

Laser-Flash Photolysis of Naphthyl Diselenides; Reactivities of Naphthylseleno Radicals

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ABSTRACT: Transient absorption spectra of 1-naphthylseleno (1-NaphSe[•]), and 2-naphthylseleno (2-NaphSe[•]) radicals, which are generated by laser-flash photolysis of the corresponding diselenides, were observed. The reactions of 1-NaphSe[•], and 2-NaphSe[•] with 2-methyl-1,3-butadiene and α -methylstyrene were investigated by following the decay rates of these seleno radicals. By both steady-state and laser-flash photolysis, it is proved that these seleno radicals add to alkenes in a reversible manner. The reaction rate constants for such reversible addition reactions were determined by conducting the reaction in the presence of O₂, which traps selectively the carbon-centered radicals formed by the addition reaction of the seleno radicals to the alkenes. The reactivity of 2-NaphSe[•] is higher than that of 1-NaphSe[•], both of which are less reactive than PhSe[•]. These reactivities were interpreted with the properties of SOMO calculated by MO method. © 1998 John Wiley & Sons, Inc. *Int J Chem Kinet* **30**: 193–200, 1998.

INTRODUCTION

Organic seleno radicals have been recognized as important intermediates in the photochemistry of organic selenium-compounds [1,2]. In general, flash-photolysis studies are useful to obtain direct information about the properties of the free radicals [3–6]. Among the chalcogen-atom centered radicals, the organic thio radicals have been studied extensively by the flash (laser)-photolysis [7–12]. However, in spite of the importance of the organic selenium-centered radicals in the various fields of chemistry, only a few flash pho-

tolysis studies have been reported on the selenium-centered radicals [13–15]. One of the important properties of the selenium-centered radicals is their reactivities to alkenes; reversible addition process has been reported by observing *cis-trans* isomerization of stilbene [16,17]. Therefore, it is interesting to observe such reversibility in direct kinetic study such as laser-flash photolysis method. Comparison of the reactivities of the selenium-centered radicals with corresponding sulfur analogues is also important for the better understanding of the selenium-centered radicals. For the comparison of different radicals, it is essential to determine the absolute rate constants of the radicals in a common reaction. Such rate constants of thio radicals in the addition reaction to alkenes, in which the addition reaction proceeded in a reversible fashion, have been directly obtained by the application of flash photolysis [18–20].

In this study, we report the formation of 1-

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naphthylseleno radical (1-NaphSe[•]), 2-naphthylseleno radical (2-NaphSe[•]) by a nano-second laser photolysis of the corresponding diselenides. By following the decay behavior of these seleno radicals, we determined the absolute rate constants of these radicals in the addition reaction to alkenes. We also performed some MO calculations to confirm the electronic properties of these free radicals.

EXPERIMENTAL

Materials

Naphthyl diselenides (NaphSe)₂ were prepared from commercially available bromonaphthalenes following the procedure reported for the preparation of phenyl diselenide [21]. They were used after purification by recrystallization from benzene. Commercially available phenyl diselenide was used as received. 2-Methyl-1,3-butadiene (isoprene) and α -methylstyrene were used after distillation. Solvents were of spectroscopic grade. The O₂-concentration in the solution was calculated by the Henry law using the reported coefficients [22].

Apparatus

Steady-light photolysis were performed in THF solutions of 0.02 mM diselenides with Xe—Hg lamp (150 W) by irradiating the light longer than 270 nm at 23°C; the UV absorption changes were followed by a UV/Vis spectrometer.

Laser-flash photolysis apparatus was a standard design with Nd:YAG laser of 6 ns duration. Diselenides of 0.2–2 mM were photolyzed with THG light (355 nm). Since the absorbance < 1 at 355 nm of 1 mM of diselenides, the transient species may be formed homogeneously in 10 cm rectangular optical cell. The monitoring light, which was perpendicular to the laser light, was selected with a monochromator. The transient spectra were measured with a multi-channel photodiode array (MCPD) with an image intensifier [23]. The time profiles were followed by a photomultiplier (PM) system. All the measurements were performed at 23°C.

MO Calculation

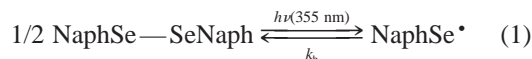
The MO calculations were performed with PM3 method using MOPAC Version 6 presented by Japan Program Exchange Association [24].

RESULTS AND DISCUSSION

Transient Absorption Spectra

The steady-state absorption spectra of (NaphSe)₂ and (PhSe)₂ are shown in Figure 1. The absorption peaks around 300 nm of (NaphSe)₂ are ascribed to the naphthalene moiety. The absorption tails extending from about 350 to 400 nm are attributed to Se—Se moiety. For phenyl diselenide (PhSe)₂, the absorption bands at 240 nm is due to the phenyl moiety and broad band from 300 to 400 nm to Se—Se moiety. Thus, laser photolysis was performed with 355 nm light, which predominantly excites Se—Se moiety.

The transient absorption spectra observed by the laser photolysis of (1-NaphSe)₂ with 355 nm light are shown in Figure 2, in which absorption peaks at 680 and 420 nm appear. The shape of the time-resolved spectra in the region of 500–750 nm measured by MCPD detector is similar to that measured by PM detector. In the wavelength region longer than 800 nm, no appreciable transient absorption was observed. The main absorption peaks at 420 nm and 680 nm are similar to those of 1-naphthylthio and 1-naphthyloxy radicals [25,26]. These absorption bands were observed even in the presence of O₂, suggesting that 1-NaphSe[•] is not reactive to O₂. This observation is similar to that of PhSe[•] [13,27]. The low reactivity to O₂ was also reported for the aryloxy and arylthio radicals [15,16]. Thus, the absorption bands in Figure 2 are attributed to 1-NaphSe[•] (eq. (1)).



Naph; 1-Naph and 2-Naph

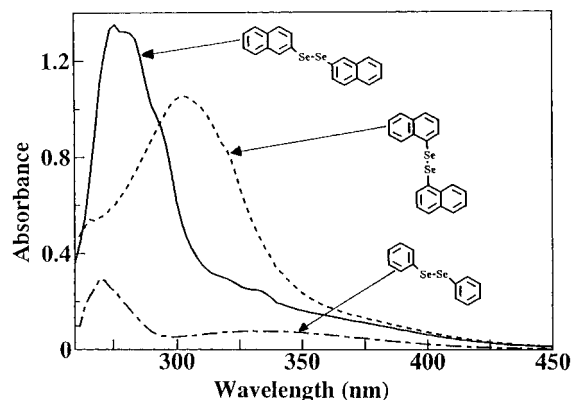


Figure 1 Absorption spectra of diselenides (0.02 mM) in THF in 10 mm of optical cell length.

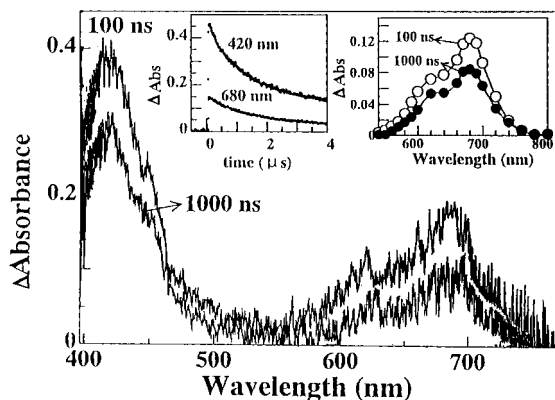


Figure 2 Transient absorption spectra obtained after laser photolysis (355 nm) of 1 mM of (1-NaphSe)₂ in deaerated THF (MCPD-detector): Insert: transient spectra measured by PM-detector and decay profiles at 420 and 680 nm in Ar-bubbled solution.

For (2-NaphSe)₂, the main absorption peaks appeared at 490 and 680 nm (Fig. 3). At the shorter region than 420 nm, other transient absorption band seems to be hidden. The spectral feature is similar to those of 2-naphthylthio and 2-naphthylthio radicals [25,26]. Thus, these absorption bands are attributed to 2-NaphSe[•] (eq. (1)).

The transient absorption spectra observed by the laser photolysis of (PhSe)₂ with 355 nm-light show peaks at 440 and 490 nm (Fig. 4). The decay profiles suggests that PhSe[•] is low reactive to O₂, which is in accord with the observed low reactivity to O₂ for aryloxy radicals, arylthio radicals, and arylseleno rad-

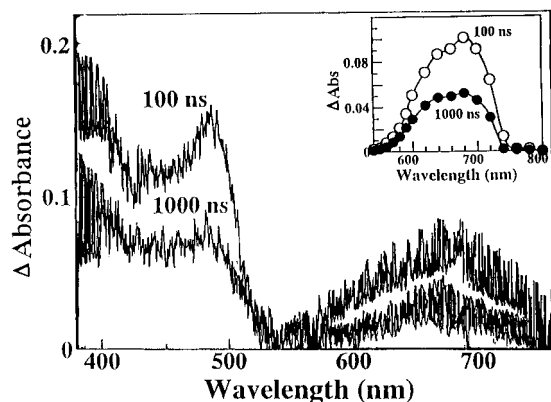


Figure 3 Transient absorption spectra obtained after laser photolysis (355 nm) of 1 mM (2-NaphSe)₂ in deaerated THF (MCPD-detector): Insert: Transient spectra measured by PM-detector.

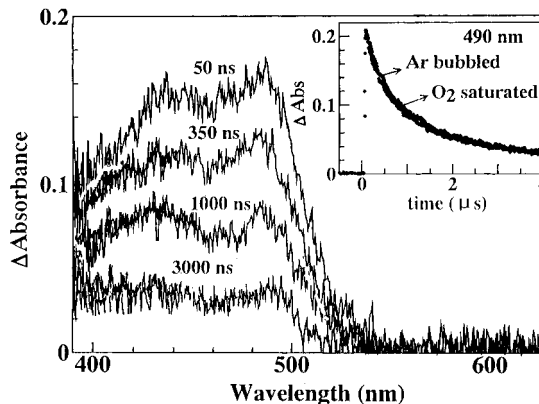


Figure 4 Transient absorption spectra obtained after laser photolysis (355 nm) of 1 mM (PhSe)₂ in deaerated THF (MCPD-detector): Insert: Decay profiles at 490 nm in Ar- and O₂-saturated solution.

ical [11]. Thus, the absorption bands in Figure 4 are attributed to PhSe[•] (eq. (2)).

With the delay time, the absorption band at 490 nm decays without shifting the absorption maxima. With decay of the absorption at 440 nm, on the other hand, the absorption maximum tends to shift to the shorter wavelength. Since this shift was observed only when the concentration of (PhSe)₂ was higher than 1 mM, this may be related to the radical adducts such as PhSe—Se[•](Ph)SePh (eq. (2)) as suggested by Burkey and Griller for PhS[•] [28].

The decay time-profiles of PhSe[•] in THF are shown (Fig. 5) with changing the concentration of (PhSe)₂, with which the initial absorption intensities

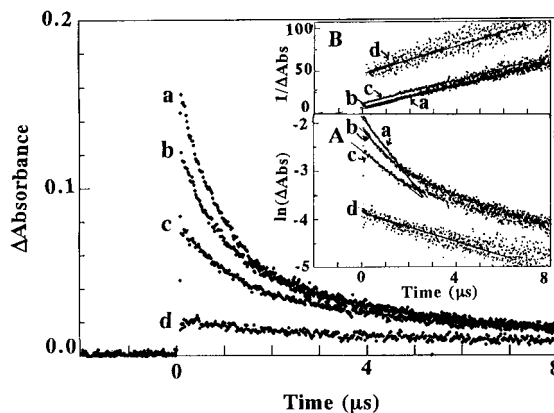
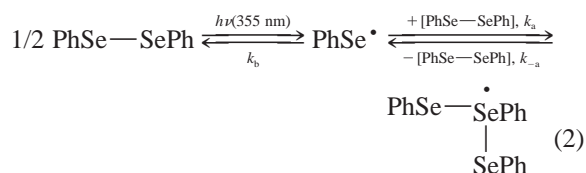


Figure 5 Concentration dependence of decay profiles of PhSe[•] at 485 nm in THF: (a) 2; (b) 1; (c) 0.5; and (d) 0.2 mM. Insert: (A) First-order plots and (B) second-order plots.

increase. In the inserted first-order plots (Fig. 5), each decay curve can not be fitted with a single exponential, which indicates that after the initial reaction of PhSe^\bullet with $(\text{PhSe})_2$, the equilibrium may be established. By the plots of the slopes obtained from the initial part of the first-order plots with the concentration of $(\text{PhSe})_2$, the second-order rate constant was evaluated to be $k_a = 1.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In second-order plots, good linear relations were obtained with the same slopes even the concentration of $(\text{PhSe})_2$ was varied. This suggests that the self-recombination of PhSe^\bullet becomes the rate determining step, since the reverse reaction of the radical adduct is very fast. This implies that it is difficult to observe the radical adduct in the considerable high concentration.



For NaphSe^\bullet , the change of the transient absorption spectra with the concentration of diselenide was not found, because of the complex absorption bands. Although the decay profiles show similar behavior to that of PhSe^\bullet , the bulky naphthalene group may hinder the formation of radical adducts.

Linear lines were obtained for the second-order plots for the decays of 1-NaphSe $^\bullet$, 2-NaphSe $^\bullet$, and PhSe $^\bullet$, suggesting that they predominantly recombine into the diselenide. The slopes give the ratio of recombination rate constant (k_b) to molar extinction coefficient (ϵ), $2k_b/\epsilon$. For 1-NaphSe $^\bullet$, $2k_b/\epsilon$ of the 680 nm band is about four-fold larger than that of 420 nm band, which indicates that the ϵ at 680 nm is 1/4 of that at 420 nm. This is in fair agreement with the ratio of the observed initial absorption intensities at 420 and 680 nm, which is ca. 1/3. This clearly supports that both bands are attributed to a species, 1-NaphSe $^\bullet$.

The ratios of $2k_b/\epsilon$ are summarized in Table I. The $2k_b/\epsilon$ of 2-NaphSe $^\bullet$ in viscous cyclohexane is smaller than that in less viscous THF, suggesting that recombination reaction of the free radicals is controlled by the diffusion rate of the two radicals. In order to evaluate the ϵ values, the laser-flash photolysis experiments of the diselenides were performed in the presence of electron donors such as tetramethyl-*p*-phenylenediamine (TMPD), no electron transfer reaction from TMPD to the seleno radicals was observed. In the presence of electron acceptor such as tetracyanoquinodimethane (TCNQ), evidence of the electron transfer from the seleno radical to TCNQ was not ob-

Table I Rate Constants (k_b) for Recombination of Seleno Radicals (RSe^\bullet)

RSe^\bullet	Solvent	η	$2k_b/\epsilon (\lambda_{\text{max}})$
		cP	$\text{cm s}^{-1} (\text{nm})$
1-NaphSe $^\bullet$	THF	0.55	1.3×10^6 (410)
1-NaphSe $^\bullet$	CH	0.98	5.5×10^5 (420)
2-NaphSe $^\bullet$	THF	0.55	6.7×10^6 (480)
2-NaphSe $^\bullet$	CH	0.98	4.1×10^6 (480)
PhSe $^\bullet$	THF	0.55	8.2×10^6 (480)
PhSe $^\bullet$	CH	0.98	6.4×10^6 (480)

CH; cyclohexane. $k_D = 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in THF and $k_D = 6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in CH. On assuming $k_D = k_b$, ϵ can be evaluated. From the ϵ values, initial concentration of the seleno radical by a laser exposure for 1 mM of diselenide with 10 mJ laser pulse is evaluated to be ca. 0.01 mM.

tained. Thus, it was difficult to evaluate the ϵ values of the seleno radicals. It is to be suggested that the k_b values are close to the diffusion-controlled limits (k_D), which can be calculated to be $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in THF and to be $6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in cyclohexane by Debye's equation ($k_D = 8 RT/3000\eta$ where η is solvent viscosity) [29].

In Figure 6, the decay curves of 2-NaphSe $^\bullet$ in the presence of reactive alkenes such as 2-methyl-1,3-butadiene (isoprene) are shown in the form of first-order plot. The decay rate of 2-NaphSe $^\bullet$ was not accelerated (Fig. 6(a)) compared with that in the absence of isoprene; upward curved line in the first-order plot indicates that the second-order process is included. In aerated and O_2 -saturated solutions, on the other hand, 2-NaphSe $^\bullet$ showed fast decay (Fig. 6(b) and (c)). The first-order rate constants (k_{1st}) was separated from the

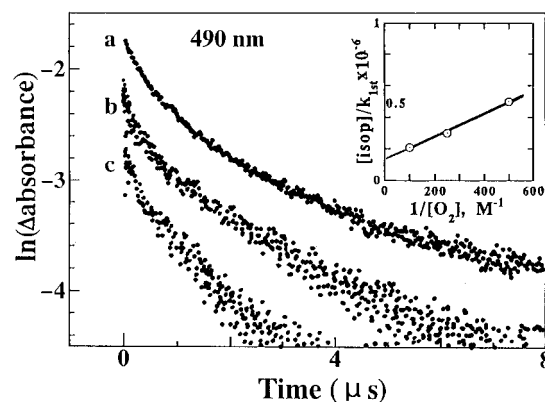
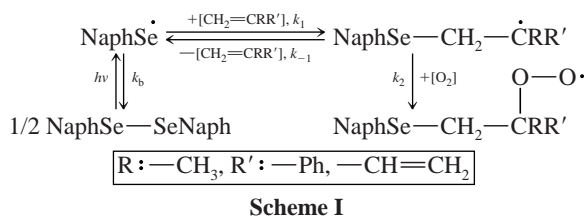


Figure 6 First-order decay plots of absorption band at 490 nm of 2-NaphSe $^\bullet$ in the presence of 50 mM of isoprene (a) in deaerated THF, (b) in aerated solution and (c) in O_2 -saturated solution. Insert: Plot of $[\text{isoprene}]/k_{1st}$ vs. $1/[\text{O}_2]$.

second-order rate constant (k_b) by curve-fitting method. The k_{1st} was proportional to both concentrations of isoprene and O_2 . Similar behavior was observed for α -methylstyrene (α -MSt)-2-NaphSe \cdot , isoprene-PhSe \cdot , and α -MSt-PhSe \cdot . In the case of 1-NaphSe \cdot , the decay rates were accelerated only slightly on addition of these alkenes, even in O_2 -saturated solution, indicating the low reactivity of 1-NaphSe \cdot .

This indicates that addition reaction of the seleno radicals to the alkenes proceeds in a reversible mode as indicated from *cis-trans* isomerization of stilbene [16,17]. Here, O_2 acts as a selective trapping agent for the carbon centered radicals which are generated by the addition reaction [30]. The selectivity of the carbon radical trapping by O_2 is quite high because O_2 is reactive only to the carbon-centered radicals [31], but not to the seleno radicals. These processes are illustrated in Scheme I, in which NaphSe \cdot adds to the terminal olefinic carbon in an anti-Markovnikov manner similar to the thio radicals [2,32].



As reported, *cis-trans* isomerization of stilbene photosensitized with (PhSe) $_2$ strongly indicates that the addition process is reversible [16,17]; i.e., the addition reaction of PhSe \cdot to stilbene produces the carbon-centered radical [PhSe-CHPh-C \cdot HPh], in which rotation around the C-C bond and successive elimination of PhSe \cdot induces *cis-trans* isomerization in the absence of O_2 . When O_2 is present in solution, isomerization was inhibited [16,17], indicating that O_2 traps the carbon-centered radical as shown in Scheme I.

To confirm Scheme I, the steady-light photolysis of (NaphSe) $_2$ was performed. The absorption spectra practically did not change even after the irradiation of (NaphSe) $_2$ for more than 25 min with > 270 nm light both in aerated and deaerated solutions. This is in accord with the laser-flash photolysis experiments, showing that NaphSe \cdot , which is unreactive to O_2 , is predominantly recombined back to the starting (NaphSe) $_2$. The small change in the spectrum by prolonged irradiation of more than 1 h may be due to the photochemical reactions such as change into mono-selenide [33,34]. In the presence of isoprene in deaerated

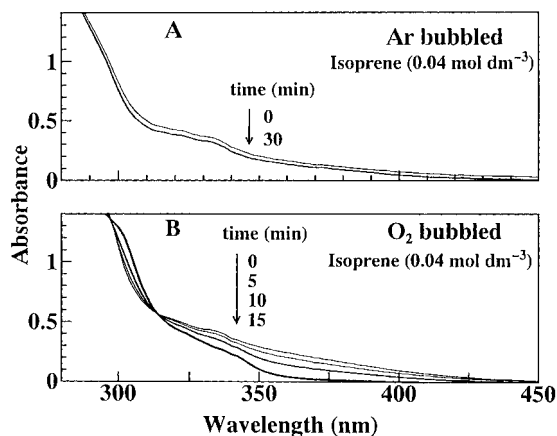


Figure 7 UV/Visible absorption spectral changes by photolysis of 0.05 mM (2-NaphSe) $_2$ with light (> 270 nm) in THF at 23°C in the presence of isoprene (A) in deaerated solution and (B) in O_2 -saturated solution.

ated solution, the absorption of (NaphSe) $_2$ was only slightly changed as shown in Figure 7(a); this corresponds with the laser-flash photolysis experiments in Figure 6(b) and (c). On the other hand, the absorption band of (NaphSe) $_2$ decreased rapidly in the presence of both isoprene and O_2 (Fig. 7(b)) with half-time ($t_{1/2}$) of 10 min. This phenomenon is corresponding to the laser-flash photolysis experiment (Fig. 6). These findings are supporting the reaction processes as shown in Scheme I.

Similarly, the absorption spectral changes were observed by the steady-light photolysis of (1-NaphSe) $_2$ as shown in Figure 8. The final spectrum indicates that

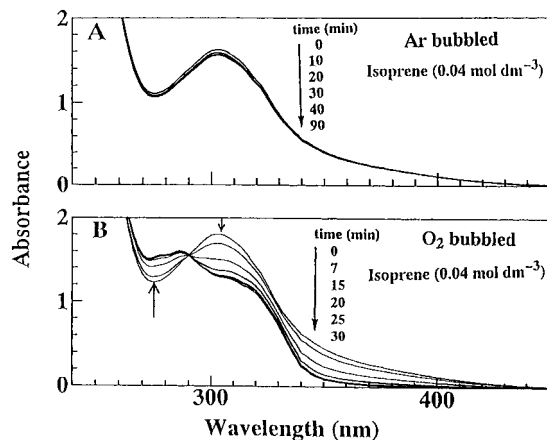


Figure 8 UV/Visible absorption spectral changes by photolysis of 0.05 mM (1-NaphSe) $_2$ with light (> 270 nm) in THF at 23°C in the presence of isoprene (A) in deaerated solution and (B) in O_2 -saturated solution.

the product also contains the naphthalene moiety. In the presence of isoprene in deaerated solution, the absorption band of (1-NaphSe)₂ was practically unchanged during the photolysis for 90 min with >270 nm light. In the presence of both isoprene and O₂, the absorption bands of (1-NaphSe)₂ decreased in a slower rate (*t*_{1/2} = 15 min) than that of (2-NaphSe)₂, although the acceleration of the decay rate of 1-NaphSe[•] was not observed in the laser-flash photolysis experiments even in the presence of O₂.

The steady kinetic analysis, which follows a decrease in diselenide or an increase in the product with steady-light photolysis, was reported for the addition reaction of the phenylthio radical to styrenes [35]; it was pointed out that evaluation of the relative rate constants was very difficult. Thus, only when bold assumptions that irreversibility is low for conjugated olefins were applied to the reversibility of addition process, the relative rate constants for addition reactions were evaluated [36]. In this study, on the other hand, since we could follow the decays of NaphSe[•] directly, kinetic analysis to obtain the rate constants may be possible by the selective radical trap method developed by us [8].

On the application of the steady-state approximation with respect to the intermediate [NaphSe—CH₂—C[•]RR'] in Scheme I, eq. (3) can be derived [8],

$$-d[\text{NaphSe}^{\bullet}]/dt = k_b[\text{NaphSe}^{\bullet}]^2 + k_1\{1 - k_{-1}/(k_{-1} + k_2[\text{O}_2])\}[\text{CH}_2=\text{CRR}'] \times [\text{NaphSe}^{\bullet}] \quad (3)$$

The observed actual decay curves are mixed order of the first-order and the second-order with respect to [NaphSe[•]] giving eq. (4),

$$-d[\text{NaphSe}^{\bullet}]/dt = k_{2\text{nd}}[\text{NaphSe}^{\bullet}]^2 + k_{1\text{st}}[\text{NaphSe}^{\bullet}] \quad (4)$$

where *k*_{2nd} = *k*_b, and

$$k_{1\text{st}} = k_1\{1 - k_{-1}/(k_{-1} + k_2[\text{O}_2])\} \times [\text{CH}_2=\text{CRR}'] \quad (5)$$

The following eq. (6) is derived from eq. (5). Thus, the *k*₁ value can be obtained by the extrapolation of the plots of [CH₂=CRR']/*k*_{1st} against 1/[O₂] as shown in the insert of Figure 6 *k*₋₁/*k*₁*k*₂ can be obtained from the slope.

$$[\text{CH}_2=\text{CRR}']/k_{1\text{st}} = 1/k_1 + k_{-1}/(k_1k_2[\text{O}_2]) \quad (6)$$

For isoprene and α-methylstyrene, the *k*₁ values are summarized in Table II for 2-NaphSe[•] and 1-NaphSe[•] with PhSe[•]. For 1-NaphSe[•], the dependence of *k*_{1st} values on [O₂] is too small to be observed by this method; thus, the *k*_{1st} observed in O₂-saturated THF was put equal to *k*₁. These *k*₁ values are less than about 5 × 10⁵ M⁻¹ s⁻¹.

The *k*₋₁ values are also listed in Table II; the *k*₋₁ values are calculated from the observed slope (*k*₋₁/*k*₁*k*₂) by substituting with observed *k*₁ and reported *k*₂; in Table II, *k*₂ = 2 × 10⁹ M⁻¹ s⁻¹ was adopted by averaging the representative reported values [31]. The *k*₋₁ values, which are in the order of 5 × 10⁶ – 10⁷ M⁻¹ s⁻¹, indicate that the equilibrium of the addition is established within 0.1–0.2 μs.

The *k*₁ values in Table II indicate that the addition reactivities of the seleno radicals increase in the order; 1-NaphSe[•] < 2-NaphSe[•] < PhSe[•]. The reactivity of NaphSe[•] was found to be lower than the corresponding NaphS[•] by one order in magnitude [26,37].

In the case of the reaction of NaphSe[•] with isoprene and α-methylstyrene, both the addition and H-atom abstraction reactions would be anticipated, because both reactions produce conjugated allyl and benzyl radicals having high resonance stability. In order to evaluate the H-atom abstraction ability of NaphSe[•], the decay rates of NaphSe[•] were observed in the presence of 1,4-cyclohexadiene, which is known as a strong hydrogen-atom donor [38]. It was observed that the decay rates were not accelerated in the pres-

Table II Rate Constants for Addition Reaction of Seleno Radicals with Isoprene and α-Methylstyrene in THF

RSe [•]	Isoprene		α-Methylstyrene	
	<i>k</i> ₁ M ⁻¹ s ⁻¹	<i>k</i> ₋₁ s ⁻¹	<i>k</i> ₁ M ⁻¹ s ⁻¹	<i>k</i> ₋₁ s ⁻¹
1-NaphSe [•]	<5 × 10 ⁵	----- ^a	<1 × 10 ⁵	----- ^a
2-NaphSe [•]	7.1 × 10 ⁶	(1.0 × 10 ⁷) ^b	7.0 × 10 ⁵	(1.6 × 10 ⁶) ^b
PhSe [•]	1.8 × 10 ⁷	(4.0 × 10 ⁶) ^b	3.0 × 10 ⁶	(1.0 × 10 ⁷) ^b

^a Variation of *k*_{1st} with changing [O₂] was too small to observe.

^b *k*₂ = 2 × 10⁹ M⁻¹ s⁻¹ [31].

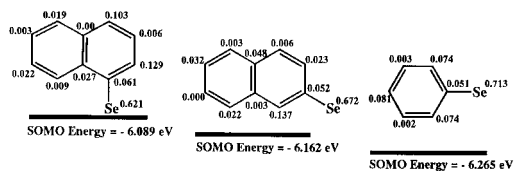


Figure 9 SOMO energies and their unpaired electron densities of NaphSe• and PhSe•.

ence of 1,4-cyclohexadiene, indicating that the H-atom abstraction abilities of these seleno radicals are quite low. This is also supported by the steady-light photolysis; in the presence of 1,4-cyclohexadiene, the decrease in the absorption bands of the diselenides was not observed. Therefore, the addition reaction is the only reaction responsible for the observed decay of NaphSe• besides the recombination reaction (Scheme I).

The molecular orbital (M.O.) energies and electron densities of NaphSe• were calculated by semiempirical restricted Hartree–Fock method using the optimized geometry obtained by PM3 method [24]; the results are shown in Figure 9. The reactivities of the radicals can be explained from these MO parameters [39]; the unpaired electron density of SOMO at Se atom increase in the order of 1-NaphSe• < 2-NaphSe• < PhSe•, which seems to be in accord with the observed reactivities.

Since the S-centered radical has highly electrophilic character, it would be expected that the seleno radicals also have similar character in some extent. In the addition reaction to alkenes, it has been anticipated that the contribution of polar resonance structure in the transition state of the reaction lowers the activation energy [40]. The higher the electrophilicity of the seleno radical, the lower the SOMO energy. The order of the SOMO energy is also in accord with the increasing reactivity of the radicals obtained by the experiments.

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