pulse radiolysis

The pulse radiolysis setups at Interdisciplinary Group, Time Resolved Spectroscopy, University of Leipzig, Leipzig, Germany (1 MeV, 15 ns electron pulse) and at Radiation & Photochemistry Division, Bhabha Atomic Research Center, Mumbai (7 MeV, 50 ns electron pulse) were used and are described elsewhere.[20,21]

The uncertainty in the measurements of wavelength, transient absorption, lifetime, and rate constants are 5 nm, $\sim$10%, $\sim$10%, and $\sim$15%, respectively.

Chemicals

Sesamol of highest commercially available purity (>98%) from Fluka was used as received. All the solvents were of spectroscopy grade. All other chemicals were of Analytical Reagent grade. N_2 and O_2 used were of highest available purity (99%).

RESULTS AND DISCUSSION

In the present work, absorption and fluorescence of SOH in H_2O, cyclohexane (C_6H_{12}), and benzene (C_6H_6) have been studied before time resolved studies to understand the solvent effect on these parameters and are reported in Table 1. SOH has been found to have fluorescence maximum (λ_f) at 335 nm ($\lambda_{ex} = 303$ nm) with $\tau_f \sim 0.9$ ns in cyclohexane. It can be seen from Table 1 that increase in solvent dipole moment or polarity function decreases τ_f. Reduction in fluorescence lifetime (τ_f) with increase in solvent dipole moment or polarity function from C_6H_{12} (C_6H_6) $\rightarrow$ H_2O shows the presence of vibrational de-excitation channels with H_2O molecules because of hydrogen bonding of phenolic and methylenedioxy groups. Similarly, a small red shift in fluorescence maxima with increase in polarity has been also observed which may be due to change in electronic structure of excited state with respect to ground state (figure not shown).

Laser flash photolysis studies

Laser photolysis (7 ns pulse of 5.3 mJ, 266 nm) of de-aerated solution of SOH in cyclohexane produced

Table 1. Photophysical properties of SOH in different solvents

Solvent	Dipole moment (D)	Polarity function (Δf)	λ_{max}^{flu} (nm)	τ_{flu} (ns)
Water	78.54	0.406	345	0.78
Benzene	2.275	0.116	339	0.96
Cyclohexane	2.015	0.0998	335	0.91

absorption spectrum having λ_{max} at 320, 405, 425, and 480 nm at 450 ns after the pulse (Fig. 1A, trace a).

The absorption bands at 320 and 425 nm are similar to those observed earlier for sesamolyl radical (SO·)[22,23] but those at 405 and 480 nm are new absorption bands. Further, laser photolysis in oxygen-saturated solution (a triplet quencher, $E^T = 1\,eV$)[24] produced absorption bands at 320 and 425 nm only and not at 405 and 480 nm (Fig. 1A, trace b). Quenching of absorption bands at 405 and 480 nm by oxygen suggests that these may be due to sesamol triplet. A comparison of curves 'a' and 'b' in Fig. 1A also shows that triplet absorption spectrum of SOH is quite broad.

The absorption band at 480 nm was found to decay faster ($t_m = 2.6\,\mu s$) as compared to that at 425 nm ($t_m = 6.4\,\mu s$) (Fig. 1B). Therefore, the difference spectrum (trace c in Fig. 1A) has been drawn to get the absorption spectrum of sesamol triplet (SOH^T). The spectrum beyond 10 μs has been found to be similar to that of phenoxyl radical of SOH (sesamolyl radical, SO·) observed earlier.[22,23] The decay kinetics of the absorption band at 480 nm was further investigated by laser photolysis (7 ns pulse of 5.3 mJ, 266 nm) of SOH in cyclohexane under different concentrations of oxygen (Fig. 1C). It can be seen from Fig. 1C that the decay rate of transient having λ_{max} at 480 nm increases with increase

in the concentration of oxygen. This confirms that absorption band at 480 nm is due to sesamol triplet, which is quenched by oxygen in a concentration dependent manner with $k = 1.15 \times 10^9\,dm^3\,mol^{-1}\,s^{-1}$. Further, the measured triplet state lifetime for SOH in organic solvent (cyclohexane) is close to those reported for phenol derivatives in aqueous solution.[10]

In order to get the value of triplet energy level of SOH, energy transfer from SOH^T to other quenchers has been also studied. Absorption band of SOH^T has been quenched by anthracene (at [SOH]/[anthracene] ~ 10) with a bimolecular rate constant of $1.75 \times 10^{10}\,dm^3\,mol^{-1}\,s^{-1}$ to produce a spectrum of anthracene triplet ($E^T = 1.85\,eV$, $\lambda_{max} = 425\,nm$)[25] (Fig. 2). Energy transfer from SOH^T to anthracene is also evident by the kinetic traces observed at 425 nm in the presence and absence of quencher. A sharp decay in absorption followed by growth at 425 nm observed in the presence of anthracene (inset in Fig. 2) shows energy transfer from SOH^T to anthracene. However, SOH^T has not been quenched by biphenyl ($E^T = 2.85\,eV$).[25] This suggests that energy level of SOH^T lies in between anthracene triplet (1.85 eV) and biphenyl triplet (2.85 eV).[24,25]

The mechanism of formation of SOH^T and SO· has been studied by measuring the absorption at 480 and 425 nm, respectively with increase in excitation energy per laser pulse. A plot of the absorptions at 480 and
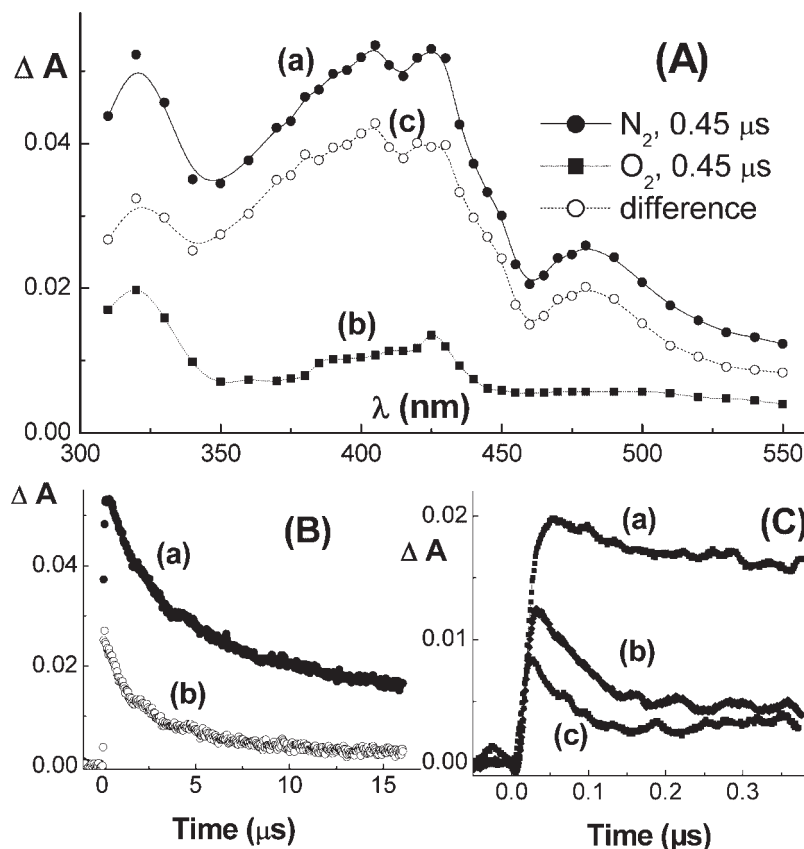

Figure 1. (A) Transient absorption spectrum obtained from photolysis of SOH ($1 \times 10^{-3}\,mol\,dm^{-3}$) in cyclohexane (a) in de-aerated condition, (b) in oxygen-saturated condition, and (c) the difference of spectra (a)–(b). Kinetic traces obtained on photolysis of SOH ($1 \times 10^{-3}\,mol\,dm^{-3}$) in de-aerated cyclohexane: (B) at (a) 425 and (b) 480 nm; (C) 480 nm for (a) de-aerated, (b) aerated, and (c) oxygen-saturated solution
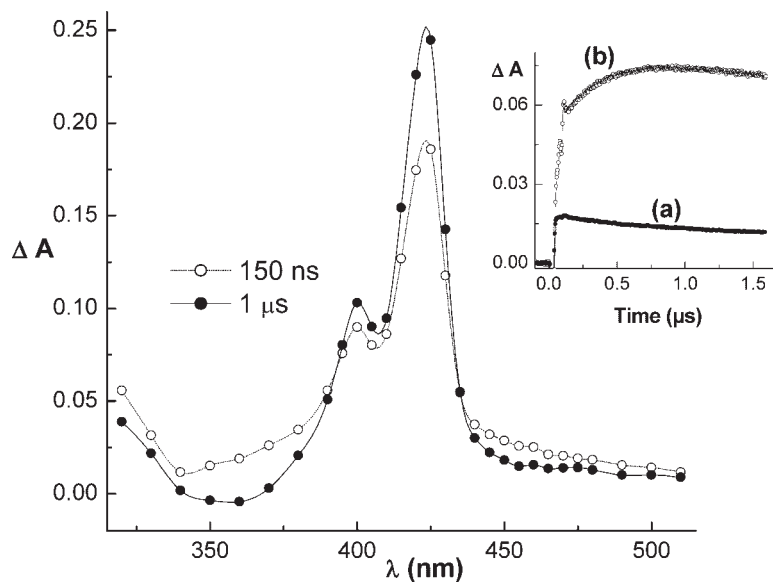
Figure 2. Transient absorption spectrum obtained from photolysis of de-aerated SOH (1.58×10^{-3} mol dm^{-3}) and anthracene (1.6×10^{-4} mol dm^{-3}) in cyclohexane. Inset: Traces at 425 nm from a solution of SOH (1.58×10^{-3} mol dm^{-3}) (a) in absence and (b) in presence of anthracene (1.6×10^{-4} mol dm^{-3}) under identical conditions

425 nm with increase in laser energy from 1 to 10 mJ per pulse (Fig. 3a and 3b) shows a linear fit. Further, a plot of $\log(\Delta A)$ against $\log$(laser power) has been also found to be linear (i.e., $\Delta A \propto$ (laser power)$^n \Rightarrow n = 1$). This suggests that the processes of triplet as well as radical formation are mono-photonic (from 1 to 10 mJ per pulse) as reported earlier for phenols also.[2,14,15] However, at 15 mJ/pulse energy there is some deviation from linearity suggesting that other mechanisms also occur.

In the present study, SOH^T (405 and 480 nm) as well as SO$^.$ (320 and 425 nm) appeared simultaneously on photolysis of SOH at 0.45 μs after the laser pulse. The absorption bands for SOH^T and SO$^.$ have been produced by mono-photonic processes on laser photolysis at 266 nm and 5.3 mJ per pulse. This suggests simultaneous formation of SOH^T and SO$^.$ [Eqns (3, 4)].[15] The formation of SO$^.$ could also take place by triplet state H-abstraction reaction [Eqn (6)] as observed earlier for SOH in aqueous solution.[13] Photolysis of SOH in organic solvents has been found to produce both triplet and phenoxyl radical of SOH (SO$^.$) which may affect the use of SOH as a photo-protector. In order to further estimate the energy of SOH^T, energy transfer from various sensitizers to SOH has been attempted using pulse radiolysis technique.

Electron pulse radiolysis studies

Pulse radiolysis of de-aerated solution of SOH in cyclohexane produced transient absorption spectrum
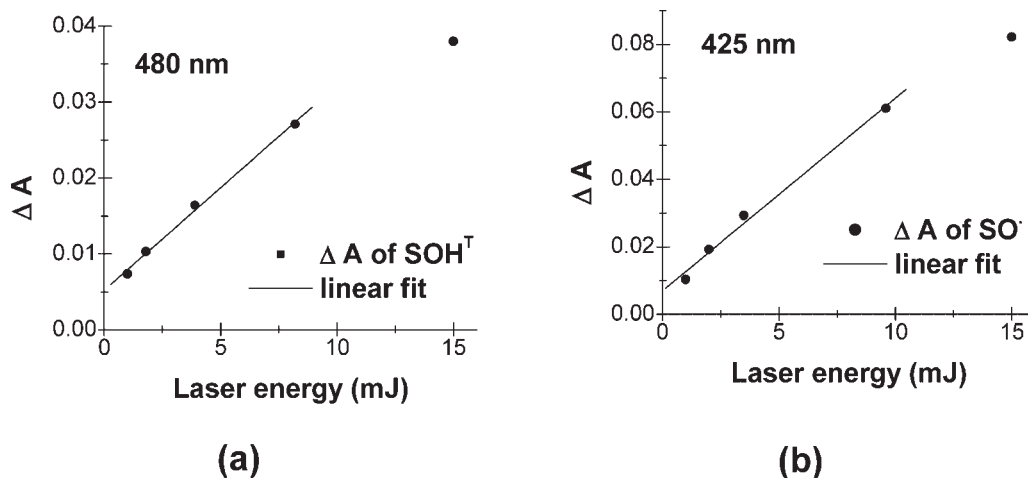

Figure 3. Laser intensity dependence of formation of (a) SOH^T and (b) SO$^.$
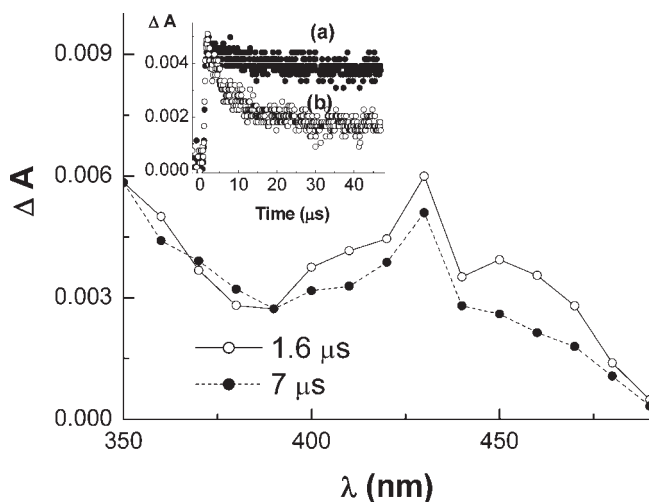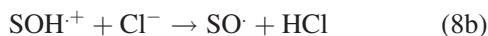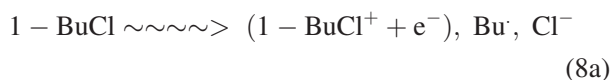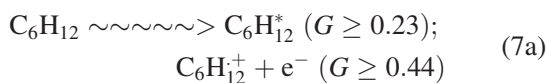
Figure 4. Transient absorption spectrum obtained on electron pulse radiolysis of de-aerated solution of SOH $(1 \times 10^{-2} \, \text{mol dm}^{-3})$ in cyclohexane. Dose $= 40$ Gy. Inset: Absorption traces at (a) 420 nm and (b) 450 nm under similar conditions. Dose $= 40$ Gy

Figure 5. Transient absorption spectrum observed in the pulse radiolysis of de-aerated solution of SOH $(2 \times 10^{-2} \, \text{mol dm}^{-3})$ in benzene. Dose $= 100$ Gy

with maximum at 430 and 450 nm (Fig. 4). Radiolysis of cyclohexane is known to produce excited states and radical cation of solvent molecule [Eqn (7a)], which react with solute to produce solute transients. In an earlier study, solvent radical cation of 1-BuCl has been found to produce SOH$^{\cdot+}$ ($\lambda_{max} = 455$ nm, $t_m \sim 2.2 \, \mu$s) and SO$^{\cdot}$ ($\lambda_{max} = 430$ nm) in the first step followed by deprotonation of SOH$^{\cdot+}$ to produce SO$^{\cdot}$ in the second step.[23] Therefore, radiolysis of SOH in cyclohexane has been assumed to produce sesamol radical cation (SOH$^{\cdot+}$, $\lambda_{max} = 450$ nm) and sesamolyl radical (SO$^{\cdot}$, $\lambda_{max} = 430$ nm) in the same way.

$$C_6H_{12} \sim\sim\sim\sim\sim> C_6H_{12}^* \, (G \geq 0.23);$$
$$C_6H_{12}^+ + e^- \, (G \geq 0.44) \quad (7a)$$

$$C_6H_{12}^+ + SOH \rightarrow C_6H_{12} + SOH^{\cdot+}, \, (SO^{\cdot} + H^+) \quad (7b)$$

$$1 - BuCl \sim\sim\sim\sim> \, (1 - BuCl^+ + e^-), \, Bu^{\cdot}, \, Cl^- \quad (8a)$$

$$SOH^{\cdot+} + Cl^- \rightarrow SO^{\cdot} + HCl \quad (8b)$$

The absorption band at 450 nm due to SOH$^{\cdot+}$ has been found to decay faster than that due to SO$^{\cdot}$ (430 nm) (inset of Fig. 4) in this case also. Longer lifetime of SOH$^{\cdot+}$ ($t_m \sim 5.0 \, \mu$s) has been observed in cyclohexane as compared to that in 1-BuCl ($t_m \sim 2.2 \, \mu$s). This could be due to charge neutralization reaction of SOH$^{\cdot+}$ with Cl$^-$, which is produced in the radiolysis of 1-BuCl solvent [Eqn (8a, b)]. Radiolysis of SOH in cyclohexane has not produced absorption band for SOH^T (Fig. 4).

On the other hand, pulse irradiation of SOH in de-aerated benzene produced a transient absorption spectrum with bands at 330 and 430 nm only (Fig. 5).
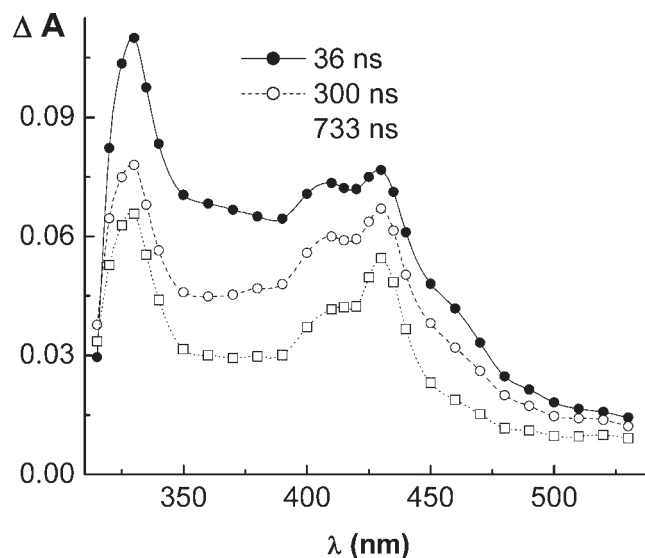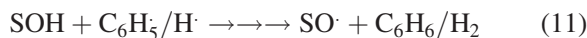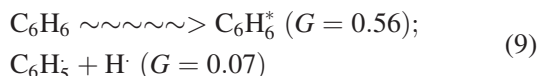
Radiolysis of benzene is known to produce excited singlet state ($G = 0.15 \, \mu$mol J^{-1}, $E = 4.77$ eV, $\tau = 27$ ns), excited triplet state ($G = 0.41 \, \mu$mol J^{-1}, $E = 3.69$ eV, $\tau = 3.4$ ns), and solvent radicals[25–32] [Eqn (9)]. The triplet forms an excimer by coupling with a ground-state benzene molecule, which decays with a lifetime of about 4.9 ns.[30] The excited singlet state is reported to produce molecular hydrogen and acetylene,[31] whereas the excited triplet state is believed to decay to a phenyl radical and H atom.[27,28] The total radical yield (phenyl radical and hydrogen atom) in benzene radiolysis is known to be about 0.07 μmol J^{-1}.[32] Further, pulse radiolysis studies in liquid benzene have shown that the rate coefficient for the reaction of phenyl radicals with the solvent (benzene) is low (3.1×10^5 dm^3 mol^{-1} s^{-1}).

In the present work, absence of absorption band/shoulder of SOH^T ($\lambda_{max} = 480$ nm) in the radiolysis of SOH (2×10^{-2} mol dm^{-3}) in benzene could be due to energy transfer process [Eqn (10)] followed by fast H-atom abstraction by SOH triplet [Eqn (6)]. The radiation dose (100 Gy) used in the present work coupled with radical yield in benzene radiolysis (0.07 μmol J^{-1}) suggest that the phenyl and H radical produced in the radiolysis of benzene react with SOH to directly produce SO$^{\cdot}$ radical (330, 430 nm) [Eqn (11)]. An overlapping absorption has been observed in the 300–500 nm region with absorption band of SO$^{\cdot}$ (330, 430 nm). This overlapping absorption in the 350–500 nm region could be due to the absorption of phenyl radical (C_6H_5) adduct of SOH in benzene. This is assumed on the basis of formation of solvent radicals ($C_6H_5^{\cdot}$, H$^{\cdot}$) in the radiolysis of benzene.

Sesamolyl radical SO$^{\cdot}$ has been found to decay, like other phenoxyl radicals, in a second order manner

with $2k = 3 \times 10^9 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$. Radiation-induced formation of excited states and radicals with their yield for benzene are shown in Eqn (9).

$$
\begin{aligned}
&C_6H_6 \sim\sim\sim\sim\sim> C_6H_6^* \; (G = 0.56); \\
&C_6H_5^\cdot + H^\cdot \; (G = 0.07)
\end{aligned} \tag{9}
$$

$$
C_6H_6^* + SOH \rightarrow C_6H_6 + SOH^* \tag{10}
$$

$$
SOH + C_6H_5^\cdot/H^\cdot \rightarrow\rightarrow\rightarrow SO^\cdot + C_6H_6/H_2 \tag{11}
$$

The quantities in the parenthesis are radiation chemical yield in the unit of µmol per Joule of absorbed energy. The yield of SO· on radiolysis of SOH in cyclohexane and benzene has been found to be 0.027 and 0.138 µmol J^{-1} of absorbed energy. This calculation is based on the assumption that molar absorption coefficient of SO· is the same ($\varepsilon_{430 \, nm} = 5540 \, \mathrm{mol^{-1} \, dm^3 \, cm^{-1}}$) as that observed in aqueous medium.[22] Similarly, the yield of SOH·$^+$ in the radiolysis of SOH in cyclohexane has been found to be 0.02 µmol J^{-1} of absorbed energy. This has been calculated by taking molar absorption coefficient of SOH·$^+$ in cyclohexane similar to that observed in 1-BuCl ($\varepsilon_{455 \, nm} = 4500 \, \mathrm{mol^{-1} \, dm^3 \, cm^{-1}}$).[23] There is no correspondence of G-values of SO· or SOH·$^+$ with the G-values of either excited state or radical of the solvent. This difference in G-values further suggests that excited state of solvent directly produces SO· radical as observed in the photolysis of SOH in cyclohexane (reported in earlier section).

Energy transfer studies

Energy transfer from triplet state of benzophenone ($E^T = 3.03 \, \mathrm{eV}$), biphenyl ($E^T = 2.85 \, \mathrm{eV}$), and naphthalene ($E^T = 2.64 \, \mathrm{eV}$) to SOH has been also studied to get triplet state energy of SOH.[24,25] These sensitization studies have been performed in benzene solutions and the energy transfer rate constants have been measured by following the decay of the absorption of sensitizing triplet. A step-wise energy transfer occurs from benzene to sensitizer followed by sensitizer to SOH. The observed rate constants have been found to decrease with decrease in triplet energy of the sensitizers. The measured rate constants for energy transfer from triplet state of benzophenone and naphthalene to SOH are 5.4×10^9 and $2.0 \times 10^6 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$, respectively. It has to be noted that no increase in absorption has been observed at 430 nm (λ_{max} of SO·) in energy transfer studies suggesting against an H atom abstraction by the sensitizers.

SUMMARY

SOH has been found to produce excited states and reactive phenoxyl radicals on photolysis in organic solvents. It has been found to have λ_f at 335 nm

($\lambda_{ex} = 303 \, \mathrm{nm}$) with $\tau_f \sim 0.9 \, \mathrm{ns}$ in cyclohexane. Laser photolysis of SOH in cyclohexane produced triplet (SOH^T, $t_m = 2.6 \, \mu\mathrm{s}$) and phenoxyl radical (SO·) of SOH. SOH^T is quenched by anthracene with $k = 1.75 \times 10^{10} \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$. Formation of SOH^T and SO· radical in the photolysis of sesamol in cyclohexane has been found to be mono-photonic processes. On the other hand, pulse radiolysis of SOH in cyclohexane produced radical cation SOH·$^+$ and SO· radical. Radiolysis of SOH in benzene produced SO· only. Energy transfer from triplet state of benzophenone and naphthalene to SOH has been found to take place at 5.4×10^9 and $2.0 \times 10^6 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$, respectively. Energy level of triplet state of SOH is estimated to lie between 1.85 and 2.64 eV.

Acknowledgements

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