Radiolytically generated benzene triplets as sensitizers for energy and combined electron/proton transfer processes

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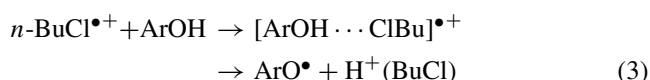
Abstract

Pulse radiolysis technique has been employed to investigate energy and electron transfer reactions involving triplets of naphthols and hydroxybiphenyls. The transient absorption spectra obtained on pulse radiolysis of N_2-saturated solution of naphthols and hydroxybiphenyls in benzene are assigned to triplet–triplet absorption. It was found that biphenyl triplets undergo energy transfer to naphthols and hydroxybiphenyls forming the acceptor triplets. On the other hand, benzophenone triplets, favor electron transfer followed by H^+ transfer reaction forming benzophenone ketyl radical and phenoxyl radical of the acceptor. An analogous sequence mimics with 2-naphthol triplets and using benzophenone, acetophenone or chloranil as electron acceptor. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Owing to the low ionization potential and weak O–H bond, phenols and their bulky substituted derivatives are used as stabilizers in polymer, food and oil industry [1,2]. The antioxidant action of phenol is understood in terms of electron and $H^\bullet$ atom donor ability [3–6]. The electrons generated on radiolysis of a non-polar solvent such as n-butyl chloride (n-BuCl) are immediately scavenged by dissociative electron capture process to yield Cl^-. The highly mobile positively charged holes moves through the solvent and are localized as solvent radical cation (reaction 1). Radiolysis of phenolic compounds, ArOH, (phenols, naphthols, hydroxybiphenyls) in n-butyl chloride gave evidence for the formation of solute radical cation (reaction 2) and phenoxyl radicals via a special encounter geometry controlled state (reaction 3) [7–9].

$$n\text{-BuCl} \rightarrow n\text{-BuCl}^{\bullet+} + e_{solv}^- \tag{1}$$

$$n\text{-BuCl}^{\bullet+} + \text{ArOH} \rightarrow \text{ArOH}^{\bullet+} + n\text{-BuCl} \tag{2}$$

$$n\text{-BuCl}^{\bullet+} + \text{ArOH} \rightarrow [\text{ArOH} \cdots \text{ClBu}]^{\bullet+}$$
$$\rightarrow \text{ArO}^\bullet + \text{H}^+(\text{BuCl}) \tag{3}$$

In contrast to this, benzene because of the extremely high mobility of the primarily formed ions, singlet and triplet excited states dominate (reaction 4) [10–13]. Mostly the excited singlet and triplet species are produced directly via geminate ion recombination in the primary process of benzene radiolysis (reaction 4).

$$\text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_6^+ + e^-) \rightarrow {}^3(\text{C}_6\text{H}_6)^* \tag{4}$$
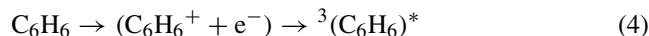
Benzene singlet immediately forms excimer and intersystem crossing of benzene would not be important. On the other hand, radiolysis of N_2-saturated neutral aqueous solution leads to the formation of three highly reactive species ($H^\bullet$, $^\bullet OH$, e_{aq}^-) in addition to the formation of less reactive or inert molecular products (H_2, H_2O_2) (reaction 5) [14].

$$\text{H}_2\text{O} \rightarrow \text{H}^\bullet, {}^\bullet\text{OH}, e_{aq}^-, \text{H}_2, \text{H}_2\text{O}_2, \text{H}_3\text{O}^+ \tag{5}$$
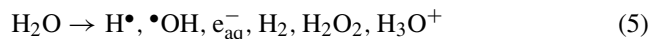
In the pulse radiolysis of benzene, Thomas and Mani [12] found benzene biradicals and singlet excimers as products of the original electronically excited states. In laser photolysis of benzene, its triplet could be characterized by Bensasson et al. [11] as a very short-lived intermediate, decaying under the formation of a biradical (reaction 6) with $k_6 = 1.8 \times 10^7$ dm^3 mol^{-1} s^{-1}.

$$^3(\text{C}_6\text{H}_6)^* + \text{C}_6\text{H}_6 \rightarrow (\text{C}_6\text{H}_6)_2^{\bullet\bullet} \tag{6}$$
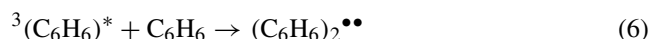
Pulse radiolysis of N_2-saturated benzene (Fig. 1) showed absorption bands at 500 (singlet excimer) and 320 nm (biradical). The lifetime of benzene singlet, which is considered
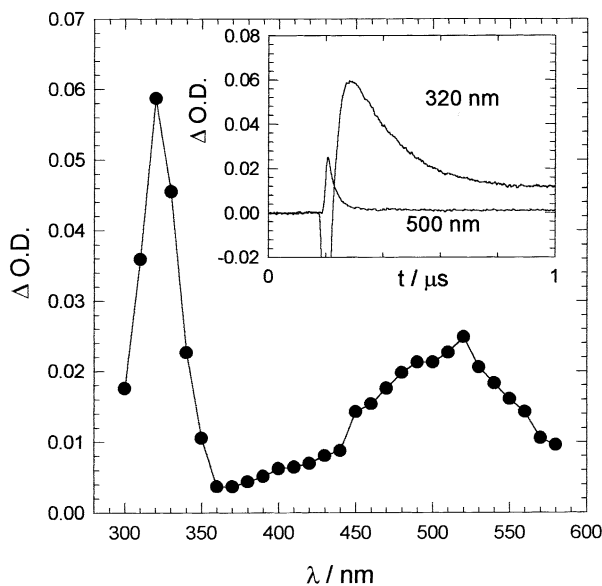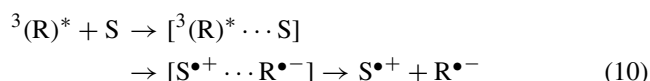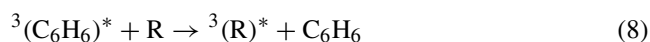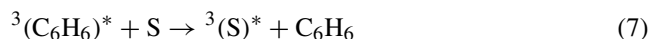
Fig. 1. Transient absorption spectra obtained on pulse radiolysis of N_2-saturated benzene; 300–360 nm region — 80 ns and 370–580 nm region — 14 ns after the pulse. Inset show absorption–time profiles at 320 and 500 nm.

as that of excimer, is about 30 ns. Despite of short lifetime of benzene triplet of only a few nanosecond (3.4 ns), using relatively high concentration of the solute (S), the benzene triplet can be used for generating solute triplets (reaction 7). In the presence of a second sensitizer (R), benzene triplet can also serve as sensitizer for generating solute triplets (reactions 8 and 9) subsequently initiating triplet induced electron (reaction 10) and $H^\bullet$ atom transfer (reaction 11) processes.

$$^3(C_6H_6)^* + S \rightarrow {}^3(S)^* + C_6H_6 \tag{7}$$

$$^3(C_6H_6)^* + R \rightarrow {}^3(R)^* + C_6H_6 \tag{8}$$

$$^3(R)^* + S \rightarrow {}^3(S)^* + R \tag{9}$$

$$^3(R)^* + S \rightarrow [^3(R)^* \cdots S]$$
$$\rightarrow [S^{\bullet+} \cdots R^{\bullet-}] \rightarrow S^{\bullet+} + R^{\bullet-} \tag{10}$$

$$[^3(R)^* \cdots S] \rightarrow S(-H)^\bullet + RH^\bullet \tag{11}$$

Therefore, radiolysis of phenolic compounds in benzene can also result in electron transfer processes via benzene triplet. Hydrogen atom transfer reactions of the triplet states of phenolic compounds to aromatic carbonyl compounds can proceed by either hydrogen atom or electron transfer followed by proton transfer process [15–22]. In this paper, we report on pulse radiolysis studies of naphthols and hydroxybiphenyls in benzene and various modes of triplet sensitized reactions with different acceptors are discussed.

2. Experimental

2.1. Chemicals

Naphthols (1- and 2-NpOH) and hydroxybiphenyls (2-, 3- and 4-ByOH) were of high purity and used without

further purification. Benzene (HPLC grade, >99.9%) was obtained from Sigma Chemicals. *n*-Butyl chloride (Merck) was additionally purified by passing it through a column of an activated molecular sieve. Benzophenone was purified by recrystalization. All other chemicals used were also of high purity. Chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone) was obtained from Fluka. Freshly prepared solutions were used for each experiment.

2.2. Pulse radiolysis

Pulse radiolysis experiments at Leipzig were carried out with high energy electron pulses (1 MeV, 16 ns) generated from pulse transformer type accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia). The dose delivered per pulse was measured with an electron dosimeter and was usually around 50 Gy per pulse. The detection of the transient species was carried out by the optical absorption technique, which consist of a pulsed xenon lamp (XBO 900, Osram), a Spectra Pro-500 monochromator (Acton Research Corporation), an IP28 photomultiplier (Hamamatsu Photonics), and a 1 GHz digitizing oscilloscope (TDS 640, Tektronix). Further details are given elsewhere [1].

Pulse radiolysis experiments at BARC were carried out using a linear electron accelerator (Ray Technologies, UK) giving electron pulses of 7 MeV (50 ns) [23,24]. The transient species were monitored using a 450 W xenon arc lamp and a Hamamatsu R-955 photomultiplier as the detector. The photomultier output was digitized using a 100 MHz storage oscilloscope (Iwatsu Model 8123) and analyzed for kinetic informations with an IBM compatible microcomputer. Dosimetery was carried out using an aerated aqueous solution of potassium thiocynate (1×10^{-2} mol dm^{-3}) with a $G\varepsilon$ value of 21,520 dm^3 mol^{-1} cm^{-1} for the transient $(SCN)_2^{\bullet-}$ at 500 nm.

2.3. Laser photolysis

Laser flash photolysis experiments were carried out at Leipzig using the fourth harmonic (266 nm) from a Quanta Ray GCR-11 Nd:YAG laser (Spectra-Physics Lasers). The pulse width (FWHM) was measured to be 3 ns and the pulse energy was 10 mJ. The N_2-saturated solution was continuously flowed through a quartz cell (0.3 cm × 0.3 cm). The probe light of a pulsed 400 W xenon lamp (XBO-400, Osram) passed through a Spectra Pro-275 monochromator (Acton Research Corporation) to a R955 photomultiplier tube (Hamamatsu Photonics). The output signals were recorded on a 500 MHz digitizing oscilloscope (DSA 602 A, Tektronix). All other details are given elsewhere [1].

3. Results and discussion

The radiolysis of benzene produces its triplets with high yield and energy ($E_{T1} = 85$ kcal mol^{-1}) and therefore, can transfer energy to various solutes of lower E_{T1}.
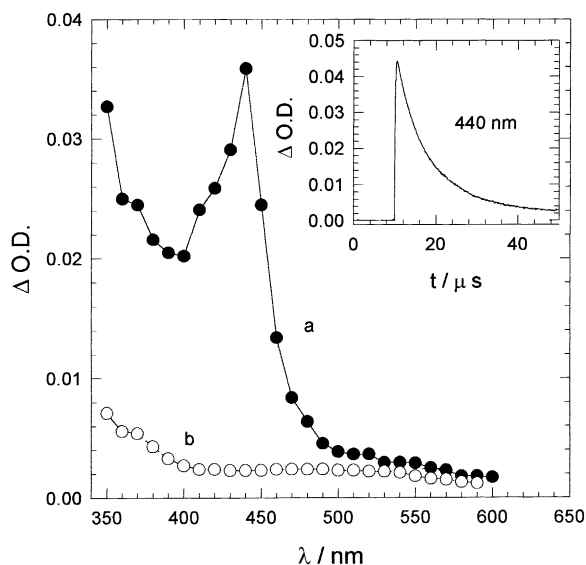
Fig. 2. Transient absorption spectra obtained on pulse radiolysis of 2-NpOH (5×10^{-3} mol dm^{-3}) in benzene under N$_2$ (a); aerated (b) conditions. Inset shows absorption–time profile at 440 nm.

3.1. Formation of triplet states

Fig. 2a shows the transient absorption spectrum obtained on pulse radiolysis of N$_2$-saturated solution of 2-NpOH (5×10^{-3} mol dm^{-3}) in benzene, which exhibits a absorption band at 440 nm. The entire spectrum decayed by first-order kinetics with $k = 1.1 \times 10^5$ s^{-1} (inset of Fig. 2). This transient absorption is completely quenched in O$_2$-saturated solution (Fig. 2b). Therefore, the transient observed in N$_2$-saturated solution is assigned due to a triplet–triplet absorption as it matched with the triplet–triplet absorption spectrum of 2-NpOH produced on laser flash photolysis studies [25]. The confirmative evidence for the formation of triplet state has come from energy transfer studies to and from a solute with well characterized triplet state (see text).

Analogous studies with 1-NpOH, hydroxybiphenyls (Fig. 3) and dihydroxybiphenyls (Fig. 4) have also been carried out and kinetic and spectral parameters of the corresponding states are shown in Table 1. In each case, the transient absorption was quenched in aerated solutions and therefore the species are assigned to

triplet–triplet absorption. The transient absorption spectra obtained on laser flash photolysis of N$_2$-saturated solution of hydroxybiphenyls in cyclohexane (Fig. 5) were same as those obtained on pulse radiolysis (Fig. 3), thus also supporting the assignment to triplet–triplet absorption. Hence, the singlet–triplet intersystem crossing efficiency appears to be very high.

Although, the G value of the excited singlet state of benzene (excimer state) is about one-third the triplet state, but
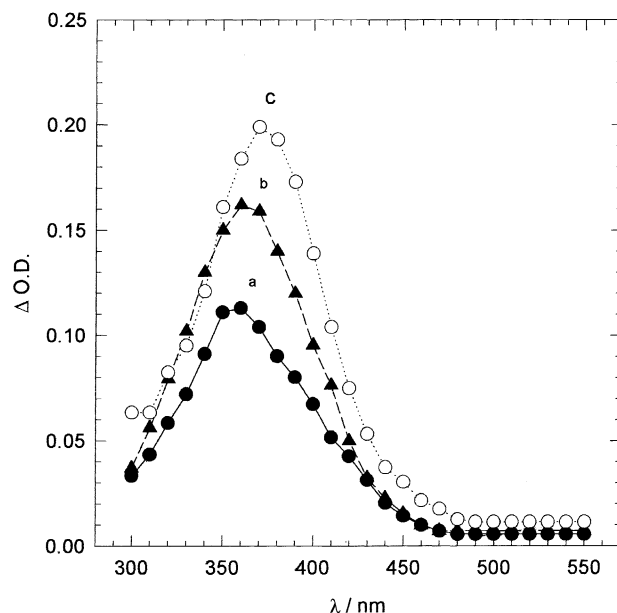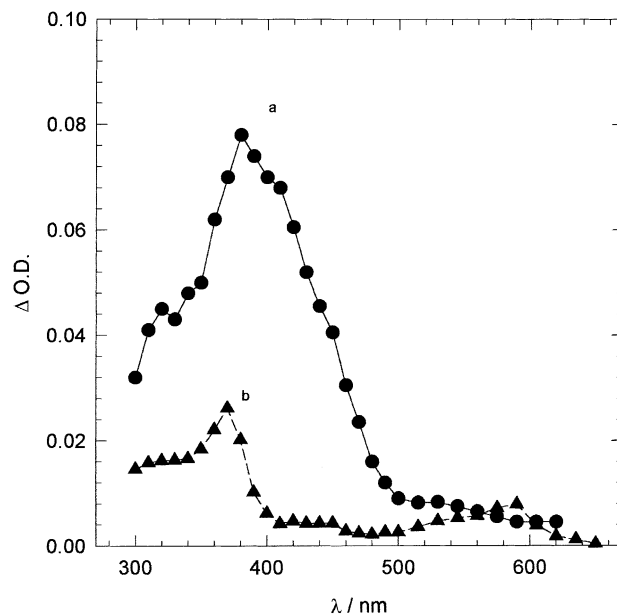

Fig. 3. Transient absorption spectra obtained on pulse radiolysis of N$_2$-saturated solution of 2-ByOH (a); 3-ByOH (b); 4-ByOH (c) in benzene.

Table 1
Kinetic and spectral parameters of the triplets produced on pulse radiolysis of N$_2$-saturated solutions of naphthols and hydroxy biphenyls

No.	Solute	λ_{max} (nm)	k (s^{-1})
1	1-NpOH	370–460	1.1×10^5
2	2-NpOH	440	1.0×10^5
3	2-ByOH	360	1.0×10^5
4	3-ByOH	360	1.1×10^5
5	4-ByOH	370	1.2×10^5
6	2,2′-By(OH)$_2$	410	4.8×10^5
7	4,4′-By(OH)$_2$	370	1.2×10^4

Fig. 4. Transient absorption spectra obtained on pulse radiolysis of N$_2$-saturated solution of 2,2′-By(OH) (a); 4,4′-By(OH)$_2$ (b) in benzene.
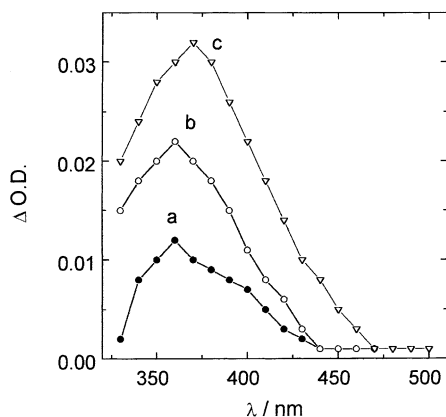
Fig. 5. Transient absorption spectra obtained on laser flash photolysis ($\lambda_{ex} = 266$ nm) of N_2-saturated solution of 2-ByOH (a); 3-ByOH (b); 4-ByOH (c) in cyclohexane.

due to its low lifetime of a few nanosecond, the energy transfer to the solute may be possible only if the energy transfer rate constant is $>10^{10}$ dm^3 mol^{-1} s^{-1} even at high solute concentration (10^{-2} mol dm^{-3}) [26,27]. The solute triplets would then transfer their energy to second acceptor molecule present in the system. The contribution of energy transfer from excited singlet state of benzene to second acceptor molecule is expected to be negligible as the results reported here are in microsecond time scale. In the present studies, reported in this manuscript, energy transfer from benzene takes place to a solute which in turn transfer energy to the second molecule.

3.2. Decay kinetics

The decay kinetics of the transient absorption band, formed on pulse radiolysis of these solutes in benzene was found to be sensitive not only to the presence of oxygen but also to solute concentration and dose rate i.e. to the concentration of the initially formed triplet. Therefore, in addition to the normal first-order decay of the triplets to the ground state (reaction 12), other possible processes contributing to the decay of triplets might be triplet–triplet annihilation (reaction 13) and quenching by the ground state (reaction 14).

$$^3(S)^* \rightarrow S + h\nu \tag{12}$$

$$^3(S)^* + {}^3(S)^* \rightarrow 2S \tag{13}$$

$$^3(S)^* + S \rightarrow 2S \tag{14}$$

$$3(S)^* + O_2 \rightarrow S + O_2{}^* \tag{15}$$

The triplet–triplet annihilation rate constant (k_{13}) was determined by monitoring the decay of triplet absorption band as a function of dose rate at a constant solute concentration. The concentration of the initially formed triplet was determined from the observed transient absorbance at 430 nm ($\varepsilon = 9 \times 10^3$ dm^3 mol^{-1} cm^{-1}). The decay of

the transient absorption band of ^{3}(1-NpOH)* at 430 nm increased from 0.96×10^5 to 2.2×10^5 s^{-1}, when the concentration of the initially formed triplet increased from 1.7×10^{-6} to 8.5×10^{-6} mol dm^{-3}. The value of the triplet–triplet annihilation rate constant was estimated to be 1.8×10^{10} dm^3 mol^{-1} s^{-1}. The value is close to the diffusion control limit in benzene (1.1×10^{10} dm^3 mol^{-1} s^{-1}).

The self quenching rate constant (k_{14}) was determined on monitoring the triplet decay for various solute concentrations. The decay of the transient band of ^{3}(1-NpOH)* at 430 nm increased from 8×10^4 to 4.5×10^5 s^{-1}, when the solute concentration was increased from 2.5×10^{-4} to 5×10^{-3} mol dm^{-3}. From the linear plot of first-order decay rate (k_{obs}) versus solute concentration, the quenching rate constant was calculated to be 7.7×10^7 dm^3 mol^{-1} s^{-1}. The value of the rate constant, obtained on extrapolation of the line upto zero solute concentration was 0.65×10^5 s^{-1}. This can be taken as a rough estimate of the value of the triplet decay rate constant (k_T). The inverse of k_T is the lifetime (15 μs) of ^{3}(1-NpOH)* in the absence of reactions (12) and (14).

The reactivity of ^{3}(1-NpOH)* with oxygen (reaction 15) was determined on following its decay as a function of O_2 concentration. The bimolecular rate constant, determined from the linear plot of first-order rate versus oxygen concentration was 1.5×10^9 dm^3 mol^{-1} s^{-1}.

The absorbance of ^{3}(1-NpOH)* ($\lambda = 430$ nm), formed on pulse radiolysis of N_2-saturated solution in benzene increased with solute concentration reaching a saturation value after 3×10^{-2} mol dm^{-3}. Under these conditions, the entire benzene triplets have transferred their energy to 1-NpOH. Using the value of molar absorptivity of 9000 dm^3 mol^{-1} cm^{-1} for ^{3}(1-NpOH)* at 430 nm, the G value is estimated to be around 0.4.

3.3. Energy transfer studies

When the difference in the triplet energy of donor and acceptor is more than 5 kcal mol^{-1}, the energy transfer is nearly diffusion controlled. The concentration of the donor is kept at least 40 times more than that of acceptor so that initially only the donor triplets are formed, which in turn transfer energy to acceptor molecules [7].

The absorption–time profiles ($\lambda = 380$ nm) obtained on pulse radiolysis of N_2-saturated solution of biphenyl (1×10^{-2} mol dm^{-3}) in benzene, was observed to become faster on addition of low concentration (3×10^{-4} mol dm^{-3}) of 2-NpOH. Simultaneously, the absorption at 440 nm was observed to grow. Time-resolved studies (Fig. 6) indicate energy transfer from biphenyl triplets to 2-NpOH and formation of ^{3}(2-NpOH)* as the transient absorption spectrum (Fig. 6b) matched with that of ^{3}(2-NpOH)*. The energy transfer rate constant was determined from the linear plot of k_{obs} versus solute concentration (inset of Fig. 6) and the value is given in Table 2. Analogous studies have been carried out also with hydroxybiphenyls and the energy transfer
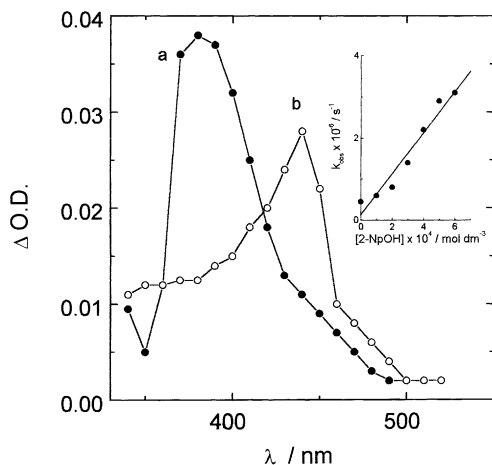
Fig. 6. Transient absorption spectra obtained on pulse radiolysis of N_2-saturated solution of biphenyl (1×10^{-2} mol dm^{-3}) and 2-NpOH (3×10^{-4} mol dm^{-3}) 0.1 μs (a); 0.7 μs (b) after the pulse. Inset shows variation of k_{obs} as a function of 2-NpOH concentration.

rate constant values are given in Table 2. In each case, the transient absorption spectrum obtained on energy transfer from donor to the acceptor matched with that of known acceptor triplet (see Figs. 2 and 3).

The triplet energy of 2-NpOH (54 kcal mol^{-1}) is higher than that of anthracene triplet (44 kcal mol^{-1}) and, therefore, 2-NpOH triplets should be able to transfer energy to anthracene. Hence, on addition of low concentration of anthracene, the decay of 2-NpOH triplet at 440 nm became faster and an energy transfer rate constant of 1.5×10^9 dm^3 mol^{-1} s^{-1} (Table 2) was determined.

3.4. Triplet sensitized electron/H$^+$ transfer reactions

Benzophenone (BP) has a first triplet energy of 68 kcal mol^{-1} and exhibits a $T_1–T_n$ absorption at $\lambda_{max} =$ 330 and 525 nm. By reason of sample self absorption, in our experiments, the UV band could not be seen. The transient absorption band obtained on pulse radiolysis of N_2-saturated solution of benzophenone (1×10^{-2} mol dm^{-3}) in benzene showed accelerated decay on addition of low concentrations

Table 2
Bimolecular triplet energy transfer rate constants

No.	Donor	Acceptor	k ($\times 10^{-9}$) (dm^3 mol^{-1} s^{-1})
1	Biphenyl	2-NpOH	4.6
2	Biphenyl	1-NpOH	5.0
3	p-Terphenyl	2-ByOH	3.7
4	p-Terphenyl	3-ByOH	4.1
5	p-Terphenyl	4-ByOH	3.1
6	p-Terphenyl	2,2′-By(OH)$_2$	2.5
7	p-Terphenyl	4,4′-By(OH)$_2$	3.3
8	2-NpOH	Anthracene	1.5[a]

[a] Determined over a narrow range of acceptor concentration due to close proximity of triplet absorption bands of donor and acceptor.
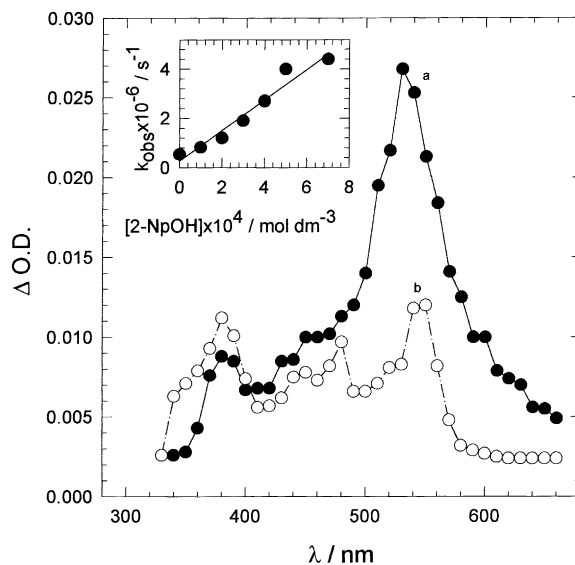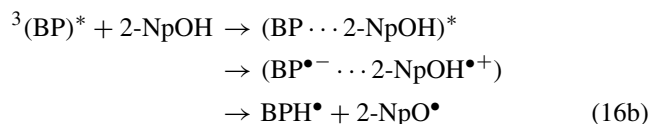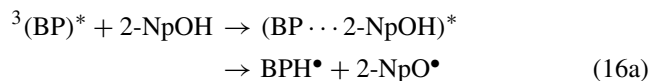

Fig. 7. Transient absorption spectra obtained on pulse radiolysis of N_2-saturated solution of benzophenone (1×10^{-2} mol dm^{-3}) and 2-NpOH (5×10^{-4} mol dm^{-3}) 0.1 μs (a); 0.7 μs (b) after the pulse. Inset shows variation of k_{obs} as a function of 2-NpOH concentration.

of 2-NpOH $(1–7) \times 10^{-4}$ mol dm^{-3}. The rate constant, determined from the linear plot of pseudo-first-order rate (k_{obs}) versus 2-NpOH concentration (inset of Fig. 7), was 5.4×10^9 dm^3 mol^{-1} s^{-1}. According to products derived of 2-NpOH, transient absorption bands at 380, 470 and 550 nm (Fig. 7b) appeared. The transient absorption bands at 380 and 470 nm match with those of 2-NpO$^\bullet$ radical. Furthermore, the benzophenone ketyl radical is known to have an absorption band around 550 nm. So the product transient spectrum (Fig. 7b) could be understood to consist of 2-NpO$^\bullet$ and benzophenone ketyl radical absorptions, formally explained by H$^\bullet$ atom transfer from 2-NpOH to the benzophenone triplet (reaction 16). The intermediate encounter complex gives rise for formation of 2-NpO$^\bullet$ and benzophenone ketyl either directly (reaction 16a) or via an encounter contact ion-pair complex (reaction 16b) with H$^+$ transfer.

$$^3(BP)^* + 2\text{-NpOH} \rightarrow (BP \cdots 2\text{-NpOH})^*$$
$$\rightarrow BPH^\bullet + 2\text{-NpO}^\bullet \qquad (16a)$$

$$^3(BP)^* + 2\text{-NpOH} \rightarrow (BP \cdots 2\text{-NpOH})^*$$
$$\rightarrow (BP^{\bullet-} \cdots 2\text{-NpOH}^{\bullet+})$$
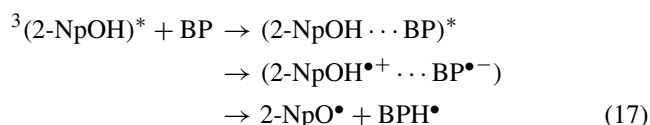$$\rightarrow BPH^\bullet + 2\text{-NpO}^\bullet \qquad (16b)$$

H$^\bullet$ atom abstraction by BP triplet is an activation energy controlled process and in ethanol as solvent, it takes place with a rate constant of 1.2×10^7 dm^3 mol^{-1} s^{-1} [20]. The rate constant determined in the present case looks diffusion controlled ($k_{16} = 5.4 \times 10^9$ dm^3 mol^{-1} s^{-1}). So it would appear to explain the reaction mechanism with electron transfer and immediately following proton transfer (reaction 16b).

Table 3
Triplet sensitized electron/H$^\bullet$ atom transfer rate constants

No.	Donor	Acceptor	$k \ (\times 10^{-9})$ $(\mathrm{dm^3 \, mol^{-1} \, s^{-1}})$
1	Benzophenone	2-NpOH	5.4
2	Benzophenone	1-NpOH	5.0
3	2-NpOH	Benzophenone	1.0
4	1-NpOH	Benzophenone	2.8
5	Chloranil	2-NpOH	5.6
6	Chloranil	1-NpOH	4.7
7	1-NpOH	Chloranil	4.5
8	2-NpOH	Chloranil	6.3
9	Benzophenone	2-ByOH	3.5
10	Benzophenone	3-ByOH	2.1
11	Benzophenone	4-ByOH	2.9
12	Benzophenone	2,2′-By(OH)$_2$	4.1
13	Benzophenone	4,4′-By(OH)$_2$	3.3
13	Acetophenone	2-NpOH	2.5
14	2-NpOH	Acetophenone	1.8
15	Chloranil	3-ByOH	5.2
16	3-ByOH	Chloranil	4.7
17	3-ByOH	Benzophenone	1.1

An analogous process is expected to take place between naphthol triplets and benzophenone. This process was studied on monitoring the decay of naphthol triplet ($\lambda = 440 \, \mathrm{nm}$), formed on pulse radiolysis of N$_2$-saturated solution of 2-NpOH ($5 \times 10^{-2} \, \mathrm{mol \, dm^{-3}}$) in benzene in the presence of low concentration of benzophenone ($2 \times 10^{-3} \, \mathrm{mol \, dm^{-3}}$). From the accelerated decay of 2-NpOH triplet, a rate constant of $1 \times 10^9 \, \mathrm{dm^3 \, mol^{-1} \, s^{-1}}$ was determined (Table 3). In course of this reaction transient absorption bands at 380, 470 and 550 nm appeared. The bands at 380 and 470 nm match with that of 2-NpO$^\bullet$ radical whereas the band at 550 nm is assigned to that of the benzophenone ketyl radical. This is coincident with reaction sequence 17.

$$^3(2\text{-NpOH})^* + BP \rightarrow (2\text{-NpOH} \cdots BP)^*$$
$$\rightarrow (2\text{-NpOH}^{\bullet +} \cdots BP^{\bullet -})$$
$$\rightarrow 2\text{-NpO}^\bullet + BPH^\bullet \qquad (17)$$

The energy transfer rate constant values (Table 3) are observed to remain independent of energy difference between donor and acceptor. The triplet energy of 2-NpOH ($54 \, \mathrm{kcal \, mol^{-1}}$) is less than that of benzophenone ($68 \, \mathrm{kcal \, mol^{-1}}$) and still electron/H$^+$ transfer is observed. This is due to the formation of an intermediate encounter complex and contact ion-pair complex. The electron/H$^+$ transfer is taking place through these intermediates. The high electron affinity of chloranil (see text) has shown high rate constant value and thus support the results that electron/H$^+$ transfer is taking place through these intermediate encounter and contact ion-pair complex.

Because of its high electron affinity, chloranil (CA; 2,3,5,6-tetrachloro-1,4-benzoquinone) is known to undergo easily triplet sensitized electron transfer reaction. The transient absorption spectra obtained on pulse radiolysis of N$_2$-saturated solution of 2-NpOH ($1 \times 10^{-2} \, \mathrm{mol \, dm^{-3}}$)
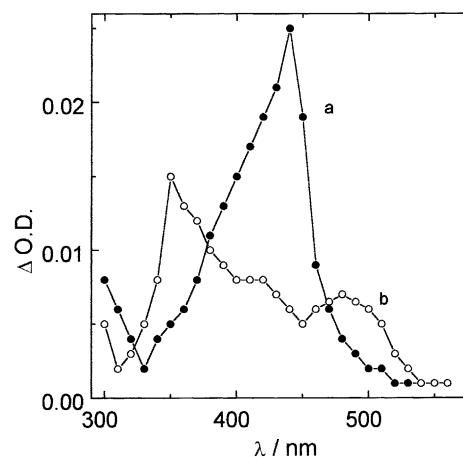

Fig. 8. Transient absorption spectra obtained on pulse radiolysis of N$_2$-saturated solution of 2-NpOH ($1 \times 10^{-2} \, \mathrm{mol \, dm^{-3}}$) and acetophenone ($3 \times 10^{-4} \, \mathrm{mol \, dm^{-3}}$) 0.1 μs (a); 0.7 μs (b) after the pulse.

in benzene containing CA ($6 \times 10^{-4} \, \mathrm{mol \, dm^{-3}}$), showed primarily 2-NpOH triplet at 440 nm and with its decay absorption bands at 360, 440 and 480 nm and a long tail to the red region appeared. The bands at 360 and 480 nm corresponds well to those of 2-NpO$^\bullet$ radical. The 440 nm band and the flat tail between 500 and 600 nm is due to a semiquinone radical (CAH$^\bullet$) formed analogous to reaction sequence (17) i.e. by electron transfer from 2-NpOH triplet to CA and subsequent H$^+$ transfer [28]. The corresponding rate constant values are given in Table 3.

Hydroxybiphenyls were also observed to undergo triplet sensitized electron transfer reaction with benzophenone and chloranil followed by deprotonation of the radical cation and resulted in the formation of phenoxyl radical of hydroxybiphenyls. The energy transfer rate constant values are given in Table 3.

Acetophenone is also known to form triplets with $\lambda_{\max} = 330 \, \mathrm{nm}$ ($E_{T1} = 74 \, \mathrm{kcal \, mol^{-1}}$, $\varepsilon_T = 7160 \, \mathrm{dm^3 \, mol^{-1} \, cm^{-1}}$) [25]. Pulse radiolysis of N$_2$-saturated solution of 2-NpOH ($1 \times 10^{-2} \, \mathrm{mol \, dm^{-3}}$) containing low concentration of acetophenone ($3 \times 10^{-4} \, \mathrm{mol \, dm^{-3}}$) showed the formation of transient absorption bands at 350, 420 and 490 nm with a shoulder at 390 nm (Fig. 8b) on decay of 2-NpOH triplet at 440 nm (Fig. 8a). The bands at 350 and 490 nm with a shoulder at 390 nm are known to be due to 2-NpO$^\bullet$ radical whereas the band at 415 nm is due to acetophenone ketyl radical. Therefore, on electron transfer from 2-NpOH triplet to acetophenone and followed by a fast deprotonation, 2-NpO$^\bullet$ and acetophenone ketyl radical are formed by a reaction mechanism analogous to reaction (17).

4. Conclusions

Pulse radiolysis of solutions of naphthols or hydroxybiphenyls in benzene resulted in the observation of the first

excited triplet state of these scavengers. In the presence of low concentrations of benzophenone or acetophenone, a subsequent quenching reaction was observed, which from the product side gives evidence for sensitized electron transfer followed by immediate proton transfer. Using scavenger such as polyphenyls, the triplet energy transfer from the sensitizer to this substrate dominates by far. Overall, on some examples, we demonstrated that pulse radiolysis in benzene solution enables the study of the kinetic rate of the first excited triplet state of appropriate solute.

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