Photochemistry of Nitrobenzenethiol. Selective Generation of the Thio Radical and Thione Triplet State as a Function of Solvent Polarity

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Transient absorption spectra of *p*-nitrobenzenethiol (NBSH) have been measured by the nanosecond laser flash photolysis method. In nonpolar and less polar solvents, nitrobenzenethio radical (NBS$^•$) was predominantly formed by the homolytic fission of the S−H bond of NBSH. In protic polar solvents, on the other hand, formation of the triplet state of deprotonated nitrobenzenethione [^{3}(NBT$^-$)*], which was confirmed by triplet quenching experiments with O_2 and β-carotene, was observed. Quantum yield of intersystem crossing (Φ_T) and the lowest triplet energy (E_{T1}) of ^{3}(NBT$^-$)* were evaluated to be 0.36 and 58 kcal/mol, respectively, in ethanol. In aprotic polar solvents such as acetonitrile, both ^{3}(NBT$^-$)* and NBS$^•$ were produced in the same time. Electron transfer occurs from donors to ^{3}(NBT$^-$)* and to NBS$^•$. For an electron acceptor, the electron-transfer reaction takes place from only ^{3}(NBT$^-$)* and not from NBS$^•$. Thus, NBSH can be used as a selective generator of the thione triplet and thio radical by changing the properties, such as polarity and protic/aprotic character, of the solvents used.

Introduction

Photochemistry of aromatic thiols and disulfides has been extensively studied.[1−8] The sulfur compounds are known to be an effective source of sulfur-centered free radicals and ion radicals, which are important intermediates in photochemical reactions and also in kinetic investigations.[2−5] Flash photolysis methods using lasers and Xe lamps as excitation sources have been employed as attractive techniques to detect reactive intermediates such as free radicals and ion radicals of the sulfur compounds.[1−3,5−8] Arylthiols with electron-donating and electron-withdrawing substituents such as NH_2 and Cl are known to produce S-centered radicals by direct transient observations.[1−3]

In the ground state, the substituted benzenethiols are more likely to exist as the nondissociated thiol in various solvents because of their high pK_a values.[9−11] On the other hand, *p*-nitrobenzenethiol (NBSH) exhibits an acid/base equilibrium (Scheme 1) in polar solvents and in protic solutions because of the low pK_a, ranging from 5.6 to 4.7,[9−11] of NBSH. It has been demonstrated that the (NBT$^-$) resonance structure makes a larger contribution than does the thiolate form (NBS$^-$) in protic polar solvents because of the high electron-withdrawing ability of the NO_2 group (Scheme 1).[11]

Although a photochemical investigation of NBSH to produce the thio radical (NBS$^•$) has been reported in nonpolar solvent,[2] a detailed study in polar solvents and in protic solutions has not been reported. It would be anticipated from the equilibrium above that multiple reactive species were produced as a function of the fractions of NBSH and NBT$^-$ (or NBS$^-$) in polar and in protic/aprotic solvents.[9−11] Recently, the importance of thione photochemistry in chemical and biological viewpoints has been recognized for various thiol−thione tautomers.[12,13] In particular, the participation of triplet states of thiones in various chemical and biochemical reactions has been frequently pointed out.[12,13]

In the present study, we have investigated the photochemistry of NBSH, including the influences of the nature of solvents (polar/nonpolar and protic/aprotic) on its photochemistry. The transient intermediates produced by the different forms of NBSH have been identified and spectroscopically characterized. In addition, we reported their reactivities, such as energy-transfer and electron-transfer reactions toward various substrates.

Materials and Methods

Commercially available *p*-nitrobenzenethiol (NBSH), *p*,*p*-dinitrobenzene disulfide (NBDS), 3,3′,5,5′-tetramethylbenzi-

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[1] (a) Oswald, A. A.; Griesbaum, K.; Hudson, B. E. *J. Org. Chem.* **1963**, *28*, 2361. (b) Thyrion, F. C. *J. Phys. Chem.* **1973**, *77*, 1478. (c) Takakura, T.; Tagami, M.; Okuyama, M.; Kamada, H. *J. Spectrosc. Soc. Jpn.* **1975**, *24*, 282.

[2] (a) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 1815. (b) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732. (c) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1981**, *103*, 5871. (d) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1982**, *104*, 1815.

[3] Burkey, T. J.; Griller, D. *J. Am. Chem. Soc.* **1985**, *107*, 246.

[4] (a) Newcomb, M.; Park, U. *J. Am. Chem. Soc.* **1986**, *108*, 4132. (b) Newcomb, M.; Kaplan, J. *Tetrahedron Lett.* **1987**, *28*, 1615.

[5] (a) Scott, T. W.; Liu, S. N. *J. Phys. Chem.* **1989**, *93*, 1393. (b) Bohne, C.; Boch, R.; Scaiano, J. C. *J. Org. Chem.* **1990**, *55*, 5414.

[6] Alam, M. M.; Watanabe, A.; Ito, O. *J. Org. Chem.* **1995**, *60*, 3440.

[7] (a) Aveline, B. M.; Kochevar, I. E.; Redmond, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 9699. (b) Aveline, B. M.; Kochevar, I. E.; Redmond, R. W. *J. Am. Chem. Soc.* **1996**, *118*, 10113.

[8] (a) Alam, M. M.; Watanabe, A.; Ito, O. *Photochem. Photobiol.* **1996**, *63*, 53. (b) Alam, M. M.; Konami, H.; Watanabe, A.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 263. (c) Alam, M. M.; Watanabe, A.; Ito, O. *Int. J. Chem. Kinet.* **1996**, *28*, 405.

[9] Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1911.

[10] De Maria, P.; Fini, A.; Hall, F. M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1969.

[11] Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224.

[12] (a) Ramamurthy, V.; Steer, R. P. *Acc. Chem. Res.* **1988**, *21*, 380. (b) Maciejewski, A.; Steer, R. P. *Chem. Rev.* **1993**, *93*, 67. (c) Lapinski, L.; Prusinowska, D.; Nowak, M. J.; Bretner, M.; Felczak, F.; Maes, G. Adamiwciz, L. *Spectrochim. Acta, Part A* **1996**, *52*, 645.

[13] (a) Alam, M. M.; Fujitsuka, M.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1998**, *102*, 1338. (b) Alam, M. M.; Fujitsuka, M.; Watanabe, A.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1998**, 817.

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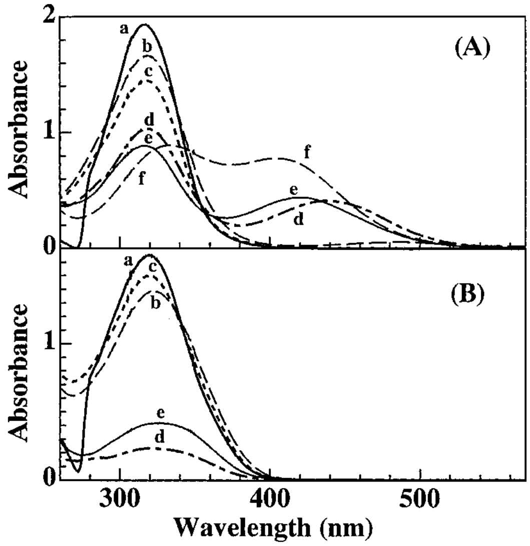
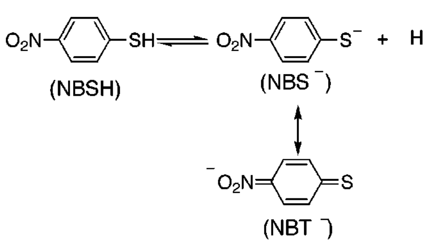


Figure 1. Steady-state absorption spectra of (A) NBSH (0.1 mM) and (B) NBDS (0.1 mM) were recorded in various solvents: (a) benzene, (b) acetonitrile, (c) THF, (d) 2-propanol, (e) ethanol, and (f) water. NBDS is sparingly soluble in ethanol and 2-propanol and insoluble in water.

Scheme 1



dine (TMB), *p*-dinitrobenzene (DNB), and other aromatic hydrocarbons were used after recrystallization. *N*,*N*-Dimethyl-*p*-nitroso-aniline (RNO), 1,3-diphenylisobenzofuran (DPBF), and β-carotene were purchased from Aldrich Chemical Co. Solvents used for the transient absorption measurements were of spectroscopic grade.

The laser flash photolysis apparatus was a standard design with Nd:YAG laser (fwhm 6 ns).[6,8] The solutions were photolyzed with light (355 nm) from a third-harmonic generator (THG). The time profiles in the visible region were followed by a photomultiplier tube (PMT) as a detector for monitoring light from a continuous Xe monitor lamp (150 W). In the visible and near-IR regions (350−1000 nm), a Si−PIN photodiode attached to a monochromator was also employed as a detector to monitor the probe light from a pulsed xenon flash lamp. The output signal from the detector was recorded with a digitizing oscilloscope and analyzed using a personal computer.[14] The laser photolysis was performed for deaerated and O_2-saturated solutions obtained by Ar and O_2 gas bubbling, respectively, in a rectangular quartz cell with a 10 mm optical path at 23 °C. The phosphorescence spectrum was measured at 77 K in glassy ethanol.

Results and Discussion

Table 1. Steady-State Absorption Properties of NBSH and NBDS in Various Solvents

	λ_{max} [ϵ (M^{-1} cm^{-1})]^a	
solvent	NBSH	NBDS
benzene	316 [19300]^b	320 [16500]
THF	317 [14400]^b	321 [15000]
acetonitrile	319 [16600]^b; 485 [500]^c	322 [13900]
ethanol	318 [8800]^b; 422 [4300]^c	326^d
2-propanol	319 [10300]^b; 440 [4100]^c	326^d
water	332 [8850]^b; 410 [7700]^c	e

^{a} Errors on ε values are ≤5%. ^{b} Absorption peak is due to NBSH form. ^{c} Absorption peak is due to NBT^- form. ^{d} Sparingly soluble in ethanol and in 2-propanol. ^{e} Not soluble in water.

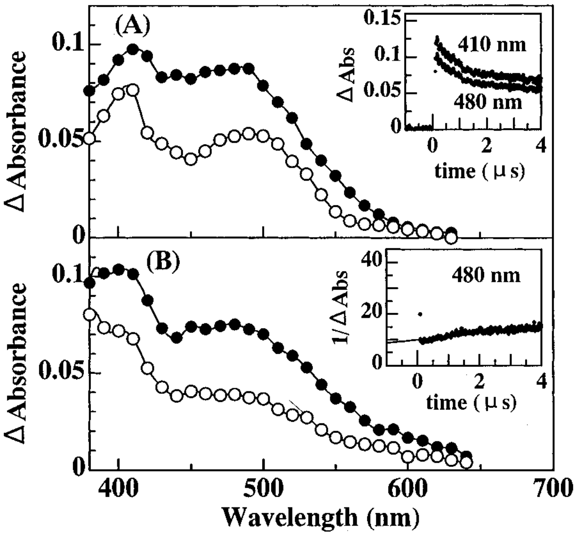
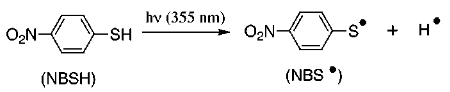


Figure 2. Transient absorption spectra observed by laser photolysis with 355 nm light in Ar-saturated THF: (●) 0.25 μs and (○) 2.5 μs. (A) NBSH (0.2 mM) and decay-time profiles (inset). (B) NBDS (0.2 mM) and second-order plot (inset).

Steady-State Absorption Spectra. The steady-state UV/visible absorption spectra of the thiol (NBSH) measured in different solvents are shown in Figure 1A. The absorption peak at 316 nm in nonpolar benzene was attributed to the thiol form (NBSH),[1−3,9−11] which shifted to a longer wavelength with the appearance of another broad absorption band in the region of 400−500 nm in polar solvents and in aqueous solution. The broad absorption band in the longer wavelength region is characteristic of a >C=S chromophore,[11−13] indicating that the (NBT^-) resonance structure makes a larger contribution than does (NBS^-), and has been seen previously in polar solvents and in aqueous solution.[11] In the absorption spectra of the disulfide (NBDS), such an appearance of new absorption in the longer wavelength was not observed, as shown in Figure 1B. In all cases, the Beer−Lambert law was demonstrated in the concentration range of 0.05−1.0 mM. The λ_{max} values are listed in Table 1 with their molar absorption coefficients (ε).

Transient Spectra in Less Polar Solvents. The transient absorption spectra observed by the laser flash photolysis of NBSH in Ar-saturated THF with 355 nm light exhibit two absorption bands at 410 and 480 nm, as shown in Figure 2A. The absorption intensities of both bands that appeared immediately after the laser pulse decay in the same rate, as shown in the time profiles in the inset in Figure 2A. Both bands were attributed to p-$O_2NC_6H_4S^\bullet$ ($NBS^\bullet$) formed by the homolytic S−H bond fission of NBSH as in eq 1,[2] because similar transient



(1)

absorption bands from the laser photolysis of NBDS were

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(14) Fujitsuka, M.; Sato, T.; Shimidzu, T.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1997**, *101*, 1056.

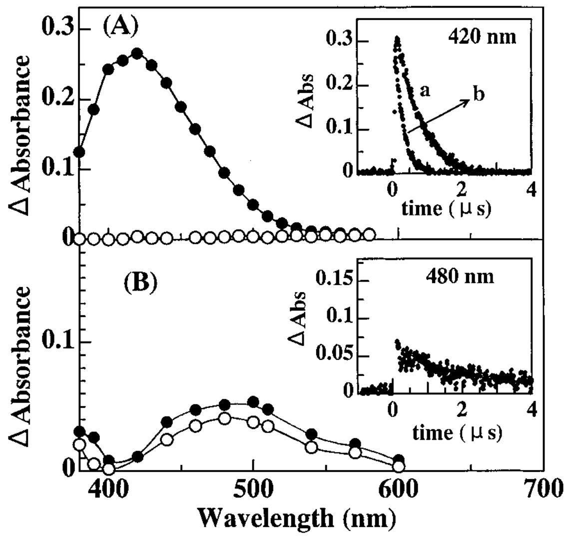
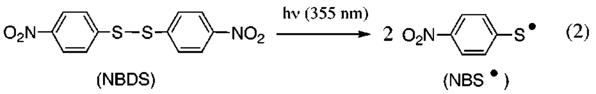


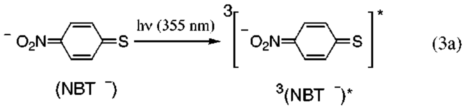
Figure 3. Transient spectra in Ar-saturated ethanol: (●) 0.25 μs and (○) 2.5 μs. (A) NBSH (0.5 mM; exists as NBT^-); the decay-time profiles in (a) deaerated and (b) aerated solutions (inset). (B) NBDS (0.4 mM) and decay-time profile (inset).

observed in Ar-saturated THF (Figure 2B), in which $NBS^\bullet$ was formed by homolytic photodissociation at the S−S bond of NBDS (eq 2).[2c] The decay rates of the absorption



bands of $NBS^\bullet$ at 410 and 480 nm were not affected by the addition of O_2 into the solution, showing the low reactivity of $NBS^\bullet$ to O_2, which is one of the characteristics of arylthio radicals.[6,8,15] The decay of $NBS^\bullet$ was attributed to recombination yielding or returning the disulfide as presumed from the second-order plot (inset of Figure 2B), in which the initial decay seems to be slightly faster than the later part.

Triplet Formation in Protic Polar Solvents. Figure 3A shows the time-dependent transient absorption spectra recorded in Ar-saturated ethanol after laser photolysis (355 nm excitation light) of NBSH, which exists mainly as NBT^-.[11] The broad transient absorption band in the region of 380−500 nm decays quickly within 3 μs (inset in Figure 3A). The absorption band was effectively quenched by O_2 and other triplet quenchers, suggesting that the transient absorption band was due to the triplet−triplet (T−T) absorption of $^3(NBT^-)^*$, as shown in eqs 3a and 3b.



$$^3(NBT^-)^* + O_2 \xrightarrow{k_{O2}} NBT^- + {}^1O_2 \qquad (3b)$$

Similarly, in 2-propanol and water solutions, where NBT^- is predominant,[9−11] and in buffer solution (pH = 9.18, in which NBT^- exists explicitly), only the T−T absorption band of $^3(NBT^-)^*$ was observed in the region of 400−480 nm by laser photolysis (355 nm light). The decay of the absorption bands of $^3(NBT^-)^*$ increases with an increase in polarity and protic nature of the solvents, probably due to ionic interaction and/or hydrogen bonding between $^3(NBT^-)^*$ and the solvents.

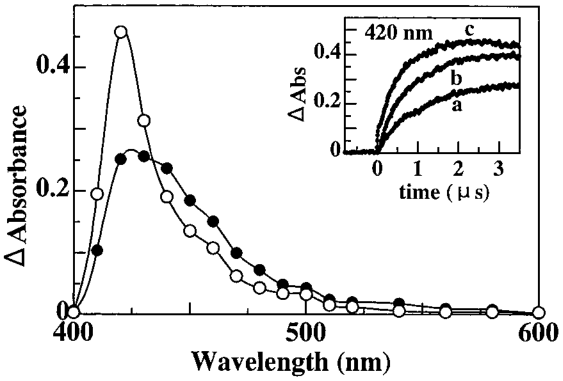


Figure 4. Transient spectra recorded by laser photolysis of NBSH (0.3 mM; exists as NBT^-) in the presence of anthracene (0.5 mM) with 355 nm light in Ar-saturated ethanol: (●) 0.25 μs and (○) 2.5 μs. Inset: growth of $^3An^*$ at 420 nm; [An], (a) 0.1, (b) 0.3, and (c) 0.5 mM.

In the case of NBDS in ethanol, spectra quite different from those of $^3(NBT^-)^*$ were observed, as shown in Figure 3B. The transient absorption band at 500 nm observed with NBDS in ethanol was attributed to $NBS^\bullet$ because of low reactivity to O_2, although a shift to a longer wavelength was observed compared with that in THF. On comparison with the spectra at 2.5 μs in Figures 3A and 3B, $NBS^\bullet$ formation from NBT^- in ethanol was excluded because of the absence of the NBSH form in protic solvents (Scheme 1).[11]

From the increase in the decay rates of $^3(NBT^-)^*$ by O_2, the second-order triplet-quenching rate constant (k_{O2} in eq 3b) was evaluated to be 2.7×10^9 M^{-1} s^{-1} for O_2 in ethanol. In this study, the formation of singlet O_2 was confirmed by consumption of 1,3-diphenylisobenzofuran (DPBF) and *N*,*N*-dimethyl-*p*-nitrosoani-line (RNO), which are known to react with singlet O_2.[13,16,17]

In transient spectra of $^3(NBT^-)^*$ in the presence of anthracene (An) in Ar-saturated ethanol, a slow rise was observed at 420 nm (Figure 4). The rise of the absorption band can be attributed to the T−T absorption band of anthracene ($^3An^*$).[18a] Figure 4 indicates the occurrence of energy transfer from $^3(NBT^-)^*$ to anthracene (eq 4).

$$^3(NBT^-)^* + \text{quencher} \xrightarrow{k_{ent}} NBT^- + {}^3(\text{quencher})^* \qquad (4)$$

The absorption band of $^3An^*$ at 420 nm seems to rise without showing the decay due to consumption of $^3(NBT^-)^*$, which indicates that the band of $^3(NBT^-)^*$ is overlapped with the strong band of $^3An^*$ at 420 nm (ϵ_T = 52 000 M^{-1} cm^{-1}).[18a] The rate constants of energy transfer (k_{ent}) for several triplet quenchers were evaluated from the slope of the pseudo-first-order plots of the first-order rate constants (k_{first}) obtained by curve-fitting with a

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(15) Chatgilialoglu, C.; Asmus, K.-D. *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; NATO ASI Series A: Life and Science Vol. 197; Plenum Press: New York, 1990; pp 327−340.

(16) Wasserman, H. H.; Murray, R. W. In *Singlet Oxygen*; Academic Press: New York, 1979; Chapters 5, 6, 8, and 9.

(17) Hemmens, V. J.; Moore, D. E. *Photochem. Photobiol.* **1986**, *43*, 247.

(18) (a) Kikuchi, K. *Joem Handbook 1, Triplet−triplet Absorption Spectra*; Bunshin Pub. Co.: Tokyo, Japan, 1989; p 54. (b) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker Inc.: New York, 1973.

Table 2. Rate Constants for Energy Transfer (k_{ent}) of $^3(NBT^-)^*$ with Triplet Quenchers at 23 °C in Ethanol

quenchers	E_{T1} (kcal mol^{-1})	k_{ent} (M^{-1} s^{-1})[a]
β,β-carotene	19.4[b]	3.1×10^9
O_2	22.5[c]	2.7×10^9
ferrocene	42.9[d]	1.8×10^9
anthracene	42.7[c]	1.1×10^9
benzil	54.3[c]	9.5×10^7

[a] Estimation error is ±5%. [b] Refs 13 and 24a. [c] Ref 18b. [d] Ref 24b.

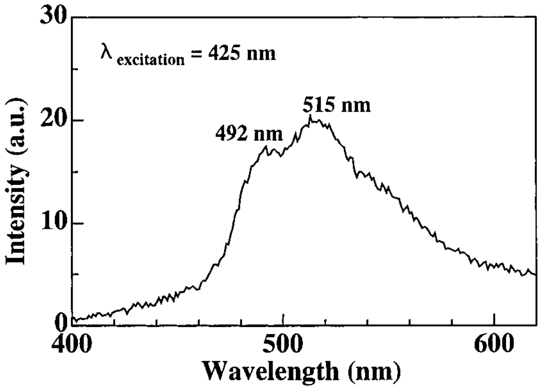

Figure 5. Phosphorescence spectra recorded for NBSH in glassy ethanol at 77 K.

single exponential the rise in the curve of $^3An^*$ at 420 nm. The k_{ent} values are summarized in Table 2. Although the k_{ent} value for anthracene (1.1×10^9 M^{-1} s^{-1}; E_{T1} = 42.7 kcal mol^{-1})[18b] is close to the diffusion-controlled limit ($k_{diff} = 5.6 \times 10^9$ M^{-1} s^{-1} in ethanol),[6] the k_{ent} value for benzil (9.5×10^7 M^{-1} s^{-1}; E_{T1} = 54.3 kcal mol^{-1})[18b] is about $^1/_{60}$ of the diffusion limit (k_{diff}), indicating that E_{T1} of $^3(NBT^-)^*$ is close to 57.7 kcal mol^{-1}, as calculated from the Sandros equation.[19]

To confirm the formation of $^3(NBT^-)^*$ in protic polar solvents, the phosphorescence spectrum was measured. A phosphorescence band observed at 492 nm in glassy ethanol at 77 K (Figure 5) confirmed the formation of $^3(NBT^-)^*$. From the phosphorescence peak at 492 nm, the lowest triplet energy (E_{T1}) of $^3(NBT^-)^*$ was calculated to be 58.1 ± 0.2 kcal mol^{-1}, which is in good agreement with the E_{T1} value evaluated by quenching of $^3(NBT^-)^*$ within ca. 0.4 kcal mol^{-1}.

In nonpolar and in less polar solvents such as benzene and THF, in which NBS$^•$ was predominantly formed, neither energy transfer nor phosphorescence was observed; this also confirmed the formation of $^3(NBT^-)^*$ due to the NBT$^-$ form in protic polar solvents, water, and buffer (pH = 9.18) solution.

Triplet Quantum Yield. The quantum yield (Φ_T) of $^3(NBT^-)^*$ formation via intersystem crossing was evaluated by energy transfer from $^3(NBT^-)^*$ to β-carotene in ethanol by comparison with Φ_T = 1.0 of benzophenone (BP) as a standard by means of eq 5,[13,20,21] where ΔA

$$\Phi_T^{NBT} = \Phi_T^{BP} \frac{\Delta A^{NBT}}{\Delta A^{BP}} \frac{k_{obs}^{NBT}}{k_{obs}^{NBT} - k_0^{NBT}} \frac{k_{obs}^{BP} - k_0^{BP}}{k_{obs}^{BP}} \qquad (5)$$

values are the respective maximal absorption intensities observed by the laser excitation of NBSH (0.1 mM) and BP (1.0 mM), k_{obs} is the pseudo-first-order rate constant for the growth of the β-carotene triplet in solutions containing BP or NBSH (optically matched at the excitation wavelength 355 nm), and k_0 is the rate constant for the decay of the triplet energy donors in the absence of β-carotene. The direct excitation of only β-carotene solution did not result in any significant triplet formation because of negligible triplet yields.[13,20] Thus, the Φ_T value in ethanol was evaluated to be 0.36 for $^3(NBT^-)^*$.

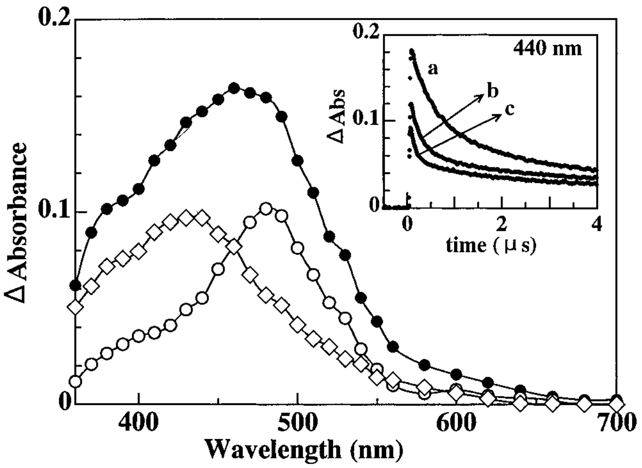

Figure 6. Transient absorption spectra observed after laser photolysis of NBSH (0.3 mM; mixture with NBT$^-$) with 355 nm light in Ar-saturated acetonitrile: (●) 0.25 μs, (○) 2.5 μs, and (◇) simulated spectrum from the difference 0.25 − 2.5 μs. Inset: decay time-profiles in (a) Ar-saturated, (b) air-saturated, and (c) O_2-saturated solutions.

The triplet extinction coefficient (ϵ_T) of $^3(NBT^-)^*$ was also estimated from the reported ϵ value of $^3BP^*$ as a standard (7220 M^{-1} cm^{-1}) by substituting the observed Φ_T and ΔA values.[13,20,21] The ϵ_T value in ethanol was determined to be 3600 M^{-1} cm^{-1} for $^3(NBT^-)^*$ at 420 nm.

Transient Spectra in Aprotic Polar Solvents. In acetonitrile, NBSH may be present with NBT$^-$ as a mixture.[11] The transient absorption spectra show a broad absorption band in the region of 380−550 nm (Figure 6). The absorption intensity of the broad band decreases with two different decay components (fast and slow decay parts, as in the inset of Figure 6), indicating the formation of two different transient species. The fast decay part was effectively quenched by O_2 and other triplet quenchers (inset in the Figure 6), suggesting that the fast decay part is due to T−T absorption of $^3(NBT^-)^*$.

The decay rate of the slow decay part (inset in Figure 6) was not affected in the presence of triplet quenchers (such as O_2, ferrocene, and β-carotene), but it decayed in a similar rate with NBS$^•$ in THF. Thus, the slow decay part is attributed to NBS$^•$ produced concomitantly with the triplet $^3(NBT^-)^*$ in polar acetonitrile (Scheme 2). Only NBS$^•$ was observed by the laser photolysis of NBDS in acetonitrile, as in other solvents.

Photoinduced Electron Transfer. Transient absorption spectra of $^3(NBT^-)^*$ observed in the presence of 3,3′,5,5′-tetramethylbenzidine (TMB; 0.2 mM) in Ar-saturated ethanol are shown in Figure 7. The absorption peak at around 400 nm due to $^3(NBT^-)^*$ was replaced with new transient absorption bands appearing at 460,

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(19) Sandros, K. *Acta Chem. Scand.* **1964**, *18*, 2355.

(20) Kumar, C. V.; Qin, L.; Das, P. K. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 783.

(21) Lamola, A. A.; Hammond, G. S. *J. Chem. Phys.* **1965**, *43*, 2129.

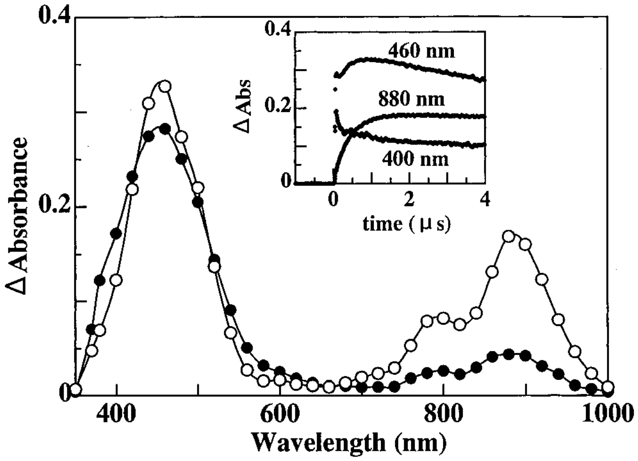
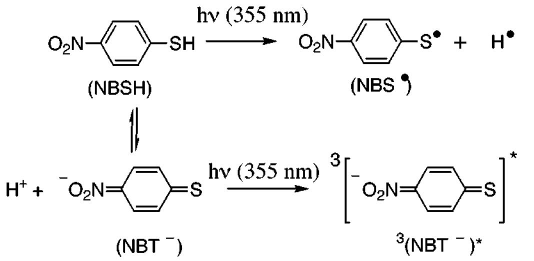
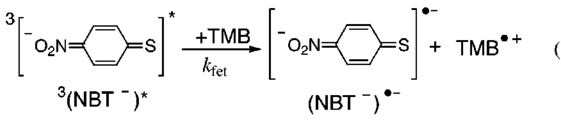


Figure 7. Transient absorption spectra in the visible and near-IR regions obtained by 355 nm laser photolysis of NBSH (0.2 mM; exists as NBT^-) in the presence of TMB (0.2 mM) in Ar-saturated ethanol: (●) 0.1 μs and (○) 1.0 μs, (detector, Si–PIN). Inset: time profiles of absorption bands.

Scheme 2. Photoprocess in Aprotic Polar Solvents (Acetonitrile)



800, and 880 nm (inset in Figure 7) due to $TMB^{\bullet+}$.[13,22] This indicates that the electron-transfer reaction occurs from TMB to $^3(NBT^-)^*$, as in eq 6.



(6)

The time profile at 400 nm (inset in Figure 7) is complex because the initial rapid decay of $^3(NBT^-)^*$ is overlapped with the rise of $TMB^{\bullet+}$.[13,22] Thus, the rate constant for electron transfer (k_{fet}) was evaluated from the rise in the curve of $TMB^{\bullet+}$ at 880 nm by curve fitting with a single exponential, as listed in Table 3.

For $NBS^\bullet$ that was produced by laser photolysis of NBDS, electron-transfer reaction from TMB was also proved by the appearance of $TMB^{\bullet+}$ in acetonitrile. Thus, it is evident that $NBS^\bullet$ can also accept an electron from TMB in polar solvents, as in eq 7. The ϵ value of $NBS^\bullet$

$$\text{NBSH (or NBDS)} \xrightarrow{h\nu} \text{NBS}^\bullet \xrightarrow[k_{fet}]{\text{TMB}} \text{NBS}^- + \text{TMB}^{\bullet+} \quad (7)$$

was evaluated to be 1700 $M^{-1}\ cm^{-1}$ by the relative method from the electron-transfer reaction between $NBS^\bullet$ and TMB, using $\epsilon_{TMB^{\bullet+}} = 20\,000\ M^{-1}\ cm^{-1}$ at 880 nm in acetonitrile.[13,22] Figure 6 shows that the absorption intensities of $NBS^\bullet$ (spectrum at 2.5 μs) and $^3(NBT^-)^*$ (simulated spectrum) are almost same, from which the ratio of the concentrations of $NBS^\bullet$ and $^3(NBT^-)^*$ can be calculated to be 2:1 in acetonitrile (ϵ of $^3(NBT^-)^* = 3600\ M^{-1}\ cm^{-1}$ as evaluated in this study above).

Table 3. Rate Constants for Forward-Electron-Transfer Reactions (k_{fet}) and Back-Electron-Transfer Reactions (k_{bet})[a]

reactants	substrate	solvent[b]	k_{fet} ($M^{-1}\ s^{-1}$)	$k_{bet}/\epsilon_{radical\ ion}$[c] (cm s^{-1})	k_{bet} ($M^{-1}\ s^{-1}$)
$^3(NBT^-)^*$	TMB	EtOH	5.5×10^9	4.8×10^4	9.8×10^8
		AN	1.3×10^{10}	6.7×10^4	1.3×10^9
	DNB	AN	1.0×10^{10}	2.9×10^5	1.7×10^9
	MV^{2+}	AN + H_2O	2.3×10^9	d	d
$NBS^\bullet$	TMB	AN	1.2×10^{10}	7.2×10^4	1.4×10^9
	DNB	AN	no reaction		
	MV^{2+}	AN + H_2O	no reaction		

[a] Estimation error is ±5%. [b] Solvents; acetonitrile (AN) and AN + H_2O (9:1). [c] $\epsilon_{TMB^{\bullet+}} = 20200\ M^{-1}\ cm^{-1}$ at 880 nm[13,22] and $\epsilon_{DNB^{\bullet-}} = 5900\ M^{-1}\ cm^{-1}$ at 910 nm[13,14] in AN. [d] Values were not obtained due to slow back-electron-transfer reaction.

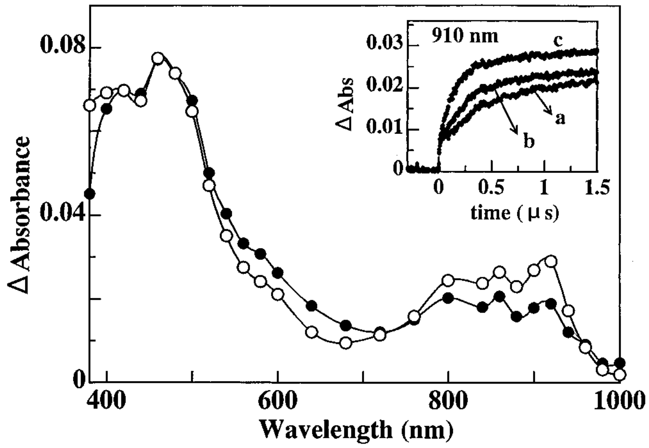
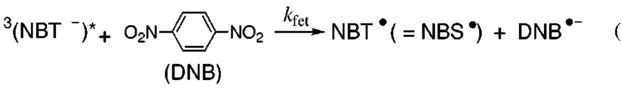


Figure 8. Transient absorption spectra in the visible and near-IR regions obtained by 355 nm laser photolysis of NBSH (0.2 mM mixture with NBT^-) in the presence of DNB (0.8 mM) in Ar-saturated acetonitrile: (●) 0.08 μs and (○) 1.2 μs, (detector, Si–PIN). Inset: rise time profiles at 910 nm with [DNB]: (a) 0.2, (b) 0.4, and (c) 0.8 mM.

Figure 8 shows the transient spectra of $^3(NBT^-)^*$ in the presence of an electron acceptor, *p*-dinitrobenzene (DNB), in acetonitrile; the fast-decay part of $^3(NBT^-)^*$ at 400 nm disappeared within a few hundred nanoseconds, leaving the slow-decay absorption part due to $NBS^\bullet$. With the rapid decay of $^3(NBT^-)^*$, new absorption bands appeared at 870 and 910 nm in the near-IR region, which are attributed to the radical anion of DNB ($DNB^{\bullet-}$).[13,14] The first-order rate constant obtained from the decay profiles of $^3(NBT^-)^*$ by DNB is in agreement with that obtained from the rise time profiles of $DNB^{\bullet-}$. Thus, it is evident that electron transfer occurs from $^3(NBT^-)^*$ to DNB, forming $DNB^{\bullet-}$ and $NBT^\bullet$ (= $NBS^\bullet$) (eq 8).[13,14] This



(8)

finding coincides with our previous observations that the triplet states of pyridinethiones and purinethione act as electron donors to DNB.[13] In addition, it is proved by the laser photolysis of NBDS in the presence of DNB that electron transfer from $NBS^\bullet$ to DNB does not occur even in polar solvents. Such electron transfer is not favorable from the electron-deficient $NBS^\bullet$.

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(22) Sasaki, Y.; Yoshikawa, Y.; Watanabe, A.; Ito, O. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2287.

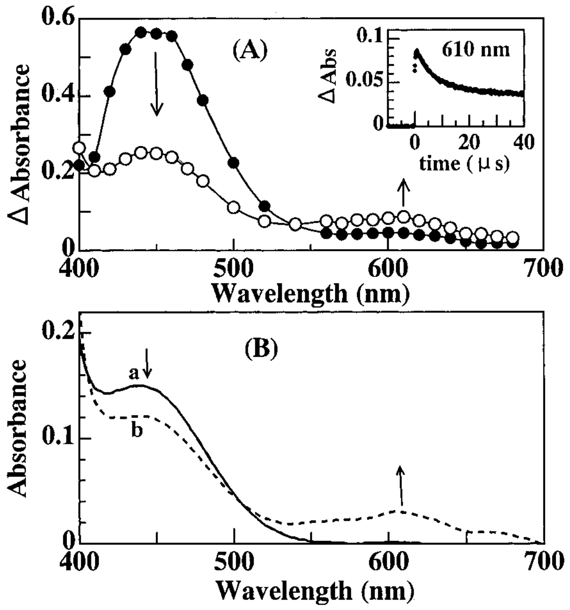


Figure 9. (A) Transient absorption spectra obtained by 355 nm laser photolysis of NBSH (0.4 mM) in the presence 0.16 mM MV^{2+} in Ar-saturated mixture of acetonitrile and water (9:1 by volume): (●) 0.1 μs and (○) 1.0 μs, (detector, Si−PIN). Inset: long decay time profile of $MV^{\bullet+}$ at 610 nm. (B) Steady-state absorption spectra (a) before and (b) after laser irradiation.

The absorption intensities of the radical and radical ions ($TMB^{\bullet+}$, $NBT^{\bullet}$, and $DNB^{\bullet-}$) decay slowly after reaching their maxima in acetonitrile. These decays obey second-order kinetics and can be attributed to the back-electron-transfer reactions (k_{bet} in eqs 9 and 10).[13,14,22]

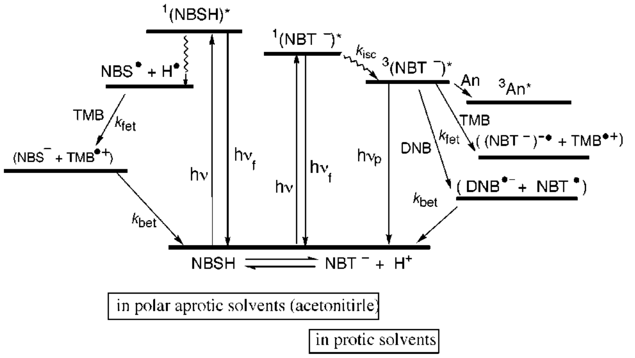
$$(NBT^-)^{\bullet-} + TMB^{\bullet+} \xrightarrow{k_{bet}} NBT^- + TMB \qquad (9)$$

$$NBT^{\bullet} + DNB^{\bullet-} \xrightarrow{k_{bet}} NBT^- + DNB \qquad (10)$$

From the slopes of the second-order plots, $k_{bet}/\epsilon_{radical\ ion}$ can be obtained as listed in Table 3. By substitution of the reported values of $\epsilon_{radical\ ion}$,[13,14,22] the k_{bet} values were evaluated for eqs 9 and 10 (Table 3).

In the case of methyl viologen (MV^{2+}), $^3(NBT^-)^*$ donates an electron to MV^{2+} in an Ar-saturated mixture of acetonitrile and water (9:1 by volume) as shown in Figure 9A. The k_{fet} was evaluated from the rise in absorption time profile of the semireduced radical cation of methyl viologen ($MV^{\bullet+}$) at 610 nm (Table 3).[23] In the case of $NBS^{\bullet}$, no electron-transfer reaction was observed with MV^{2+} in Ar-saturated solution. The absorption intensity of $MV^{\bullet+}$ at 610 nm was not decayed (inset in Figure 9A) even after a long time scale (40 μs). The steady absorption spectrum (Figure 9B) observed after laser irradiation indicates the persistence of $MV^{\bullet+}$, which may be due to the hindrance of the back-electron-transfer reaction between $MV^{\bullet+}$ and $NBT^{\bullet}$ by repulsion of the positively charged $MV^{\bullet+}$ with electron-deficient $NBT^{\bullet}$.

Scheme 3. Schematic Diagram of Photoprocesses and Photochemical Reactivities of NBSH and NBT^- in Various Reaction Media; Fluorescence ($h\nu_f$) and Phosphorescence ($h\nu_p$)



Conclusion

In the present study, it has been disclosed that the photochemical processes of NBSH are quite different from those of other arylthiols with substituents, such as NH_2, CH_3O, H, and Cl, which predominantly generate the thio radicals by the homolytic scission of the S−H bond. NBSH acts as the thio radical source in nonpolar and less polar solvents, whereas it generates the triplet state of deprotonated thione [$^3(NBT^-)^*$] in protic polar solvents. In aprotic polar solvent (acetonitrile), both the thio radical ($NBS^{\bullet}$) and $^3(NBT^-)^*$ are formed. Both $NBS^{\bullet}$ and $^3(NBT^-)^*$ act as good electron acceptors, and $^3(NBT^-)^*$ is good electron donor; however, $NBS^{\bullet}$ does not act as a donor even in polar solvents. In benzene and THF, only $NBS^{\bullet}$ was generated, but the electron-transfer reaction for $NBS^{\bullet}$ with TMB does not occur. The photochemical processes of NBSH in different solvent media are summarized in Scheme 3.

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[23] Kamphuis, J.; Bos, H. J. T.; Visser, R. J.; Huizer, B. H.; Varma, C. A. G. O. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1867.

[24] (a) Lambert, C.; Redmond, R. W. *Chem. Phys. Lett.* **1994**, *228*, 495. (b) Farmilo, A.; Wilkinson, F. *Chem. Phys. Lett.* **1975**, *34*, 575.