Laser photolysis study of naphthalene disulphides and naphthalene thiols; reactivities of naphthalenethio radicals

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Abstract

Naphthalenethio radicals (Naph-S') have been formed by laser photolysis. The transient absorption bands have been assigned by both experiment and molecular orbital (MO) calculation. The reactions of Naph-S' with vinyl monomers and dienes have been studied by laser photolysis in solution. From the decays of the bands of Naph-S', the reaction rate constants have been determined. The 2-naphthalenethio radical is more reactive than the 1-naphthalenethio radical; the resonance stability calculated by the MO method supports this finding. Upon introduction of an OH group into the naphthyl group, the reactivity of the thio radical decreases.

Keywords: Nanosecond laser photolysis; Radicals; Kinetics; Photo-addition reactions

1. Introduction

It is important to determine the reaction rate constants of free radicals as absolute values, since this makes it possible to compare the reactivities of free radicals [1,2]. We reported that the flash photolysis method was useful for evaluating the addition reactions of sulphur-centred radicals with various olefins [3]. In the case of benzyl-type radicals such as phenoxy and phenylthio radicals there have been extensive studies including the effects of substituents and solvents on the reactivities [4,5]. On the other hand, only a few studies of the reactivities of naphthyl-type radicals such as naphthenyloxy radicals have been reported [6].

There are many points to be clarified. For example, which are more reactive, benzyl-type radicals or naphthyl-type radicals? For naphthyl-type radicals it is interesting to clarify whether 1-naphthyl-type or 2-naphthyl-type radicals are more reactive and how their reactivity changes when substituents are introduced. We employed as a substituted naphthalenethio radical the 6-hydroxynaphthalene-2-thio radical (HO-Naph-S') which would be expected to be formed from 6,6'-dithiobis(2-naphthalenol) (DDD) (Scheme 1).

In our previous paper [6] we reported the results of a preliminary study using microsecond flash photolysis applied to naphthalenethio radicals (Naph-S'). In this study a nanosecond laser photolysis method was applied to addition reac-
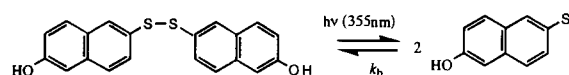
Scheme 1.

tions with various vinyl monomers. We also performed some molecular orbital (MO) calculations to confirm the electronic state of these free radicals.

2. Experimental details

2.1. Materials

Naphthalene disulphides were prepared from commercially available thiols by the oxidation of I_2; they were used after recrystallization from ethanol. 6,6'-Dithiobis(2-naphthalenol) was purchased from Aldrich Co. Ltd. Isoprene and styrene were used after distillation. Solvents were of spectroscopic grade. The O_2 concentration in solution was calculated by Henry's law using the coefficients reported in Ref. [7].

2.2. Apparatus

The laser flash photolysis apparatus was a standard design with an Nd:YAG laser of 6 ns duration. Disulphides and thiols were photolysed with third harmonic generator (THG) (355 nm) and fourth harmonic generator (FHG) (266 nm) light.

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The transient spectra were measured with a multichannel photodiode array with an image intensifier [8,9]. The time profiles were followed by a photomultiplier system in the visible region. The laser photolysis was performed on solutions in a rectangular quartz cell with 10 mm optical path. The monitoring light was selected with appropriate bandpass filters. All measurements were performed at 23 °C.

2.3. MO calculation

The MO calculations were performed by the CNDO method using MOPAC V. 6 presented by the Japan Program Exchange Association [10]. The transition energies were calculated after CI by the unrestricted Hartree–Fock method.

3. Results and discussion

3.1. Transient absorption spectra

The transient absorption spectra observed upon laser photolysis of 1,1'-dithiobisnaphthalene disulphide and 2,2'-
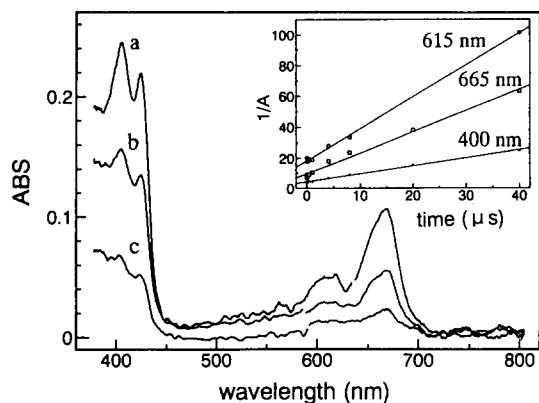

Fig. 1. Transient absorption spectra obtained after laser photolysis (355 nm) of 1,1'-dithiobisnaphthalene (1 mM) in aerated cyclohexane solution for (a) 0.05, (b) 4 and (c) 20 μs. Inset: second-order decay plots of representative absorption bands.
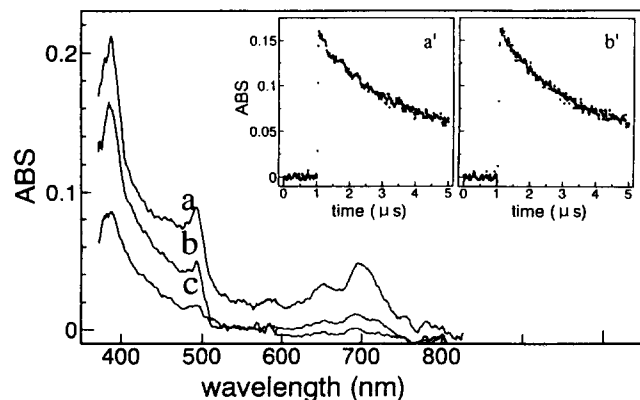

Fig. 2. Transient absorption spectra obtained after laser photolysis (355 nm) of 2,2'-dithiobisnaphthalene (1 mM) in aerated cyclohexane solution for (a) 0.05, (b) 4 and (c) 20 μs. Inset: decay profiles at 490 nm in (a') aerated and (b') nitrogen-bubbled solution.
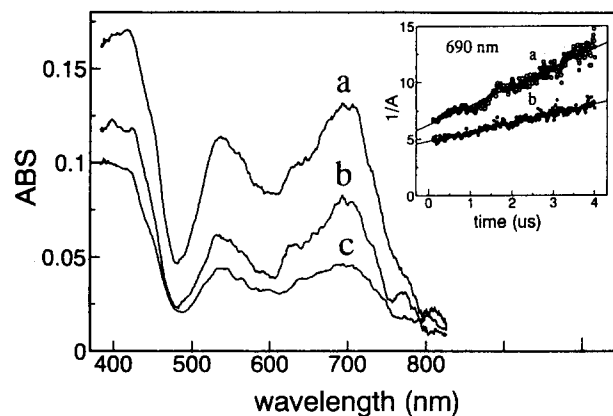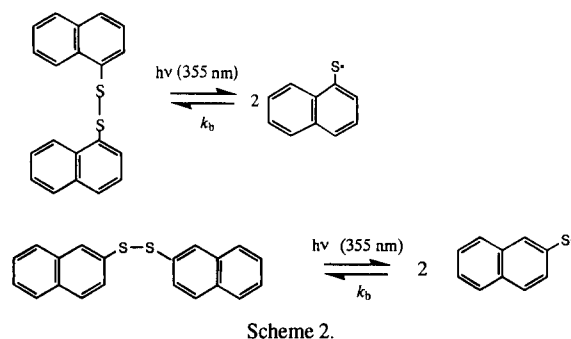

Scheme 2.

Fig. 3. Transient absorption spectra obtained after laser photolysis (355 nm) of 6,6'-dithiobis(2-naphthalenol) (2.5 mM) in aerated tetrahydrofuran solution for (a) 0.05, (b) 4 and (c) 20 μs. Inset: second-order decay plots at 690 nm in (a') tetrahydrofuran and (b') 2-propanol.

dithiobisnaphthalene disulphide with 355 nm light show sharp peaks in the visible region (Figs. 1 and 2). In the longer wavelength region above 800 nm we could not find any appreciable absorption even when using a highly sensitive photodiode detector in the near-IR region [8,9]. Upon laser photolysis of 1-naphthalene thiol and 2-naphthalene thiol, similar absorption bands to those from the corresponding disulphides were observed. Thus the absorption bands in Figs. 1 and 2 are attributed to the corresponding naphthalenethio radicals, which are abbreviated as Naph-S* (Scheme 2). These absorption bands were observed even in aerated solution, suggesting that Naph-S* is less reactive to O_2. Since arylthio radicals are known to be less reactive to O_2 [11], the transient absorption bands observed here are characteristic of aromatic thio radicals.

In the case of 6,6'-dithiobis(2-naphthalenol) the transient absorption bands appear at 400, 540 and 700 nm with a shoulder at 630 nm (Fig. 3). The longest band at 700 nm and the shoulder at 630 nm in Fig. 3 correspond to the band at 700 nm and the shoulder at 650 nm of the 2-naphthalenethio radical (2-Naph-S*). Similarly, the relatively broad bands at 530 and 400 nm in Fig. 3 correspond to the sharp bands at 495 and 400 nm of 2-Naph-S*. Therefore it is evident that the S–S bond connecting two naphthalene groups is equivocally photolysed by 355 nm laser light in solution (Scheme 2).

The absorption bands decay with second-order kinetics as shown in the insets of Figs. 1 and 3, suggesting that the

transient species decay with self-recombination. Defining the recombination rate constant as k_b and the molar extinction coefficient as ε, the $2k_b/\varepsilon$ values for 1-Naph-S$^\bullet$ are obtained as 1.6×10^6 s^{-1} at 665 nm, 2.5×10^6 s^{-1} at 615 nm and 0.6×10^6 s^{-1} at 400 nm from the slopes of the second-order plots. If these three absorption bands in Fig. 1 are attributed to the same species, the inverses of the slopes should be proportional to the absorption intensities. The relative $\varepsilon/2k_b$ values are 1.0 at 665 nm, 0.6 at 615 nm and 2.6 at 400 nm, which are in agreement with the corresponding relative absorption intensities of 1.0 at 665 nm, 0.5 at 615 nm and 2.3 at 400 nm. Therefore these three absorption bands in Fig. 1 are ascribed to one species, namely 1-Naph-S$^\bullet$.

In the inset of Fig. 3 it is seen that the second-order plot in 2-propanol is linear, suggesting that the hydrogen abstraction ability of the thio radical from 2-propanol is quite low. The slope of the second-order plot in tetrahydrofuran (THF) is steeper than that in 2-propanol; this suggests that the rate of recombination of the thio radical is close to the diffusion-controlled limit. The diffusion rate constant k_D in THF is calculated as 1.1×10^{10} M^{-1} s^{-1} at 23 °C by the Debye equation ($k_D = 8RT/3000\eta$) [12]; thus $\varepsilon = 10^4$ M^{-1} cm^{-1} at 690 nm for HO-Naph-S$^\bullet$ was calculated from $2k_b/\varepsilon = 2.1 \times 10^6$ s^{-1} cm at 23 °C. The initial concentration is assumed to be 1.4×10^{-5} M. Similarly, the ε values for 1-Naph-S$^\bullet$ were calculated as 8500 M^{-1} cm^{-1} at 665 nm, 5400 M^{-1} cm^{-1} at 615 nm and 22 700 M^{-1} cm^{-1} at 400 nm. The initial concentration of 1-Naph-S$^\bullet$ was calculated as about 10^{-5} M.

In the inset of Fig. 2 the decay profiles in degassed and aerated solutions are shown. Although the decay in aerated solution seems to be slightly faster than that in degassed solution, both decays are quite similar, suggesting low reactivity of the thio radicals to O_2.

On the other hand, upon 266 nm laser light photolysis of naphthalene thiols, extra absorption bands appear in the region of 420–440 nm, as shown in Fig. 4 for 2-naphthalene thiol as an example. In the presence of O_2 the 420 and 440 nm bands decay more rapidly than the absorption bands at

390 and 490 nm (inset of Fig. 4), whereas in degassed solution the decay rates of these bands are similar. After 4 μs the two sharp peaks in the region of 420–440 nm disappear, leaving the absorption bands attributed to Naph-S$^\bullet$ at 390, 490 and 700 nm. Thus the absorption bands in the region of 420–440 nm must be attributed to another transient species which is reactive to O_2.

The inset decay profile in Fig. 4 shows that the 420 nm band decays within 1 μs in aerated solution; the decay rate of the species at 420 nm is evaluated as about 10^7 s^{-1} in THF solution containing about 1 mM O_2. The second-order rate constant for the reaction of the 420 nm species with O_2 is evaluated as about 10^{10} M^{-1} s^{-1}. Thus one can presume the carbon-centred radical or the triplet state to be responsible for the absorption band in the region of 420–440 nm. As shown in Scheme 3, upon laser photolysis at short wavelength, C–S bond cleavage may take place in addition to the dissociation of S–H. If the triplet state is produced by the short wavelength light, the triplet state is not always a precursor of S–H bond breaking.

3.2. Reaction of thio radicals

Upon addition of styrene or isoprene, the decay rates of the transient absorption bands observed in Figs. 1–3 were accelerated with increasing concentration of additives. In Fig. 5 the first-order decay plots are shown for the reaction of 1-Naph-S$^\bullet$ with styrene. In the presence of styrene in degassed solution (curve b) the initial decay rate was accelerated compared with the decay rate without styrene (curve a). After about 1 μs the decay rate was slowed down even in the presence of styrene in degassed solution; the slope of the first-order plot becomes the same as without styrene. This may indicate that within the initial decay the Naph-S$^\bullet$ adds to the
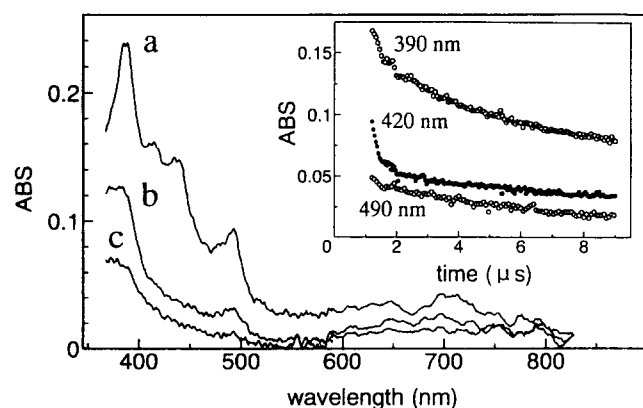
Scheme 3.

Fig. 4. Transient absorption spectra obtained after laser photolysis (266 nm) of 2-naphthalene thiol (2.5 nm) in aerated cyclohexane solution for (a) 0.05, (b) 4 and (c) 20 μs. Inset: decay profiles in aerated solution.
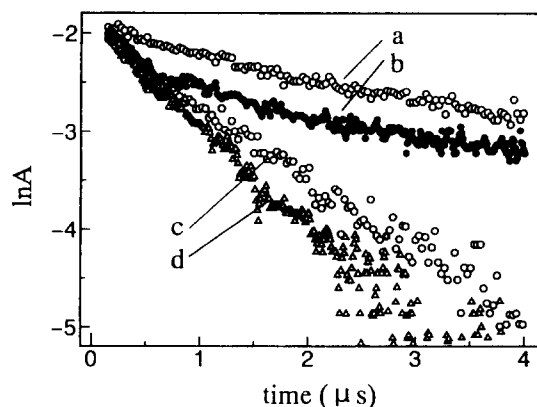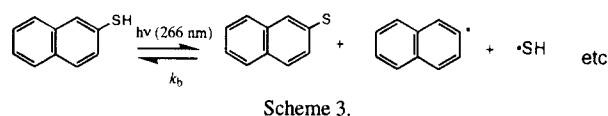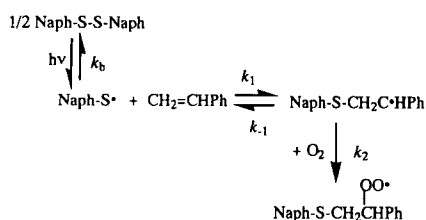
Fig. 5. Decay of the absorption band at 665 nm of the 1-naphthalenethio radical in the absence and presence of styrene (133 mM) in cyclohexane: (a) without styrene; (b) with styrene in degassed solution; (c) with styrene in aerated solution; (d) with styrene in oxygen-saturated solution.

double bond of styrene to form the adduct Naph-S–CH₂C'HPh, which in turn begins to dissociate into Naph-S* and styrene after about 1 μs. Thus the reaction becomes reversible after about 1 μs.

In aerated solution with styrene (curve c) the decay rate of 1-Naph-S* was accelerated even after 1 μs. In oxygen-saturated solution (curve d) the decay rate was further increased, showing a linear trend throughout the first-order kinetics of the whole decay curve. These findings suggest that O_2 traps the adduct carbon-centred radical selectively; the overall reactions are summarized in Scheme 4 [3].

For the fast decay within 1 μs the k_1 value can be easily obtained; after 1 μs the decay rate depends on both styrene and O_2 concentrations. The decay of [Naph-S*] can be expressed as follows [13]:

1/2 Naph-S-S-Naph

$$hv \Big\downarrow k_b$$

Naph-S* + CH₂=CHPh $\underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$ Naph-S-CH₂C•HPh

$$+ O_2 \Big\downarrow k_2$$

OO•
|
Naph-S-CH₂CHPh

Scheme 4.

Table 1
Rate constants (k_1) for addition reaction of naphthalenethio radicals with isoprene and styrene ([O_2] = 1.9 mM in aerated tetrahydrofuran [7])

Naph-S*	Styrene		Isoprene k_1 ($M^{-1} s^{-1}$)
	k_1 ($M^{-1} s^{-1}$)	k_{-1} (s^{-1})	
1-Naph-S*	6.0×10^6	1.3×10^6	3.3×10^6
2-Naph-S*	1.0×10^7	3.6×10^6	1.7×10^7
HO-Naph-S*	2.4×10^6		2.1×10^6
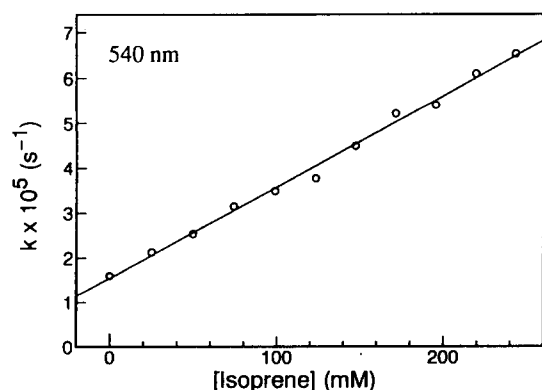
Fig. 6. Pseudo-first-order plot for the reaction of HO-Naph-S* with isoprene in aerated solution.

Naph-S* + CH₂=C(CH₃)CH=CH₂ $\overset{k_1}{\underset{}{\nearrow}}$ Naph-S-CH₂-C'(CH₃)CH=CH₂

$\searrow$ Naph-SH + CH₂=C(C'H₂)CH=CH₂
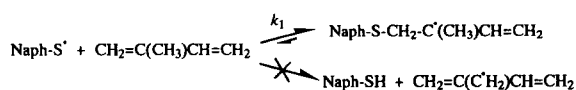
Scheme 5.

$$\frac{-d[\text{Naph-S}^*]}{dt} = k_b[\text{Naph-S}^*]^2 + k_1\left(1 - \frac{1}{k_{-1} + k_2[O_2]}\right)$$
$$\times [\text{CH}_2\text{=CHPh}][\text{Naph-S}^*]$$

The first-order rate constant (k_{first}) with respect to [Naph-S*] was separated from the second-order part (k_b) by a curve-fitting method: $k_{\text{first}} = k_1\{1 - 1/(k_{-1} + k_2[O_2])\}[\text{CH}_2\text{=CHPh}]$. Assuming the steady state approximation with respect to the intermediate [Naph-S–CH₂C'HPh], the following equation can be derived [3]:

$$\frac{[\text{CH}_2\text{=CHPh}]}{k_{\text{first}}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1 k_2[O_2]}$$

Thus the k_1 value can be obtained from the extrapolation of plots of $[\text{CH}_2\text{=CHPh}]/k_{\text{first}}$ vs. $1/[O_2]$; the k_1 values are summarized in Table 1. The k_{-1}/k_2 value can be evaluated from the slope of the plots; for 1-Naph-S* and 2-Naph-S* the k_{-1} values are listed in Table 1 on the assumption that $k_2 = 10^9$ $M^{-1} s^{-1}$ [14]. These values are in good agreement with those preliminarily evaluated by microsecond flash photolysis [6]. In the case of HO-Naph-S* the dependence of k_{first} on the O_2 concentration is small; thus the k_1 value was evaluated from $k_{\text{first}}/[\text{styrene}]$ in aerated solution.

In Fig. 6 the pseudo-first-order plot for the reaction of HO-Naph-S* with isoprene is shown; a fairly good linear relation is obtained. In the case of isoprene the dependence of the decay profiles on O_2 concentration is small, suggesting that k_{-1} is small. Thus the k_1 values are evaluated from the slope of pseudo-first-order plots like Fig. 6 in aerated solution as listed in Table 1.

In the case of the reaction with isoprene, both the addition reaction and the hydrogen abstraction reaction would be anticipated, because both reactions produce allyl-type radicals with high resonance stability. In order to evaluate the hydrogen abstraction ability of the thio radicals, the decay rates were observed in the presence of 1,4-cyclohexadiene, which is known as a strong hydrogen donor [15,16]. It was observed that the decay rates were not accelerated in the presence of 1,4-cyclohexadiene, indicating that the hydrogen abstraction abilities of these thio radicals are quite low. This finding is in good agreement with that from the product analysis, which confirms the 1,4-addition products [17]. Therefore the addition reaction is the only reaction responsible for the observed decay rates as shown in Scheme 5 [18].

If the naphthoxy-type radical HS-Naph-O* were formed from 6,6'-dithiobis(2-naphthalenol) by the photodissociation of O–H, the absorption band(s) due to the oxygen-centred radical would show an increase in decay rate(s) upon addition of 1,4-cyclohexadiene, because oxygen-centred radicals in general have a high hydrogen abstraction ability [19]. The observed transient absorption bands in Fig. 3, however, did not show such a high hydrogen abstraction ability, indicating that the naphthoxy radical is not included in the transient absorption bands in Fig. 3. Therefore it is also confirmed

Table 2
Comparison of observed transition energies with calculated ones for Naph-S*

Naph-S*	Transition energy (cm^{-1}) (relative intensity)	
	Calculated	Observed
1-Naph-S*	12800 (0.0)	–
	20400 (1.00)	15040 (1.0)
		16700 (0.5)
	—	23300 (0.1)
	23800 (5.0)	25000 (2.3)
2-Naph-S*	12050 (0.0)	–
	15200 (1.0)	14300 (1.0)
		15400 (0.6)
	—	20000 (2.0)
	30300 (5.0)	26300 (4.0)
HO-Naph-S*	10700 (0.0)	13900 (1.3)
	18000 (1.6)	18900 (1.0)
	27100 (12.3)	23300 (1.6)

that the reaction rates observed in Fig. 6 are ascribable to the addition reaction of the thio radical with isoprene.

In Table 1 the addition reactivities of the thio radicals increase in the order 2-Naph-S* > 1-Naph-S*. Compared with PhS*, the reactivity of 2-Naph-S* is lower by a factor of about . Upon introduction of the OH substituent into 2-Naph-S*, the reactivity decreases; this trend is in good agreement with the findings for PhS*, in which the introduction of an electron-donating substituent decreases the reactivity [4].

Assuming $k_2 = 10^9$ M^{-1} s^{-1} [14], the k_{-1} values for the reaction with styrene can be calculated from the observed k_{-1}/k_2 as listed in Table 1. The k_{-1} values of the order of 10^6 s^{-1} indicate that the equilibrium of the addition step is established within a few microseconds.

3. MO calculation

The electronic transition energies calculated by the MNDO method for the naphthalenethio radicals are listed in Table 2 together with the observed transition energies and the relative intensities. They correspond well with the observed transition energies and relative intensities in this study. Large transition moments are attributed to those along the long axis of the naphthalene moiety. The observed intensity of the absorption bands supports the assignment of the absorption bands. The absorption intensities of HO-Naph-S* at longer wavelength are greater than those of 2-Naph-S*; the substituent OH with lone pair electrons may decrease the transition energy.

In Table 3 some parameters calculated by the CNDO method are summarized in order to find MO parameters which predict the reactivity of the radicals. The calculated order of the height of the SOMO energy is HO-Naph-S* > 1-Naph-S* > 2-Naph-S*. The lower the SOMO energy, the more the observed reactivity with olefins seems to increase. The total energy of 2-Naph-S* is lower than that of 1-Naph-S*; a

Table 3
Calculated parameters for Naph-S*

Naph-S*	SOMO		Total energy (eV)
	Orbital energy (eV)	Unpaired π electron density on S	
1-Naph-S*	−0.276	0.386	21.465
2-Naph-S*	−0.281	0.455	20.411
HO-Naph-S*	−0.273	0.418	18.313

tendency for unstable radicals to show a high reactivity is found as presumed from the linear free-energy relationship.

The densities of the unpaired π electron calculated from the coefficients of the atomic orbital of SOMO are shown below:
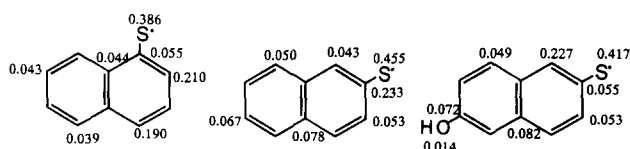
The unpaired π electron density on the S atom of 1-Naph-S* is lower than that for 2-Naph-S*; in the former radical the unpaired π electron on S delocalizes into the 1-naphthyl moiety, suggesting a low reactivity. The observed tendency is in good agreement with that anticipated by the unpaired π electron density. In HO-Naph-S* the unpaired π electron density on S is smaller than that in 2-Naph-S*, suggesting that the low reactivity is caused by the OH substituent. The actual reactivity may be determined by a combination of the MO parameters such as SOMO energy level, total energy and unpaired π electron density on the attacking atom.

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