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# Flash Photolysis Study for Substituent and Solvent Effects on Spin-trapping Rates of Phenylthiyl Radicals with Nitrones

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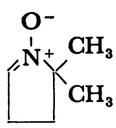
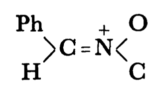
The spin-trapping rates for the reactions of para-substituted phenylthiyl radicals with nitrones have been determined by flash photolysis. For the phenylthiyl radical, the rate constant (in $mol^{-1} dm^3 s^{-1}$) in benzene for a cyclic nitrone, 5,5-dimethyl-1-pyrroline *N*-oxide, is $5.2\times10^8$, which is greater than that for acyclic one, *N*-*t*-butyl-α-toluenimine *N*-oxide ($1.1\times10^7$). The rates decrease with the solvent polarity and with the hydrogen-bonding ability; the maximum ratio of *ca.* 30 is observed for the rates between cyclohexane and methanol. Combined with the observed substituent effects, the mechanisms of the reactions and properties of the transition states are discussed.

The spin-trapping rates can be relatively determined from the stationary ESR signal intensities of the stable spin adducts,[1–4)] while, for the reactions producing the unstable spin adducts, the time dependences of decays of the attacking radicals or formations of the spin adducts must be directly followed.[5–7)] In the previous paper we have shown that the absolute rates for spin trapping of the thiyl radicals with nitroso spin-traps were determined from decay of the thiyl radicals generated by flash photolysis;[8)] however, in these reaction rates we could not find the solvent effects which were reported in the literature.[4b)] We can expect the solvent effects in polar and hydrogen-bonding solvents for more polar spin traps, nitrones ($-C=N^+-O^-$). In this study we investigate the thiyl radical-trapping reactions with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as a cyclic nitrone and *N*-*t*-butyl-α-toluenimine *N*-oxide (PBN, α-phenyl-*N*-*t*-butylnitrone) as an acyclic nitrone. From both solvent and substituent effects, the property and structure of the transition state are discussed.


DMPO


$$\overset{\text{Ph}}{\underset{\text{H}}{}}\!\!>\!C=\overset{+}{N}\!\!<\!\overset{O^-}{\underset{C(CH_3)_3}{}}$$
PBN

## Experimental

Commercially available DMPO (Aldrich) and PBN (Aldrich) were used without further purification. Diphenyl disulfides were purified by recrystallization from ethanol. Solvents were distilled when spectrophotometric grade ones were not available. Samplings and measurements were made in the dark to prevent inadvertent photolysis.

The ESR spectra of the spin adducts were measured with a Varian E4 ESR spectrometer during the photolysis of disulfides (*ca.* $10^{-3}$ mol $dm^{-3}$) with the light between 350 and 450 nm (500 W high pressure Hg lamp) in the presence of nitrones (*ca.* $10^{-3}$ mol $dm^{-3}$) in degassed solution (*ca.* $10^{-1}$ Pa). Decay of the ESR signals after cutting off the light was followed by a fast recorder or by a transient memory.

The xenon flash photolysis apparatus was of standard design;[8)] input energy was 150 J and the half-duration of xenon flash lamp (Xenon Corp. N-851 C) was *ca.* 10 μs. By the use of light filter, disulfides were flash photodecomposed with the light between 350 and 450 nm so as to avoid the photolysis of nitrones.

## Results and Discussion

*ESR Measurements.* ESR spectra were observed during the photolysis of disulfides in the presence of nitrones as shown in Fig. 1. The hyperfine splitting constants of the nitrogen atom ($a_N$) and the α-hydrogen atom ($a_H$) are summarized in Table 1. The spin adducts with PBN can be ascribed to the nitroxides, **1**, as shown in Scheme 1, since both $a_N$ and $a_H$ are in good agreement

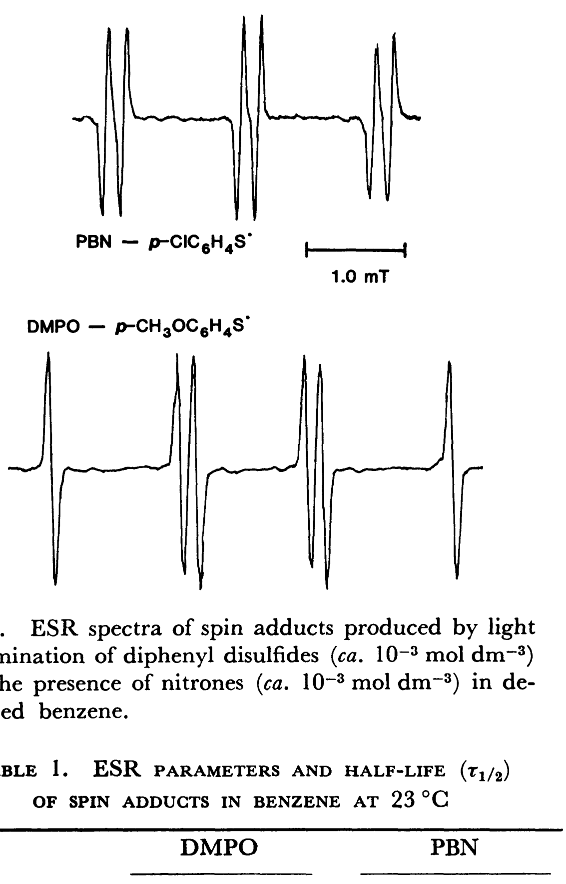
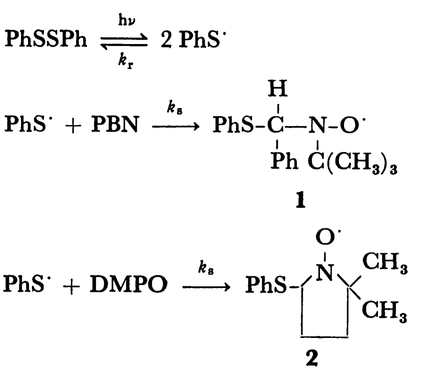


Fig. 1. ESR spectra of spin adducts produced by light illumination of diphenyl disulfides (*ca.* $10^{-3}$ mol $dm^{-3}$) in the presence of nitrones (*ca.* $10^{-3}$ mol $dm^{-3}$) in degassed benzene.

TABLE 1. ESR PARAMETERS AND HALF-LIFE ($\tau_{1/2}$) OF SPIN ADDUCTS IN BENZENE AT 23 °C

| | DMPO | | | PBN | | |
|---|---|---|---|---|---|---|
| | $a_N$ / *mT* | $a_H$ / *mT* | $\tau_{1/2}$ / *s* | $a_N$ / *mT* | $a_H$ / *mT* | $\tau_{1/2}$ / *s* |
| *p*-$ClC_6H_4S^·$ | 1.36 | 1.43 | 3.3 | 1.38 | 0.18 | 0.38 |
| *p*-$CH_3OC_6H_4S^·$ | 1.33 | 1.45 | 1.7 | 1.39 | 0.18 | 0.15 |



Scheme 1.

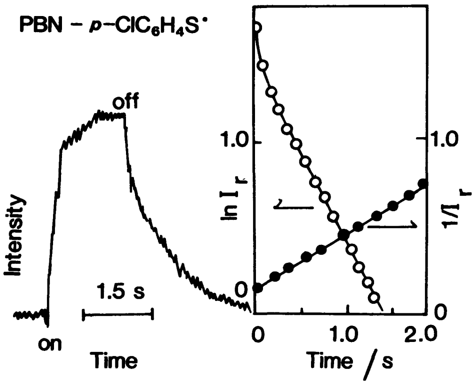


Fig. 2. Time dependence of ESR signal of the spin adduct produced by light illumination of disulfide in the presence of PBN at 23°C. The decay is plotted with the first-order (ln $I_r$ *vs.* time; $I_r$ refers to the relative signal intensity) and with the second-order (1/$I_r$).

with the reported ones.[9] The spin adducts with DMPO have large $a_H$ value characteristic to cyclic nitroxides, **2**; such large $a_H$ values come from both conformational and electronic reasons.[10]

Figure 2 shows that the growth of the ESR signal intensity reaches at the maximum within *ca.* 1 s and that the signal decays rapidly after cutting off the light. The decay curves seem to obey either one second-order kinetics or two first-order kinetics. The half-life of the spin adduct is approximately estimated from the initial part of the decay curves (Table 1). The spin adducts with DMPO are more stable than those with PBN. The substituent effects of the phenylthiyl moiety on $a_N$, $a_H$, and half-life of the nitrone adducts are smaller than those of the nitroso adducts;[8] this finding is reasonably interpreted because the C–S bond is formed at the α-carbon in the former, whereas the S atom bonds directly to the nitrogen atom in the latter.

*Transient Absorption Spectra.* Figure 3 shows transient absorption spectra observed by the flash photodecomposition of bis(*p*-*t*-butylphenyl) disulfide in the presence of PBN. The absorption band at *ca.* 510 nm observed immediately after flash (35 μs) is attributed to the *p*-*t*-butylphenylthiyl radical.[8] Similar absorption bands were observed for other phenylthiyl radicals. The decay rate of the thiyl radical in the presence of PBN (decay curve at 520 nm of Fig. 3) is faster than that without PBN. The decay curve at 520 nm is composed of the fast and slow decay parts; the slow part yielded a spectrum which is depicted with the absorbances at 400 μs after flash. This spectrum may be attributed to the spin adduct. The decay profile at 425 nm shown in a long time scale in Fig. 3 seems to obey second-order kinetics rather than first-order kinetics. The half-life evaluated from the decay at 425 nm is *ca.* 1 ms which is considerably shorter than that evaluated from the ESR signal. This suggests the presence of the fast decay process which did not appear in the decay of the ESR signal; otherwise, there may be inadvertent photolysis of the spin adducts with the monitoring light of the flash photolysis experiment. The second-order decay of the spin adducts indicates that the decomposition mechanism of the spin adducts may include the dimerization process to the diamagnetic dimers before the fission of the bonds as Grillan and Ingold suggested.[11] Similar phenomena were observed for DMPO.

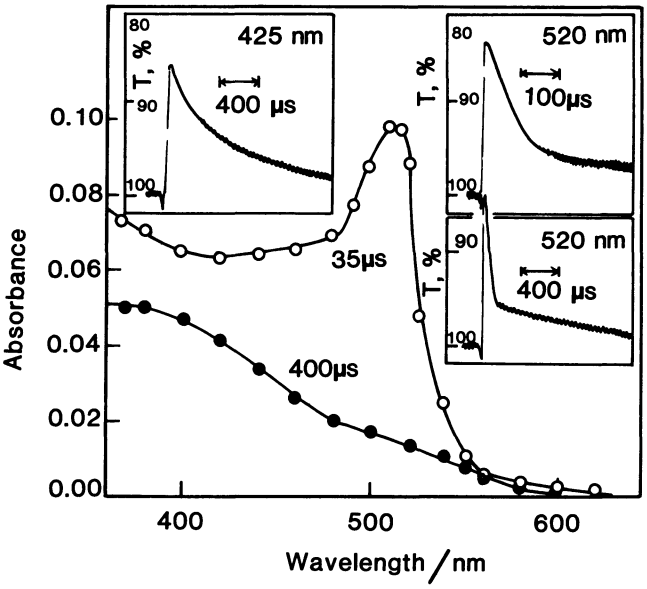


Fig. 3. Transient absorption spectra observed by flash photolysis of bis (*p*-*t*-butylphenyl) disulfide (*ca.* $10^{-4}$ mol dm$^{-3}$) in the presence of PBN ($3.0\times10^{-3}$ mol dm$^{-3}$) in benzene. The absorption band at 510 nm observed 35 μs after flash is ascribed to the *p*-*t*-butylphenylthiyl radical and the band of 400 μs after flash is ascribed to the spin adduct. Insert: The fast decay and the slow decay at 520 and 425 nm.

*Determination of Rate Constants.* The decay rate of the thiyl radical can be evaluated from the first order plots for the decay of the absorption band of the thiyl radical by the addition of nitrones (Fig. 4). The rate can be expressed as Eq. 1:

$$-\mathrm{d}[\mathrm{PhS}^\cdot]/\mathrm{d}t = 2k_r[\mathrm{PhS}^\cdot]^2 + k_s[\mathrm{PhS}^\cdot][\mathrm{nitrone}] \quad (1)$$

The processes for the reproduction of the thiyl radical with the decomposition of the adduct and the reaction of the thiyl radical with the spin adduct are omitted from the rate expression because of their small contribution.[8] By the addition of nitrones in large excess

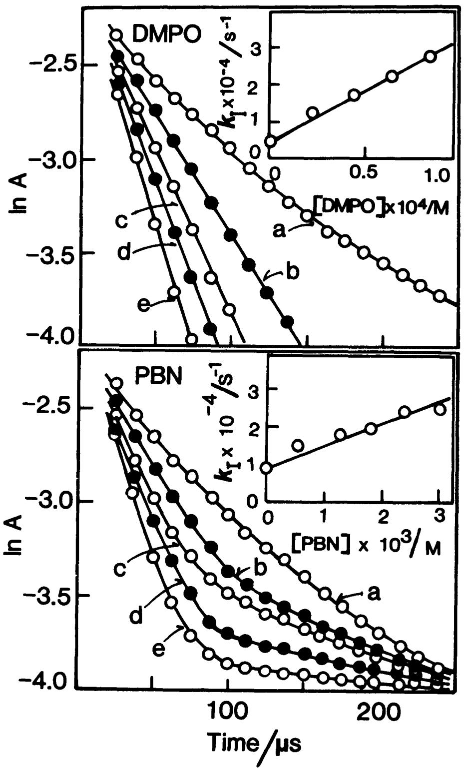


Fig. 4. The first-order plots for decay of *p*-t-butylphenylthiyl radical. [DMPO] × $10^5$ mol $dm^{-3}$: a, 0; b, 2.2; c, 4.4; d, 6.6; and e, 8.8. [PBN] × $10^3$ mol $dm^{-3}$: a, 0; b, 0.55, c, 1.3; d, 2.4; and e, 3.0. Insert: Pseudo-first-order plots; 1 M = 1 mol $dm^{-3}$.

compared with the concentration of the thiyl radical generated by one flash exposure which was estimated to be *ca.* $10^{-6}$ mol $dm^{-3}$,[8] decay kinetics approaches first order (Fig. 4). In Fig. 4, the slopes of the first-order plots ($k_I$) are plotted against [nitrone]; fairly good pseudo-first-order relationships are found. The slopes yield the rate constants for spin trapping ($k_S$). In the case of PBN, although the slow decay part disturbs the analysis, the $k_S$ values can be estimated from the slopes of the initial parts.

*Substituent Effect.* In order to clarify the contribution of the polar transition state to the reactivity, we at first examined the substituent effect of the phenylthiyl radicals. In Table 2 the rate constants for the phenylthiyl radicals with both electron-donating and withdrawing substituents are summarized. For each nitrone, the electron-withdrawing substituents accelerate the rates and *vice versa.* The Hammett plots *vs.* $\sigma^+$ (Fig. 5) yielded straight lines, whereas the plots *vs.* $\sigma$ yielded curves. This suggests that the resonance factors contribute to the reactivities in addition to the inductive effects and that, in the Yukawa-Tsuno equation, log $(k/k_0)=\rho(\sigma^{\circ}+r\Delta_{R^+})$, the $r$ value is about 1.[12] The slopes for the $k_S$ values in benzene yielded $\rho^+=0.98\pm0.02$ for DMPO and $\rho^+=1.14\pm0.02$ for PBN. The observed interval between both lines is the difference in the reactivities of two nitrones.

Although the rates decrease in methanol (Table 2), a straight line is also found in the Hammett plot for DMPO (Fig. 5); $\rho^+=1.15\pm0.02$ which is slightly greater than that in benzene. Positive $\rho^+$ values, in general, indicate that there is a contribution of the polar resonance structures to the transition state such as [$PhS^-$, nitrone$^{+\cdot}$]. In the case of the phenylthiyl radicals, however, since the thermodynamic stabilities vary with the change of the para substituents,[13] some parts of the observed $\rho^+$ value for the reactivities may come from the linear free-energy relationship and remaining parts can be attributable to the polar transition state.

Table 2. Substituent effect on spin-trapping rate constants ($k_S$) of $p$-$XC_6H_4S^\cdot$ with DMPO and PBN in benzene or in methanol at 23 °C

| X | $k_S \times 10^{-6}$ / mol$^{-1}$ dm$^3$ s$^{-1}$ DMPO[a] | | PBN[b] |
|---|---|---|---|
| | In benzene | In methanol | In benzene |
| Br | 750 | 72 | 17 |
| Cl | 700 | 60 | 12 |
| H | 520 | 54 | 11 |
| $t$-$C_4H_9$ | 260 | 26 | 5.6 |
| $CH_3$ | 300 | 19 | 5.0 |
| $CH_3O$ | 110 | 5.4 | 1.1 |

a) Estimation error is *ca.* 10%. b) Estimation error is *ca.* 20%.

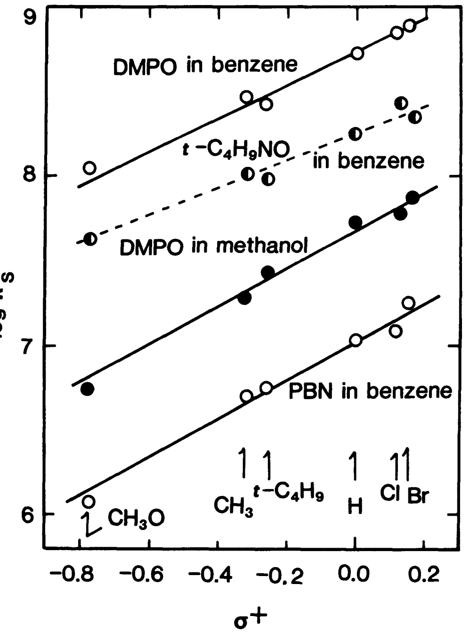
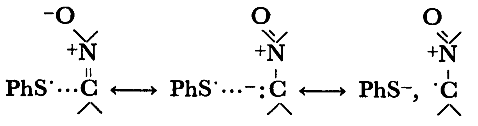


Fig. 5. The Hammett plots of log $k_S$ *vs.* $\sigma^+$. Data for $t$-$C_4H_9NO$ are cited from ref. 8.

The slope of the Hammett plot for 2-methyl-2-nitrosopropane (Fig. 5)[8] is less than those for nitrones; this indicates that the contribution of the polar resonance structure for nitrones is greater than that for nitroso compounds. The polar structures anticipated for nitrones are shown below (**3a**—**3c**), in which **3c** reasonably represents the charge transfer from nitrone to the thiyl radical. On the other hand, the polar resonance structures for the nitroso spin-trapping reactions are not so stable as nitrones. For a highly electrophilic benzoyloxyl radical-trapping with PBN, a similar tendency was reported,[1a] whereas the opposite tendency was reported for less electrophilic attacking radicals such as *t*-butoxyl radical and primary radical.[1c,4a]



**3a** **3b** **3c**

*Solvent Effect.* The $k_S$ values for the reaction of *p*-*t*-butylphenylthiyl radical with DMPO in nonpolar, polar, and alcoholic solvents are summarized in Table 3. The $k_S$ values decrease with the solvent polarity; the ratio of $k_S$ in cyclohexane to $k_S$ in 1,2-dichloroethane is *ca.* 5. Alcoholic solvents reduce the $k_S$ values in a great extent; the ratio of $k_S$ in cyclohexane to that in methanol is *ca.* 30. A similar tendency was found for the reaction system with PBN. Figure 6 shows a plot of log $k_S$ *vs.* the Kirkwood parameter, $(\varepsilon-1)/(2\varepsilon+1)$, which is one of solvent polarity parameters.[14] The points are divided into two groups; the upper group includes nonpolar and polar solvents and the lower one includes alcoholic solvents. The upper group shows a linear correlation with a slope of −2.48, which corresponds to the coefficient of the following equation derived by Stearn and Eyring.[15]

$$\ln k_s = \ln k_s^{\circ} - \frac{1}{kT}\cdot\frac{\varepsilon-1}{2\varepsilon+1}\cdot\left(\frac{\mu_s^2}{r_s^3}+\frac{\mu_n^2}{r_n^3}-\frac{\mu_{\neq}^2}{r_{\neq}^3}\right) \qquad (2)$$

where $k_s^{\circ}$ refers to the rate constant at $\varepsilon=1$; μ and r refer to the dipole moment and radius, respectively. Subscripts s, n, and ≠ refer to the thiyl radical, nitrone, and activated complex, respectively. The component of the dipole moment of the thiyl radical parallel to the C-N-O bonds of nitrone can be assumed to be zero when the thiyl radical approaches perpendiculary the C-N-O bonds as shown in **3**. Thus, by substituting $r_s=r_n=3.0$ Å, $r_{\neq}=3.5$ Å, and $\mu_n=3.55$ D,[16] we can calculated $\mu_{\neq}$ to be 3.1 D. The activated complex becomes less polar than nitrone in the reactant; this suggests that there is a contribution of the resonance structures as would be anticipated from the substituent effect, **3b** and **3c**, which do not play any important role in nitrone alone in the reactant.

Table 3. Solvent effect on spin-trapping rate constants ($k_S$) of $t$-$C_4H_9C_6H_4S^{\cdot}$ with DMPO at 23 °C

| Solvent | $k_S\times10^{-7}$ | Solvent | $k_S\times10^{-7}$ |
|---|---|---|---|
| $c$-$C_6H_{12}$ | 79 | $C_5H_5N$ | 21 |
| $CCl_4$ | 52 | $CH_3CN$ | 23 |
| $(n$-$C_3H_7)_2O$ | 43 | $(CH_3)_2SO$ | 19 |
| $(i$-$C_3H_7)_2O$ | 42 | $CH_2ClCH_2Cl$ | 16 |
| $CH_3CO_2C_2H_5$ | 30 | $(C_2H_5)_2CHOH$ | 4.3 |
| $FC_6H_5$ | 23 | $C_2H_5OH$ | 3.0 |
| $(CH_2)_4O$ | 22 | | |

Unit of $k_S$; $mol^{-1}\,dm^3\,s^{-1}$.

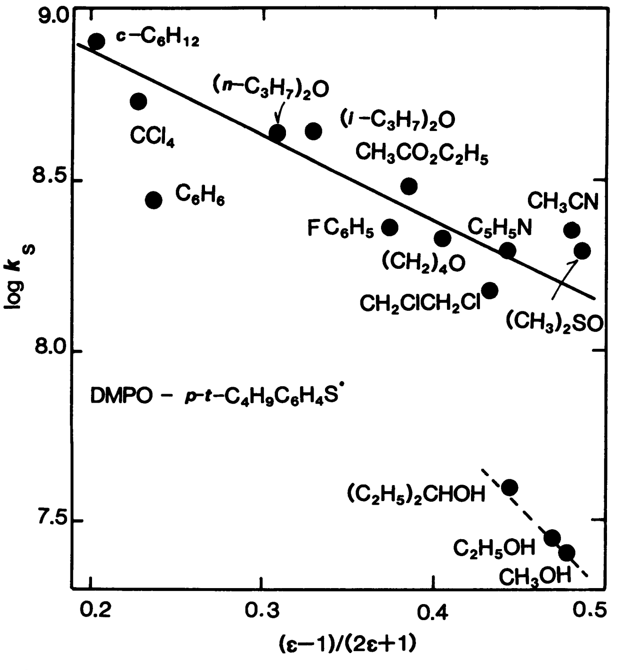


Fig. 6. Plots of log $k_S$ *vs.* the Kirkwood parameter, $(\varepsilon-1)/(2\varepsilon+1)$.

On the other hand, the thiyl radical-trapping rates with nitroso compounds did not show appreciable solvent polarity effect,[8] although the dipole moments of nitroso compounds (*ca.* 3.2 D)[17] are only slightly smaller than those of nitrones (*ca.* 3.6 D).[16] One of the reasons is that the resonance structure ($-\ddot{N}^{+}-O^{-}$) in the reactant can not be changed by the approach of the thiyl radical in the transition state.

Alcoholic solvents reduce the rates more than the rates expected only from the solvent polarity (Fig. 6). Since such a decrease in the rates was not observed for nitroso compounds,[8] this can be attributd to the strong hydrogen bonding with nitrone, not but with the thiyl radical. Hydrogen bonding may stabilize nitrone in the reactant more than that in the activated complex, because the interaction of hydrogen atom of alcohols with the anionic oxygen atom of nitrone in the former is greater than that with the neutral oxygen atom in the latter (**3b** and **3c**). The order of a decrease in the rates among three alcoholic solvents seems to correlate with the Kirkwood parameter as seen in Fig. 6, suggesting that such interaction is cooperating with the solvent polarity effect. On the other hand, the solvent effect was not observed for the rates of nitroso spin-trapping reactions even in methanol;[8] this suggests that the hydrogen-bonding ability of the nitroso group is considerably smaller than that of nitrone.

*Relative Reactivity.* Since the solvent effect on the rates was observed for nitrones but not for nitroso compounds, the order of the reactivities among various spin traps depends upon solvents. In benzene, the order toward each thiyl radical is DMPO>nitrosobenzene>*t*-$C_4H_9NO$>PBN, whereas in methanol the order changes as nitrosobenzene>*t*-$C_4H_9NO$>DMPO>PBN. The order may also change with the electrophilicity of the attacking radical; *i.e.*, the slopes of the Hammett plots for nitrones are steeper than that of nitroso compound. For less electrophilic radicals such as the primary alkyl radical, the reported order differs from that of the thiyl radical (in benzene, nitrosobenzene>$t$-$C_4H_9NO$>DMPO>PBN).[4b)] The ratio of the rates for DMPO to PBN for the thiyl radical (*ca.* 50) varies with the attacking radicals; the ratio increases with the electrophilicity of the attacking radicals (primary alkyl radical (*ca.* 20)[1b)] and $t$-butoxyl radical (*ca.* 90)).[4a)] The higher reactivity of DMPO can be attributed to the strain energy released with the change from cyclic double bond to cyclic single bond.[18,19)]

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