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Formation, excited state and electron transfer properties of the phenoxyl radical of 4,4′-thiodiphenol

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Abstract

The transient absorption bands ($\lambda_{max} = 335$, 500, 650–800 nm) formed on pulse radiolysis of N_2O-saturated basic aqueous solution of 4,4′-thiodiphenol (TDPH) are assigned to phenoxyl radical ($TDP^•$) formed on one-electron oxidation of phenoxide ion (TDP^-) of TDPH. Specific one-electron oxidants ($N_3^•$, $I_2^{•-}$, $Br^•$, $CCl_3OO^•$) also produced phenoxyl radicals with similar transient absorption spectrum. Phenoxyl radicals are able to undergo electron transfer reaction with *N,N,N′,N′*-tetramethyl-p-phenylenediamine (TMPD) with a bimolecular rate constant of 4.5×10^9 dm^3 mol^{-1} s^{-1}. Pulse radiolysis of N_2-saturated TDPH in benzene showed absorption bands at 330, 500, 650–800 nm. The second-order decay of these bands was not affected by oxygen and anthracene, well-known triplet quenchers and the transient spectrum is assigned to phenoxyl radicals formed on fast decay of solute triplets with a *G* value of 0.29. Benzophenone triplet is able to undergo energy transfer with TDPH with a bimolecular rate constant of 6×10^9 dm^3 mol^{-1} s^{-1} and formed benzophenone ketyl radical ($\lambda = 545$ nm) and phenoxyl radical ($TDP^•$, $\lambda = 500$ nm) on $H^•$ atom transfer from TDPH to benzophenone in an intermediate complex. The *G* value of phenoxyl radicals was determined to be 1.44. Picosecond laser flash photolysis of TDPH in acetonitrile failed to form any transient absorption in 450–900 nm region, supporting that only a small fraction of TDPH triplet decay to phenoxyls. Pulse radiolysis and picosecond laser flash photolysis studies indicate that the triplets of TDPH are highly unstable. The oxidation potential of TDP^-/ $TDP^•$, H^+ couple is estimated to be between 0.265 and 1.03 V. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Transient absorption bands; Radiolysis; Electron transfer properties

1. Introduction

Free radicals and radical ions generated from organic sulfur compounds have been the subject of active interest as these intermediates play an important role in understanding a number of chemical and biological processes. These studies are of relevance as sulfur centered radical species are considered as possible intermediates in redox reactions of biomolecules [1–3]. The reaction of $^•OH$ radicals and specific one-electron oxidants with dialkyl sulfides, (R_2S), result in the formation of sulfur centered dimer radical cation $(R_2S)_2^{•+}$, via a complex reaction mechanism [4–7]. The substituents are observed to affect the nature of $^•OH$ radical reaction [8]. The electron withdrawing groups lead to the formation of α-thio radicals, sulfur centered OH-adduct [9,10] and aryl substitution to monomer radical cation with stabilization on the benzene ring [11–13]. Although a large number of investigations have been made on the nature of the transients formed from alkyl derivatives of organic sulfur compounds, only a few studies are carried out on aryl substituted derivatives.

Phenols and their substituted derivatives are used in polymers, food, oil, etc. as stabilizers due to their antioxidant properties [14]. The antioxidative properties are understood in terms of electron and $H^•$ atom donor ability due to low ionization potential and weak O–H bond of phenols and their substituted derivatives [15]. Phenols and their substituted derivatives act as model systems for understanding the antioxidative mechanism. In simple phenols, phenoxyl radicals are usually the first observable oxidation products of one-electron oxidation whereas in case of naphthols and hydroxybiphenyls two channels of electron transfer are observed [16]. The $^•OH$ radicals and specific one-electron oxidants are observed to react with the phenolic form (–OH) of 4,4′-thiodiphenol by electron transfer mechanism forming solute radical cation, which on fast deprotonation is converted to phenoxyl radicals [17]. Even in 1,2-dichloro-

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ethane, the solute radical cation is converted to phenoxyl radical [17]. The phenoxide ionic form (–O$^-$) has high electron density at –O$^-$ and is expected to be the site of $^{\bullet}$OH radical attack to form the phenoxyl radicals. In this way, it might be possible to generate two different types of phenoxyl radicals on reaction of $^{\bullet}$OH radical with 4,4′-thiodiphenol. With this objective, pulse radiolysis and picosecond (ps) laser flash photolysis studies on 4,4′-thiodiphenol (TDPH) have been carried and the spectral and redox properties of the phenoxyl radicals are reported here.

2. Experimental

4,4′-thiodiphenol (TDPH), obtained from Sigma Chemicals was used without any purification. Freshly prepared solutions were used in each experiment. The studies in aqueous solutions were carried out at pH = 11, where TDPH would be present in the deprotonated form (TDP$^-$). All other chemicals used were also of high purity. The details about sample preparation are described elsewhere [10,13].

Pulse radiolysis experiments were carried out with high energy electron pulses (7 MeV, 50 ns) obtained from a linear electron accelerator whose details are given elsewhere [18]. The dose delivered per pulse was determined with aerated aqueous solution of KSCN (1×10^{-2} mol dm^{-3}) with $G\varepsilon = 21{,}520$ dm^3 mol^{-1} cm^{-1} per 100 eV at 500 nm for the transient $(SCN)_2^{\bullet -}$ species. G denotes the number of species per 100 eV of absorbed energy and ε is the molar absorptivity of $(SCN)_2^{\bullet -}$ at 500 nm. The dose per pulse was close to 15 Gy except for kinetic experiments which were carried out at a lower dose of about 10 Gy. Pulse radiolysis studies in benzene were carried out at a higher dose (45 Gy) and is mentioned in the text. The pH of the solution was adjusted with NaOH in phosphate buffer (1×10^{-3} mol dm^{-3}). The optical absorption studies were carried out with Hitachi 330 spectrophotometer.

Radiolysis of N$_2$-saturated neutral aqueous solution leads to the formation of three highly reactive species ($^{\bullet}$H, $^{\bullet}$OH, e_{aq}^-) in addition to the formation of less reactive molecular products (H$_2$, H$_2$O$_2$) [19].

$$H_2O \rightarrow {}^{\bullet}H,\ {}^{\bullet}OH,\ e_{aq}^-,\ H_2,\ H_2O_2,\ H_3O^+ \qquad (1)$$

In N$_2$O-saturated solutions, e_{aq}^- is quantitatively converted to $^{\bullet}$OH radicals with $G(^{\bullet}OH) = 5.6$ and $^{\bullet}$OH radical is the main reactive species to react with the solute. The reaction of specific one-electron oxidants ($N_3^{\bullet}$, CCl$_3$OO$^{\bullet}$, Br$^{\bullet}$, $I_2^{\bullet -}$) were carried out under conditions such that $^{\bullet}$OH radicals do not react with the solute initially, and only the one-electron oxidants react with the solute. These one-electron oxidants were generated as reported in the literature and briefly mentioned below [20,21]. $N_3^{\bullet}$ radicals were produced on pulse radiolysis of N$_2$O-saturated basic (pH = 11) aqueous solution of N_3^- (2×10^{-2} mol dm^{-3}). CCl$_3$OO$^{\bullet}$ radicals were generated on pulse radiolysis of aerated aqueous solution of isopropanol (48%, v/v), CCl$_4$ (4%, v/v). Br$^{\bullet}$ atoms were generated on pulse radiolysis of N$_2$O-saturated solution of 1,2-dibromoethane (2×10^{-2} mol dm^{-3}). $I_2^{\bullet -}$ was generated on pulse radiolysis of N$_2$O-saturated aqueous solution of I$^-$ (2×10^{-2} mol dm^{-3}).

The transient species formed on pulse radiolysis were monitored using a 450 W pulsed xenon arc lamp, monochromator (Kratos, GM-252) and a Hamamatsu R-955 photomultiplier as the detector. The photomultiplier output was digitized with a 100 MHz storage oscilloscope interfaced to a computer for kinetic analysis [22]. The rate constant values were taken from those kinetic analysis for which very good correlation was obtained between the experimental and calculated results. The bimolecular rate constant were determined from the linear regression plots of k_{obs} versus solute concentration for at least three experiments and the variation was within ±10%.

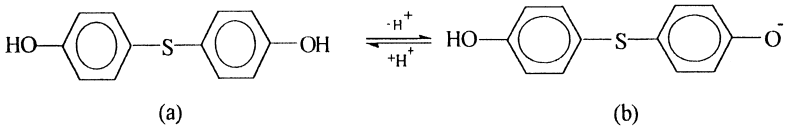
The radiolysis of a solute in aqueous solution is carried out to investigate the reaction of e_{aq}^-, $^{\bullet}$H and $^{\bullet}$OH radicals [19] whereas in a non-polar solvent such as aliphatic, alicyclic and also halo-alkanes, yields parent and free ions which can be easily used for the time-resolved study of electron transfer processes [14]. In contrast, because of the extremely high mobility of the primarily formed ions in benzene, singlet and triplet excited states dominate. The pulse radiolysis of benzene containing a relatively high concentration of solute, the benzene triplets can serve as a sensitizer for initiating the triplet induced energy transfer processes. The radiolysis of benzene produces a triplet of very high energy (353 kJ mol^{-1}) in high yield [23]. The triplet state of benzene can transfer its energy to another solute having $E_T < 353$ kJ mol^{-1} thus generating the triplet state of the latter.

3. Results and discussion

The ground state optical absorption spectrum of an aqueous solution of TDPH showed absorption bands at 228 nm ($\varepsilon = 15.3 \times 10^3$ dm^3 mol^{-1} cm^{-1}) and 244 nm ($\varepsilon = 15.5 \times 10^3$ dm^3 mol^{-1} cm^{-1}) with very little absorption at $\lambda > 300$ nm. The spectrum remained unaffected in acidic solutions but in basic solutions, it showed an absorption band at 260 nm ($\varepsilon = 25.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}) with a pK_a value of 10.1. Therefore, the solute is present in the phenolic (–OH,) form (TDPH, a, Scheme 1) in acidic solution and phenoxide ion (–O) form (TDP$^-$, b, Scheme 1) in basic solution.

3.1. Pulse radiolysis studies in aqueous medium

The pulse radiolysis experiments in N$_2$O-saturated aqueous solutions were carried out at pH = 11. At this pH the solute would be present in the phenoxide ion form and $^{\bullet}$OH radicals would be the main transient species to react with the



Scheme 1.

solute. Fig. 1 shows the transient absorption spectrum obtained on pulse radiolysis of N_2O-saturated aqueous solution of TDP^- (1×10^{-3} mol dm^{-3}, pH = 11), which exhibits absorption bands at 335, 500 nm and a broad band in 650–800 nm region. The pseudo first-order rate (k_{obs}) determined by formation kinetic studies at 335 nm was found to increase linearly with solute concentration (1–10) $\times 10^{-4}$ mol dm^{-3}. The bimolecular rate constant, determined from the slope of linear plot of k_{obs} versus solute concentration gave a value of 1.9×10^9 dm^3 mol^{-1} s^{-1}. The absorbance at 335 and 500 nm remained independent of solute concentration, suggesting that the entire yield of $^{\bullet}OH$ radicals have reacted with the solute and the concentration of $^{\bullet}OH$ radicals can be taken equal to that of the transient species formed on reaction of $^{\bullet}OH$ radicals. Under these conditions, the molar absorptivity at 335 and 500 nm was determined to be 15.6×10^3 and 7.1×10^3 dm^3 mol^{-1} cm^{-1}, respectively. The entire spectrum decayed by same kinetics (Fig. 2), second-order with $2k = 10.8 \times 10^8$ dm^3 mol^{-1} s^{-1}. The time resolved studies and decay kinetics suggest the transient spectrum to be due to one species and is assigned to phenoxyl radical formed by the following reaction.

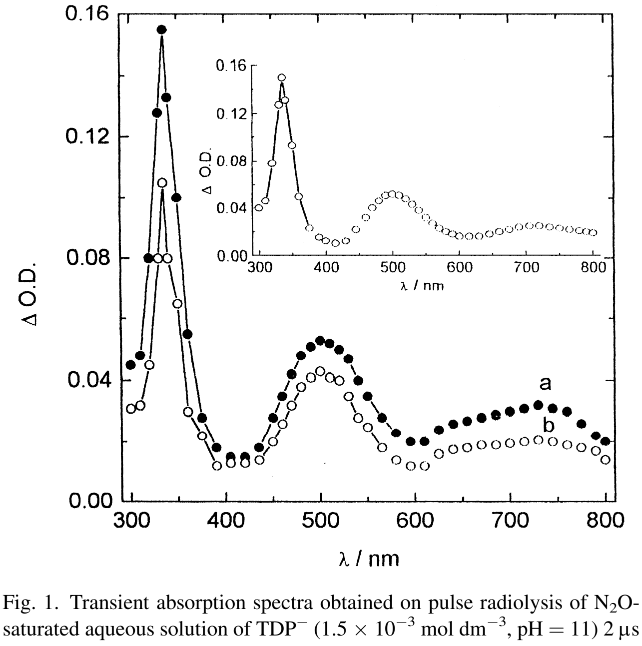


Fig. 1. Transient absorption spectra obtained on pulse radiolysis of N_2O-saturated aqueous solution of TDP^- (1.5×10^{-3} mol dm^{-3}, pH = 11) 2 μs (a) and 40 μs (b) after the pulse. Inset shows transient absorption spectrum on pulse radiolysis of N_2O-saturated aqueous solution (pH = 11) of 1,2-dibromoethane (2×10^{-2} mol dm^{-3}) containing TDP^- (5×10^{-4} mol dm^{-3}) 3 μs after the pulse. Dose: 15 Gy per pulse.

$$
\begin{aligned}
&{}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH + {}^{\bullet}OH \\
&\rightarrow [{}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH]^{\bullet +} \\
&\rightarrow {}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}O^{\bullet} + H_2O \qquad (2)
\end{aligned}
$$

The decay of the transient species remained unaffected in presence of oxygen, thus supporting its assignment to phenoxyl radicals as oxygen centered radicals are not affected by oxygen.

The solute radical cation of phenols, generated on pulse radiolysis in *n*-butyl chloride, have a lifetime of < 0.2 μs and phenoxyl radicals were the first observable transient species [14]. The lifetime of solute radical cations of naphthols and hydroxy biphenyls are increased (τ = 1–3 μs) due to the extended aromatic moiety and could be observed as the transient species [16].The radical cations decay to phenoxyl radical. The pulse radiolysis of acidic aqueous solution of TDPH, in the phenolic form, had shown transient absorption bands at 330 and 525 nm (Table 1), which decayed with a lifetime of ~330 μs [17]. These are assigned to phenoxyl radicals formed on fast deprotonation of solute radical cation (reaction (3)). The reaction of $^{\bullet}OH$ radicals with substituted aryl sulfides containing –OH group in the side chain (2-phenylthio ethanol) has shown the formation of solute radical cation with positive charge on the benzene ring. But the presence of –OH group on the benzene ring (TDPH)

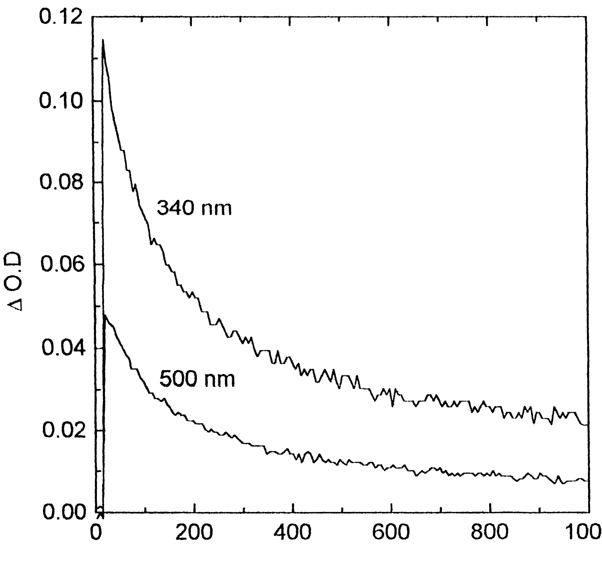


Fig. 2. Absorption–time profiles obtained on pulse radiolysis of N_2O-saturated aqueous solution of TDP^- (1.5×10^{-3} mol dm^{-3}, pH = 11) at 340 and 500 nm.

Table 1
Kinetic and spectral properties of the transients formed from TDPH/TDP^-

S. No.	Reaction	ε ($dm^3\ mol^{-1}\ cm^{-1}$)	λ_{max} (nm)	k ($dm^3\ mol^{-1}\ s^{-1}$)	Decay ($2k$) ($dm^3\ mol^{-1}\ s^{-1}$)
1	$TDP^- + {}^{\bullet}OH$	15.6×10^3	335	1.9×10^9	10.8×10^8
		7.1×10^3	500		
		–	650–800		
2	$TDP^- + Br^{\bullet}$	15.3×10^3	335	2.8×10^9	10.9×10^8
		6.8×10^3	500		
		–	650–800		
3	$TDP^- + N_3^{\bullet}$	15.3×10^3	335	6.1×10^9	10.7×10^8
		6.6×10^3	500		
		–	650–800		
4	$TDP^- + CCl_3OO^{\bullet}$	15.1×10^3	335	1.6×10^9	9.8×10^8
		6.5×10^3	500		
		–	650–800		
5	$TDP^- + I_2^{\bullet -}$	–	335	3.8×10^8	–
			500		
			650–800		
6	$TDPH + {}^{\bullet}OH^{a}$	8.5×10^3	330	5.1×10^9	3.1×10^{3b}
		2.1×10^3	525		
7	TDP in benzene	–	335	–	5.1×10^{5c}
			550		2.4×10^{6c}
			650–800		
8	TDPH in DCE	–	330	–	1.1×10^{3b}
			530		–

[a] At pH = 1.
[b] First-order (s^{-1}).
[c] Second-order decay ($2k/l\varepsilon$) (s^{-1}).

has resulted in the formation of phenoxyl radical.

$$\begin{aligned} &HO\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH + {}^{\bullet}OH \\ &\quad \rightarrow [HO\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH]^{\bullet +} \\ &\quad \rightarrow HO\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}O^{\bullet} + H_2O \qquad (3) \end{aligned}$$

This phenoxyl radical (reaction 3) is different from that obtained in basic solutions (reaction 2). In analogy with the studies on phenols and their substituted derivatives, the radical cations of TDPH are not expected to have such a high lifetime and may support the assignment of the transient absorption band to phenoxyl radical.

The additional evidence in support of the above mechanism (reaction 2) came from similarity of the transient spectrum obtained on reaction of ${}^{\bullet}OH$ radicals and specific one-electron oxidants with TDP^-. Inset of Fig. 1 shows the transient spectrum obtained on reaction of $Br^{\bullet}$ atoms with TDP^-. The spectral and kinetic parameters, which are similar to those obtained on reaction of ${}^{\bullet}OH$ radicals are shown in Table 1. The transient species is assigned to phenoxyl radicals formed by reaction (4).

$$\begin{aligned} &{}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH + Br^{\bullet} \\ &\quad \rightarrow [{}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH]^{\bullet +} \\ &\quad \rightarrow {}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}O^{\bullet} + H^+ + Br^- \qquad (4) \end{aligned}$$

The yield of the transient species formed on reaction of $Br^{\bullet}$ atoms with TDP^- was comparable to that obtained on reaction with ${}^{\bullet}OH$ radicals. It suggests that the redox potential for the couple $TDP^-/TDP^{\bullet}$, H^+ is lower than that of $Br^{\bullet}/Br^-$ couple ($E^0 = 1.9$ V).

Similar studies on the oxidation of TDP^- have been carried out with a number of specific one-electron oxidants and the results are shown in the Table 1. The kinetic and spectral parameters of the transient species ($TDP^{\bullet}$) formed were similar to those formed on reaction with ${}^{\bullet}OH$ radicals at pH = 11. The yield of the transient species formed on reaction with $I_2^{\bullet -}$ radical anion was about 80% of that obtained on reaction with ${}^{\bullet}OH$ radicals. This shows that the redox potential value of $TDP^-/TDP^{\bullet}$, H^+ couple is lower than that of $I_2^{\bullet -}/2\ I^-$ ($E^0 = 1.03$ V) couple, and the difference in redox potential value may not be very high.

The rate constant for the reaction of $I_2^{\bullet -}$ with TDP^- was determined on monitoring the decay of the transient absorption of $I_2^{\bullet -}$ as a function of TDP^- concentration. The decay ($\lambda = 380$ nm) was observed to become faster on addition of low concentration of TDP^- (Fig. 3) suggesting electron transfer from TDP^- to $I_2^{\bullet -}$ (reaction (5)).

$$\begin{aligned} &I_2^{\bullet -} + {}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH \\ &\quad \rightarrow [{}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}OH]^{\bullet +} \\ &\quad \rightarrow {}^{-}O\text{–}C_6H_4\text{–}S\text{–}C_6H_4\text{–}O^{\bullet} + H^+ + 2I^- \qquad (5) \end{aligned}$$

The pseudo first-order rate constant (k_{obs}) was observed to increase linearly with TDP^- concentration (inset of Fig. 3) and the bimolecular rate constant was determined to be $3.8 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}$. The time-resolved studies showed the formation of transient absorption bands at

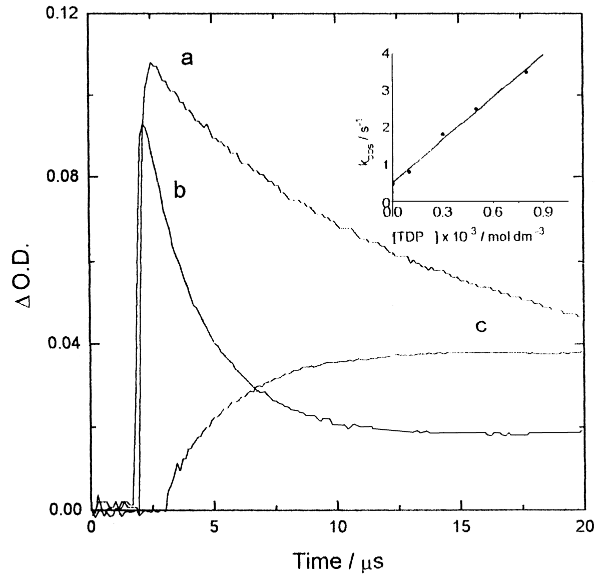


Fig. 3. Absorption–time profiles obtained on pulse radiolysis of N_2O-saturated aqueous solution of I^- (3×10^{-2} mol dm^{-3}, pH = 11, $\lambda = 380$ nm) in absence (a) and presence of TDP^- (0.2×10^{-3} mol dm^{-3}) at 380 nm (b) and at 500 nm (c). Inset shows plot of k_{obs} vs. TDP^- concentration at 380 nm. Dose: 15 Gy per pulse.

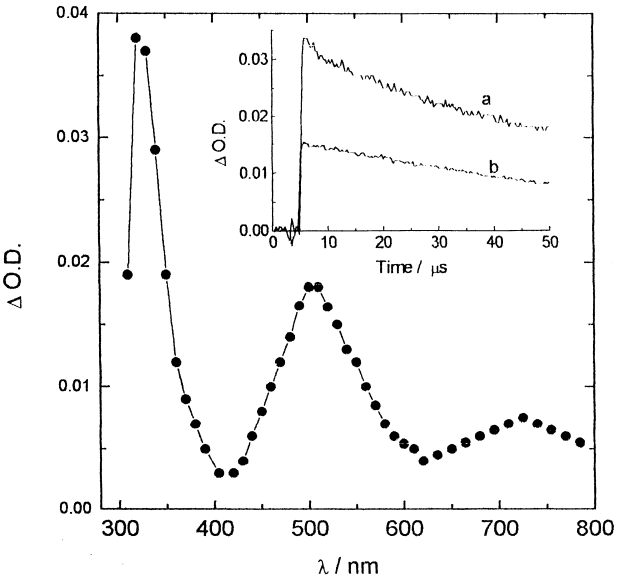


Fig. 4. Transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of TDPH (1×10^{-3} mol dm^{-3}) in benzene. Inset show absorption–time profiles at 335 nm (a) and 500 nm (b). Dose: 45 Gy per pulse.

335 and 500 nm and the transient absorption spectrum was similar to that shown in Fig. 1. The rate constant for reaction (5) was also determined from the growth of the transient absorption at 335 and 500 nm (Fig. 3(c)) and the bimolecular rate constant value was 4.5×10^8 dm^3 mol^{-1} s^{-1}, close to the value obtained from the decay of $I_2^{\bullet-}$ at 380 nm. The relatively lower bimolecular rate constant value for reaction (5) may also support the lower yield observed for this reaction. The decay of $TDP^\bullet$ radical obtained on pulse radiolysis of N_2O-saturated aqueous solution of TDP^- (2×10^{-3} mol dm^{-3}, pH = 11, $\lambda = 500$ nm) was not affected on addition of low concentration I^- (1×10^{-5} mol dm^{-3}), suggesting that the equilibrium is not established for reaction (4), under these conditions and the redox potential value of $TDP^-/TDP^\bullet$, H^+ couple is not close to that of $I_2^{\bullet-}/2I^-$ couple.

N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) is a weak reductant with $E^0 = 0.265$ V, was used to confirm the oxidizing nature of the transient $TDP^\bullet$ species. The oxidized form of TMPD ($TMPD^{\bullet+}$) has absorption bands at 335, 565 and 610 nm. The bimolecular rate constant for the oxidation of TMPD was determined on monitoring the transient absorption at 610 nm ($\varepsilon = 12{,}000$ dm^3 mol^{-1} cm^{-1}), formed on pulse radiolysis of N_2O-saturated aqueous solution of TDP^- (2×10^{-3} mol dm^{-3}, pH = 11, TMPD = 2×10^{-5} mol dm^{-3}). These experiments were carried out at a lower dose (10 Gy per pulse) to minimize the effect of radical reaction of $TDP^\bullet$. The formation of $TMPD^{\bullet+}$ was observed to take place with a bimolecular rate constant of 4.5×10^9 dm^3 mol^{-1} s^{-1} and $G(TMPD^{\bullet+}) = 5.1$. The *G* value is close to $G(^\bullet OH)$, suggesting nearly complete electron transfer from TMPD to $TDP^\bullet$. These studies suggest that the redox potential of the couple $TDP^-/TDP^\bullet$, H^+ is higher than that of $TMPD/TMPD^{\bullet+}$ couple and is expected to be between 0.265 and 1.03 V.

3.2. Pulse radiolysis studies in organic medium

Fig. 4 shows the transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of TDPH (1×10^{-3} mol dm^{-3}) in benzene, which exhibits absorption bands at 335, 500 and 650–800 nm. The bands at 500 and 335 nm were observed to decay by second-order kinetics with $2k/\varepsilon l = 2.4 \times 10^6$ and 5.1×10^5 s^{-1}, respectively. As mentioned earlier pulse radiolysis in benzene would generate solute triplets. The confirmative evidence for the formation of triplet state could be obtained on energy transfer to or from a known triplet which is already well characterized. The decay of the transient absorption was not affected in aerated solution and in presence of low concentration of anthracene ($E_T = 178$ kJ mol^{-1}). The transient decay of biphenyl triplet ($E_T = 274$ kJ mol^{-1}, $\lambda = 360$ nm, $\varepsilon = 27{,}100$ dm^3 mol^{-1} cm^{-1}), formed on pulse radiolysis of N_2-saturated solution of biphenyl (2×10^{-2} mol dm^{-3}) in benzene was also not affected in presence of TDPH (4×10^{-4} mol dm^{-3}). These energy transfer studies suggest that the transient absorption (Fig. 4) is not due to TDPH triplet. Pulse radiolysis of TDPH in 1,2-dichloroethane (DCE) has shown the formation of transient absorption bands at 330 and 530 nm, similar to those obtained on reaction of $^\bullet OH$ radicals and specific one-electron oxidants in acidic solutions and assigned to phenoxyl radicals as shown in reaction (3). The transient absorption spectrum (Fig. 4) is similar to that obtained on reaction of $^\bullet OH$

radicals and specific one-electron oxidants in basic solutions and is therefore assigned to phenoxyl radicals as shown in reaction (2). Therefore, the transient absorption spectrum (Fig. 4) may be due to phenoxyl radicals formed via reactions (6) and (7).

$$^3(C_6H_6)^* + HO{-}C_6H_4{-}S{-}C_6H_4{-}OH \rightarrow {}^3(HO{-}C_6H_4{-}S{-}C_6H_4{-}OH)^* + C_6H_6 \quad (6)$$

$$^3(HO{-}C_6H_4{-}S{-}C_6H_4{-}OH)^* \rightarrow {}^-O{-}C_6H_4{-}S{-}C_6H_4{-}O^\bullet + H^+ + H^\bullet \quad (7)$$

Based on the absorbance value at 500 nm and $\varepsilon_{500} = 6.7 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$, the G value of phenoxyl radicals was determined to be 0.29. Under the experimental conditions, entire benzene triplets must have transferred the energy to TDPH (1×10^{-3} mol dm^{-3}). The G value (=0.29) is much lower than the expected value of 4.2 of benzene triplets [23–25], suggesting that TDPH triplets are also decaying by a mechanism other than phenoxyl radical formation. Since the transient absorption spectrum of TDPH triplets could not be observed, its lifetime must be very small and must have decayed within the pulse itself.

Fig. 5(a) and Fig. 5(b) shows the transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of benzophenone (BP, 2×10^{-2} mol dm^{-3}) in benzene, 0.6 and 8 μs after the pulse. It should be due to benzophenone triplets ($\varepsilon_T = 288$ kJ mol^{-1}), which decayed by first-order kinetics with $k = 2.9 \times 10^5\ s^{-1}$. Although the initial portion of the transient absorption at 525 nm in presence of TDPH (2×10^{-4} mol dm^{-3}) was not affected (inset of Fig. 5), the transient absorption at higher time scale showed appreciably high absorption, which was relatively long lived (inset of Fig. 5). Under these conditions, the triplet energy transfer from benzene triplets would be to benzophenone alone and not to TDPH. Time resolved studies showed the formation of a transient absorption band at 330 nm and broad absorption in 450–580 nm with a peak at 545 nm (Fig. 5(c)). It should be due to the transient species formed on energy transfer from benzophenone triplets (^{3}BP) to TDPH (reactions (8) and (9)).

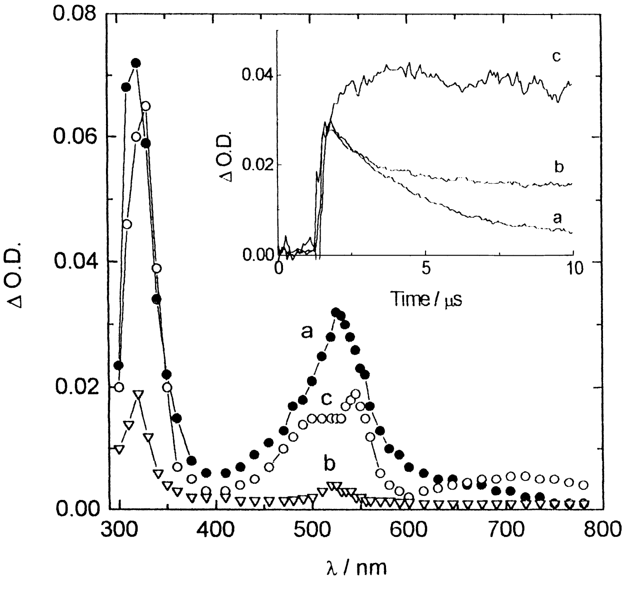


Fig. 5. Transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of benzophenone (2×10^{-2} mol dm^{-3}) in benzene 0.6 μs (a) and 8 μs (b) after the pulse and in presence of TDPH (2×10^{-4} mol dm^{-3}) 8 μs after the pulse (c). Inset shows absorption–time profiles at 525 nm in absence (a) and in presence of TDPH at 525 nm (b) and 340 nm (c). Dose: 15 Gy per pulse.

$$^3(C_6H_6)^* + BP \rightarrow {}^3(BP)^* + C_6H_6 \quad (8)$$

$$^3(BP)^* + HO{-}C_6H_4{-}S{-}C_6H_4{-}OH \rightarrow {}^3(HO{-}C_6H_4{-}S{-}C_6H_4{-}OH)^* + BP \quad (9)$$

The energy transfer rate constant, determined from formation kinetic studies at 340 nm gave a value of $6 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$. But the transient absorption spectrum (Fig. 5(c)) was not similar to that obtained on pulse radiolysis of N_2-saturated solution of TDPH in benzene (Fig. 4). Since the lifetime of solute triplet is expected to be very small, it could not be due to solute triplets. On the other hand, benzophenone ketyl radical (BPH$^\bullet$, >C$^\bullet$OH) is known to have absorption band at 545 nm and at wavelengths lower than 350 nm [26]. Benzophenone ketyl radical might be formed on H$^\bullet$ atom transfer from TDPH to BP through an intermediate complex (reactions (10) and (11)).

$$^3(BP)^* + HO{-}C_6H_4{-}S{-}C_6H_4{-}OH \rightarrow (BP \cdots HO{-}C_6H_4{-}S{-}C_6H_4{-}OH)^* \quad (10)$$

$$(BP \cdots HO{-}C_6H_4{-}S{-}C_6H_4{-}OH)^* \rightarrow BPH^\bullet + {}^-O{-}C_6H_4{-}S{-}C_6H_4{-}O^\bullet + H^+ \quad (11)$$

The broad absorption at 500 nm may therefore be due to phenoxyl radical. The position of this band matched with that obtained on pulse radiolysis studies in basic aqueous solutions (Fig. 1, Table 1). The absorption band at 330 nm may also be due to phenoxyl radical (TDP$^\bullet$) with contribution from benzophenone ketyl radicals (BPH$^\bullet$). Based on the absorbance value at 500 nm = 0.016 and $\varepsilon_{500} = 6.7 \times 10^3\ dm^3\ mol^{-1}\ cm^{-1}$, the G value of phenoxyl radicals was determined to be 1.44. The value is much higher than 0.29, observed in absence of benzophenone even at a low concentration of TDPH (2×10^{-4} mol dm^{-3}). The yield of phenoxyl radicals increased in the presence of a solute having high affinity for H$^\bullet$ atoms. From these studies, it appears that the triplet state of TDPH is unstable and it decays to phenoxyl radicals by H$^\bullet$ atom transfer mechanism. This explains the similarity of the transient absorption spectrum obtained on pulse radiolysis of N_2-saturated solution of TDPH in benzene (Fig. 4) to that in aqueous solution (Fig. 1).

In order to establish the formation of triplet state of TDPH, ps laser flash photolysis [27] of TDPH in acetonitrile ($\lambda_{ex} = 266$ nm, 35 ps, Continuum Model 501-C-10) showed very little absorption in 450–850 nm region, indicating that either the triplets are not absorbing in this region or the lifetime is very small (<50 ps). These results support the earlier observation that the triplet state of TDPH is highly unstable and is decaying by $H^{\bullet}$ atom transfer mechanism forming phenoxyl radicals. These studies also support the observation that only a small fraction of TDPH triplet decay by $H^{\bullet}$ atom transfer as the transient absorption in 450–900 nm region, on ps laser flash photolysis studies, was negligible.

4. Conclusions

One-electron oxidation of phenoxide ion of 4,4′-thiodiphenol, in basic aqueous solutions, results in the formation of phenoxyl radical and the oxidation potential of $TDP^{-}/TDP^{\bullet}, H^{+}$ couple was estimated to be between 0.265 and 1.03 V. The redox potential value for $TDPH/TDP^{\bullet}, H^{+}$ couple for the oxidation of TDPH in acidic solutions (0.97 V) was higher than that of $TDP^{-}/TDP^{\bullet}, H^{+}$ couple in basic solutions, which may be due to higher electron density at O^{-}. The triplet states of TDPH is highly unstable and a small fraction of it decay by $H^{\bullet}$ atom transfer mechanism forming phenoxyl radicals. The yield of phenoxyl radicals is increased in the presence of a solute which has high affinity for $H^{\bullet}$ atoms.

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