# Kinetic Study of Reactivities of Naphthalenylthio Radicals to Vinyl Monomers

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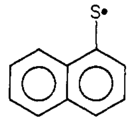
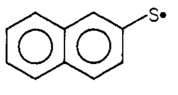
The absolute rate constants for the addition reactions of the 1- and 2-naphthalenylthio radicals to vinyl monomers have been determined by the flash photolysis technique. Since the addition reaction occurs in a reversible fashion, the reverse rate constant and the equilibrium constant have been estimated as the relative values. For each vinyl monomer the 2-naphthalenylthio radical is more reactive than the 1-naphthalenylthio radical. It is also suggested from the equilibrium constants that the latter radical is thermodynamically more stable than the former radical.

In free-radical reactions in which the naphthalene-substituted methyl and oxy radicals are produced, the 1-naphthalene derivatives are more reactive than the 2-naphthalene derivatives.[1–4] The reactivity ratios of hydrogen abstraction from methylnaphthalenes by the bromine and *tert*-butoxy radicals (1-methylnaphthalene/2-methylnaphthalene) are 1.5–2.1,[1,2] that of addition of the phenylthio radical to vinylnaphthalenes (1-vinylnaphthalene/2-vinylnaphthalene) is 1.4,[3] and that of hydrogen abstraction from naphthalenols by the *tert*-butoxy radical (1-naphthalenol/2-naphthalenol) is 2.0.[4] On the other hand, the difference in the reactivities between the 1- and 2-naphthalene-substituted radicals has not been directly estimated.

We will report here the absolute rate constants for addition of the naphthalenylthio radicals to vinyl monomers estimated by the flash photolysis technique. In addition, we can estimate the relative equilibrium constants since the thio radicals react with vinyl monomers in a reversible fashion. Therefore, we can discuss the reactivities on the basis of the thermodynamic parameters.


1-naphthalenylthio radical


2-naphthalenylthio radical

## Results and Discussion

The transient absorption spectra generated by the flash photodecomposition of naphthyl disulfides are shown in Figure 1. They are attributed to the respective naphthalenylthio radicals since the same absorption spectra were observed by the flash photodecomposition of the corresponding naphthalenethiols. The absorption bands of the 1-naphthalenylthio radical at 670 and 410 nm correspond to the bands of the 2-naphthalenylthio radical at 700 and 390 nm, respectively. We cannot detect an absorption band for the former radical at ca. 500 nm where there is a sharp band for the latter radical. The polarization of the transition moments can be inferred from the intensities of the bands; the band at 500 nm is the long-axis (along two benzene rings) transition, and the bands at 600–700 nm are the short-axis transition.

Decays of the transient absorption bands of the naphthalenylthio radicals show second-order kinetics (insert of Figure 1), suggesting that the thio radicals return to the disulfides via recombination. The slope of the second-order plot yields $2k_r/\epsilon$ where $k_r$ and $\epsilon$ refer to the rate constant for recombination and the molar extinction coefficient, respectively. The $2k_r/\epsilon$ value of the 2-naphthalenylthio radical at 400 nm in cyclohexane ($\eta$ = 0.940 cP)[5] is $5.6 \times 10^5$ cm s$^{-1}$ and that in *n*-heptane ($\eta$ = 0.407 cP)[5] is $1.1 \times 10^6$ cm s$^{-1}$ at 23 °C; such viscosity dependence indicates that recombination is diffusion controlled. From the diffusion-controlled rate constant estimated from the Debye equation ($6.8 \times 10^9$ M$^{-1}$ s$^{-1}$ in cyclohexane)[6,7] and the absorbance immediately after the flash ($A$ = 0.25 at 400 nm), the initial concentration of the naphthalenylthio radical generated by one flash exposure is estimated to be ca. $10^{-6}$ M. Since the decay curves were not affected by the presence of oxygen in solution, the reactivity of the naphthalenylthio radicals toward oxygen is low.

By the addition of vinyl monomers such as methyl methacrylate to the degassed solution, the enhancement of the decay rates of the naphthalenylthio radicals was not observed (Figure 2; decay curves a and b). When vinyl monomers and oxygen coexist, the decay rates increase with the concentrations of vinyl monomer and oxygen. Decay kinetics approach first order (decay curves c–g in Figure 2). From these findings it is suggested that the addition reaction of the naphthalenylthio radicals with vinyl monomers is a reversible process and that oxygen acts as a selective radical trap to the adduct carbon-centered radicals as shown in eq 1. Here, NaphS· refers to the naphthalenylthio radicals.

$$\mathrm{NaphS\cdot + CH_2{=}CHY \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NaphSCH_2C{\cdot}HY \xrightarrow[k_2]{O_2} peroxy\ radical} \quad (1)$$

The similarity of decay curves a and b in Figure 2 indicates that the equilibrium is established during the flash duration of the xenon lamp used in our experiment (ca. 10 μs). The reversibility of the addition process of the phenylthio radicals is confirmed by the product analysis[8–10] and by flash photolysis experiments.[11,12] The anti-Markovnikov addition products were confirmed.[13,14]

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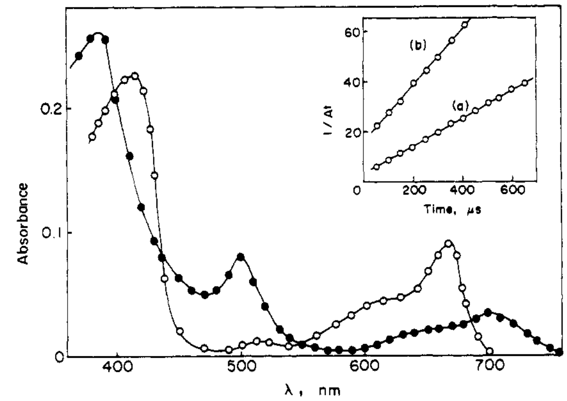

**Figure 1.** Transient absorption spectra generated by the flash photodecomposition of naphthyl disulfides (ca. $10^{-4}$ M) in aerated cyclohexane. The spectra are depicted with the absorbances at 75 μs after flash; ○ and ● denote the 1- and 2-naphthalenylthio radicals, respectively. insert: second-order plots for decay of 2-naphthalenylthio radical at 400 nm (a) in cyclohexane and (b) in *n*-heptane.

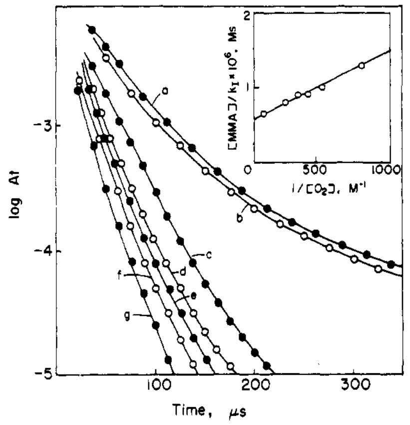

**Figure 2.** First-order plots for decay of the 2-naphthalenylthio radical at 500 nm in the presence of methyl methacrylate (MMA) and oxygen. [MMA]: a, 0; b–g, $1.2 \times 10^{-2}$ M. [$O_2$]: a and b, 0; c, $1.1 \times 10^{-3}$; d, $1.8 \times 10^{-3}$; e, $2.7 \times 10^{-3}$; f, $4.0 \times 10^{-3}$; g, $1.2 \times 10^{-2}$ M.

On the basis of the steady-state assumption with respect to the concentration of the adduct carbon-centered radical, eq 2 can be derived from the rate expression for the decay

$$[CH_2{=}CHY]/k_I = 1/k_1 + k_{-1}/k_1k_2[O_2] \qquad (2)$$

of the naphthalenylthio radicals in the reaction eq 1.[11] Here, $k_I$ refers to the first-order rate constant which can be estimated from the slope of the first-order plot. When decay kinetics are mixed-order, consisting of second-order ($2k_r[\text{NaphS}\cdot]^2$) and first-order ($k_I[\text{NaphS}\cdot]$), the $k_I$ value can be estimated with a graphic method[15] or a computer-simulation method[16] by using the $2k_r/\epsilon$ value. Insert of Figure 2 shows the plot of $[CH_2{=}CHY]/k_I$ vs. $1/[O_2]$ for the reaction of 2-naphthalenylthio radical with methyl methacrylate; a linear correlation was observed. Similar correlations were observed for other reaction systems. The $k_1$ values were directly estimated from the intercept ($1/k_1$), and the $Kk_2$ values were estimated from the slope ($k_{-1}/k_1k_2$), where the equilibrium constant $K$ is defined as $k_1/k_{-1}$. The $k_1$ and $Kk_2$ values are summarized in Table I for the 1-naphthalenylthio radical and in Table II for 2-naphthalenylthio radical. In each table, the upper five vinyl monomers are conjugated ones, and the lower two are nonconjugated ones; in each group the upper vinyl monomer has the more electron-rich double bond. The relative reverse rate constant ($k_{-1}/k_2$) can be calculated from $k_1/Kk_2$; the $k_{-1}/k_2$ values for conjugated vinyl monomers are ca. $10^{-3}$ M, and those for nonconjugated ones are ca. $10^{-2}$ M.

**Table I. Rate Constants ($k_1$) and Relative Equilibrium Constants ($Kk_2$) for the Addition Reactions of 1-Naphthalenylthio Radical to Vinyl Monomers in Cyclohexane at 23 °C[a]**

| vinyl monomer[b] | $k_1$, $M^{-1}$ $s^{-1}$ | $Kk_2$, $M^{-2}$ $s^{-1}$ |
|---|---|---|
| α-MSt | $1.3 \times 10^7$ | $1.2 \times 10^{10}$ |
| St | $4.9 \times 10^6$ | $7.0 \times 10^9$ |
| MMA | $5.7 \times 10^5$ | $2.2 \times 10^8$ |
| MAN | $3.3 \times 10^5$ | $3.3 \times 10^8$ |
| AN | $5.6 \times 10^4$ | $2.8 \times 10^7$ |
| IBVE | $1.4 \times 10^4$ | $1.2 \times 10^6$ |
| VAc | $1.3 \times 10^3$ | $1.8 \times 10^5$ |

[a] Each value contains estimation error of ca. 10%.
[b] Abbreviations of vinyl monomers: α-MSt, α-methylstyrene; St, styrene; MMA, methyl methacrylate; MAN, methacrylonitrile; AN, acrylonitrile; IBVE, isobutyl vinyl ether; VAc, vinyl acetate.

**Table II. Rate Constants ($k_1$) and Relative Equilibrium Constants ($Kk_2$) for the Addition Reactions of 2-Naphthalenylthio Radical to Vinyl Monomers in Cyclohexane at 23 °C[a]**

| vinyl monomer | $k_1$, $M^{-1}$ $s^{-1}$ | $Kk_2$, $M^{-2}$ $s^{-1}$ |
|---|---|---|
| α-MSt | $3.4 \times 10^7$ | $5.0 \times 10^{10}$ |
| St | $1.2 \times 10^7$ | $2.6 \times 10^{10}$ |
| MMA | $1.8 \times 10^6$ | $1.1 \times 10^9$ |
| MAN | $8.3 \times 10^5$ | $1.4 \times 10^9$ |
| AN | $2.1 \times 10^5$ | $1.3 \times 10^8$ |
| IBVE | $4.2 \times 10^4$ | $7.7 \times 10^6$ |
| VAc | $4.8 \times 10^3$ | $6.2 \times 10^5$ |

[a] Each value contains estimation error of ca. 10%.

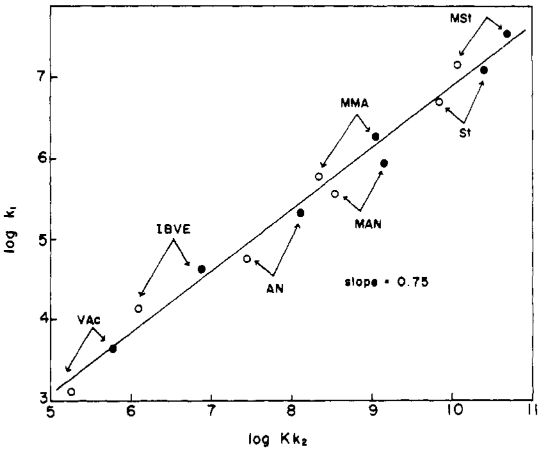

**Figure 3.** Plots of log $k_1$ vs. log $Kk_2$; ○ and ● denote the 1- and 2-naphthalenylthio radicals, respectively. Abbreviations of vinyl monomers are in footnote *b* of Table I.

Replacing the $k_2$ values by the reported one ($10^8$–$10^9$ $M^{-1}$ $s^{-1}$),[17] we can estimate the $K$ values to be $10^2$–$10^{-4}$ $M^{-1}$; for the upper two vinyl monomers the forward reactions are exothermic, and for the other vinyl monomers the reactions are endothermic. The $k_{-1}$ values are estimated to be $10^5$–$10^7$ $s^{-1}$ from tables; such fast backward reactions are compatible with our observation that the equilibrium is

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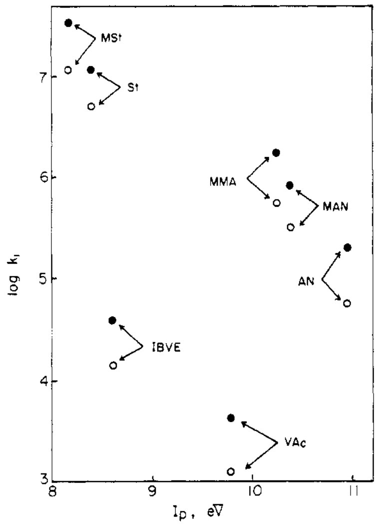

**Figure 4.** Plots of log $k_1$ vs. the ionization potentials of vinyl monomers ($I_p$); ○ and ● denote the 1- and 2-naphthalenylthio radicals, respectively.

established during the xenon flash duration (ca. 10 $\mu$s).

Figure 3 shows the plot of log $k_1$ vs. log $Kk_2$; a linear free-energy relationship is established. This suggests that the reactivities of each naphthalenylthio radical toward various vinyl monomers are mainly determined by the thermodynamic stabilities of the adduct carbon-centered radicals. On the other hand, it can be presumed that the dependence of the $k_1$ values upon the ionization potentials of vinyl monomers is a measure of the polar transition state.[18] In Figure 4, the upper group contains conjugated vinyl monomers, and the lower group contains nonconjugated ones; each group shows a negative dependence, which can be interpreted by the contribution of a polar resonance structures such as [NaphS$^-$, CH$_2$=CHY$^+\cdot$]. Thus, the both factors from the linear free-energy relationship and the polar transition state are affecting the reactivities.

For each vinyl monomer, the $k_1$ value for the 2-naphthalenylthio radical is greater than that for the 1-naphthalenylthio radical by a factor of 2.5–3.8; such a difference is sufficiently greater than the estimation error in our experiments. Although the addition of the 1-naphthalenylthio radical is considered to be entropically less favorable, it is found that such a steric factor may not influence the reactivity since the points for both the naphthalenylthio radicals in Figure 3 fit to one line. The polar nature of both the thio radicals is also same since the similar tendency is seen in Figure 4. As seen in Figure 3, the greater exothermicity of the 2-naphthalenylthio radical compared with that of the 1-naphthalenylthio radical corresponds to the higher reactivity toward each vinyl monomer; thus the 2-naphthalenylthio radical is thermodynamically less stable than the 1-naphthalenylthio radical.

The phenylthio radical is more reactive than the naphthalenylthio radicals (PhS·/2-NaphS·/1-NaphS· ratio of 6:3:1),[11] which also reflect the less stable phenylthio radical. The resonance energies calculated for the benzyl radical and the 1- and 2-naphthylmethyl radicals are (in $\beta$ units) 0.022, 0.024, and 0.026, respectively. This order is in good agreement with our observation about the stabilities of the thio radicals. It is notable that the reactions producing the naphthalene-substituted radicals as mentioned in the introduction[1-4] can also be interpreted by the linear free-energy relationship; the reactivities are proportional to the stabilities of the radicals in the products.

## Experimental Section

Naphthyl disulfides were prepared from the commercially available naphthalenethiols by the action of iodine. Vinyl monomers were used after distillation under reduced pressure. Cyclohexane and $n$-heptane used as solvents were of spectrophotometric grade.

The flash experiments were made at room temperature which was controlled at 23 ± 1 °C. The flash apparatus was of standard design; the half-duration and flash energy of the xenon flash lamp (Xenon Corp., N-851C) were ca. 10 $\mu$s and 150 J, respectively. The flash light in the range of 350–400 nm was selected by the use of appropriate light filter to prevent the excitation of the vinyl monomers. Kinetic observations were made with a continuous monitor light source and photomultiplier detection. The oxygen concentrations in solution were calculated from the Henry law by dissolving oxygen under partial pressure after degassing the solution.[19]

**Registry No.** 1-Naphthalenylthio radical, 85736-23-8; 2-naphthalenylthio radical, 85736-24-9; styrene, 100-42-5; methyl methacrylate, 80-62-6; methyacrylonitrile, 126-98-7; acrylonitrile, 107-13-1; isobutyl vinyl ether, 109-53-5; vinyl acetate, 108-05-4; $\alpha$-methylstyrene, 98-83-9.

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# Formation and Rearrangements of Blocked Aromatic Molecules Substituted with O$^-$ Groups

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Reaction of diketone **7** with strong bases results in migration of the angular methyl group to form 10-hydroxy-10-methyl-9-anthrone (**9a**). Surprisingly, no similar reaction occurs on treatment of diketone **11**, the 1-methyl analogue of **7**, with base. Reaction of **7** with base is therefore considered to result in stereospecific abstraction of the pseudoaxial $\beta$ proton to yield the blocked aromatic anion **3**. Rearrangement of diketone **15**, the 6-methyl analogues of **7**, yields 2,10-dimethyl-10-hydroxy-9-anthrone (**16**), indicating that rearrangements of **3** and **15** proceed by [1,2] migrations of the angular methyl groups.

Molecules containing "blocked aromatic"—cyclohexadienone or methylenecyclohexadiene (semibenzene)—rings undergo an exceptional variety of rearrangement processes to yield products in which the blocked aromatic

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