Characterization and reactivities of transient species generated by laser flash photolysis of *N*-hydroxypyridine-4-thione

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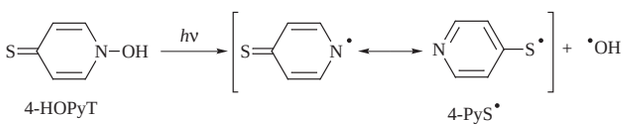
The reaction intermediates produced by the nanosecond-laser-flash photolysis of *N*-hydroxypyridine-4-thione (4-HOPyT) have been studied in aqueous and nonaqueous solutions. The pyridyl-4-thiyl radical (4-PyS$^{\bullet}$ at 420 nm) and $^{\bullet}$OH are formed by the homolytic N–OH bond cleavage of 4-HOPyT. The 720-nm band was assigned to the pyridyl-*N*-oxyl radical (4-S=PyO$^{\bullet}$) generated by the photodissociation of the O–H bond and by H abstraction from 4-HOPyT through $^{\bullet}$OH. The triplet state of 4-HOPyT [^{3}(4-HOPyT)*], confirmed by energy transfer with triplet quenchers, is also produced concomitantly with the radical species. Diffusion controlled electron-transfer reactions occur between ^{3}(4-HOPyT)* and donors (or acceptors), which may be caused by the relatively high triplet-state energy (E_{T_1} = 60.1 kcal mol^{-1}) of ^{3}(4-HOPyT)*. In aqueous alkaline solution, the solvated electron (e_{aq}^-) and the one-electron semioxidized radical of 4-HOPyT (4-S=PyO$^{\bullet}$) are produced by photoionization of the anionic form of 4-HOPyT. Thus, it is possible to control the generation of $^{\bullet}$OH and e_{aq}^- by changing the pH of the solution.

Introduction

Thiols, sulfides and disulfides with pyridine moieties have been widely recognized as useful chemical reagents for synthetic purposes (Barton's reagents).[1–6] Furthermore, since *N*-hydroxypyridinethiones (HOPyT's) are known as biologically active compounds with antifungal, antibacterial and anticancer properties,[7–10] their zinc and sodium salts have been used commercially in antidandruff shampoos.[11] Moreover, HOPyT's are capable of producing hydroxyl radical upon photolysis (Scheme 1),[6,12–17] which has special importance as a cytotoxic agent in



Scheme 1

mouse cells and Chinese hamster fibroblasts, but only in the presence of light.[14,17] For this purpose, laser flash photolysis is particularly effective for the detection of reactive intermediates such as triplet states and radicals.[15–18]

In the present study, we have applied the nanosecond-laser photolysis method to reveal the reactive species produced from *N*-hydroxypyridine-4-thione (4-HOPyT), which is known to be predominantly present as the thione form in tautomeric equilibrium with the minor thiol form in solution.[19] Thus, it is also necessary to clarify the nature of the intermediates formed by either N–O or O–H bond cleavage. 4-HOPyT also exhibits an acid–base equilibrium (pK_a = 3.82).[19] In particular it would be expected that pH changes could alter the transient species generated from 4-HOPyT. Furthermore, some MO calculations were performed to rationalize the experimental results.

Results and discussion

Steady-state absorption spectra

The UV–visible absorption spectrum of 4-HOPyT in THF (Fig. 1) shows intense absorption peaks at 300 nm (ε = 9400 mol^{-1} dm^3 cm^{-1}) and 362 nm (ε = 17 000 mol^{-1} dm^3 cm^{-1}), which suggests that both the 300- and 362-nm bands are characteristic $^1(\pi$–$\pi^*)$ transitions of the C=S chromophore of thiones.[18,20–23] The fluorescence and phosphorescence spectra of 4-HOPyT are also shown in Fig. 1, which may be emitted from the 362 nm band of 4-HOPyT. The absorption spectral shape of the dilute 4-HOPyT solution (0.05×10^{-3} mol dm^{-3}) is the same as that of the concentrated solution (up to 1.0×10^{-3} mol dm^{-3}). The absorption intensities increase proportionally with concentration and follow the Beer–Lambert law, which indicates insignificant aggregation of 4-HOPyT in the concentration range 0.05–1.0×10^{-3} mol dm^{-3}.[18]

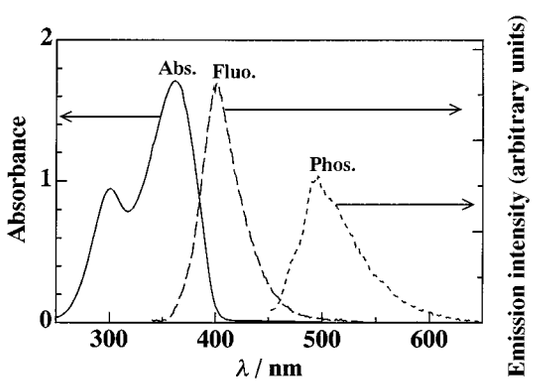


Fig. 1 Steady UV–VIS (——) and fluorescence (–––, λ_{exc} = 362 nm) spectra of 4-HOPyT (0.1×10^{-3} mol dm^{-3}) in THF (1.0-cm optical path); phosphorescence spectrum (-----, λ_{exc} = 362 nm) of 4-HOPyT in glassy frozen Me-THF at 77 K.

Transient spectra in organic solvents

The transient absorption spectra of the laser flash photolysis of 4-HOPyT (0.4×10^{-3} mol dm^{-3}) at 355 nm in Ar-saturated THF exhibit two absorption bands at 420 and 720 nm with a shoulder at 680 nm, as shown in Fig. 2. The absorption intensity of the 420-nm band decreases with a fast and a slow decay component (see inset of Fig. 2), which indicates the formation

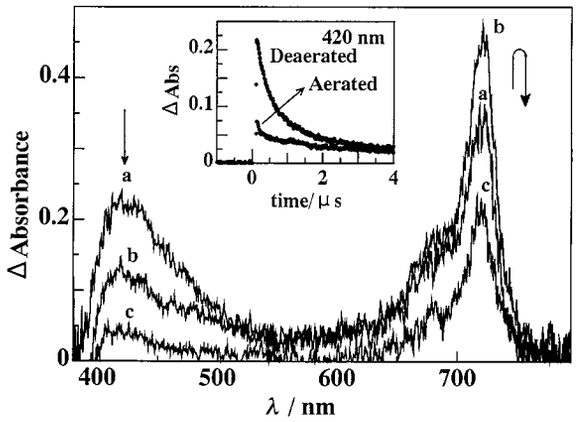
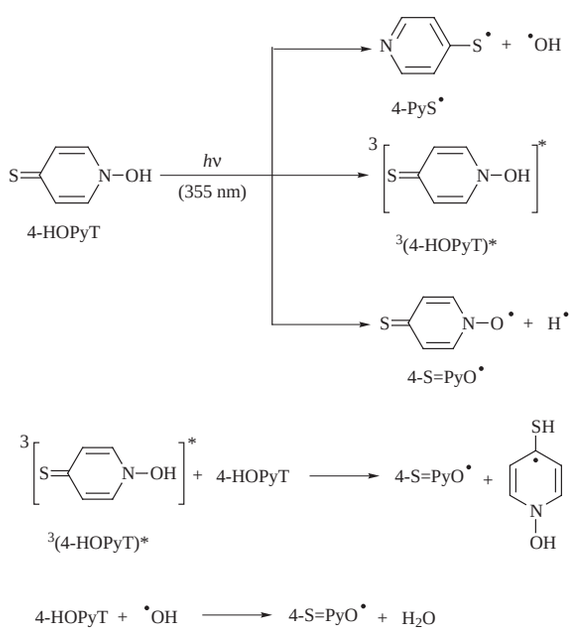


Fig. 2 Transient absorption spectra observed after laser photolysis of 4-HOPyT (0.4×10^{-3} mol dm^{-3}) at 355-nm excitation in Ar-saturated THF (detector, MCPD); (a) 50 ns, (b) 350 ns and (c) 2000 ns. Insert: time profiles of the 420-nm absorption band (detector, PMT).

of two different transient species. The fast decay component was efficiently quenched by O_2 (see inset in Fig. 2) and other triplet quenchers such as ferrocene and β-carotene, which suggests that the 420-nm band can be attributed to triplet–triplet absorption of ^{3}(4-HOPyT)*.[16,18,23] The triplet lifetime (τ_T°) was evaluated as 2.8 μs from the decay of the 420-nm transient band at low laser power (2–3 mJ pulse^{-1}) and in very dilute THF solution of 4-HOPyT using the equation $1/\tau_T = 1/\tau_T^\circ + k_{sq}$[4-HOPyT].[18,23]

The rate of the slow decay part (see inset in Fig. 2) was not affected by the presence of triplet quenchers such as O_2 and β-carotene. Thus, the slow decay component is attributed to the pyridinyl-4-thiyl radical (4-PyS$^\bullet$), which was produced concomitantly with ^{3}(4-HOPyT)*, followed by the homolytic N–OH bond fission of 4-HOPyT to afford $^\bullet$OH (Scheme 2) as



Scheme 2

reported in recent studies.[14–17] A similar transient absorption band to 4-PyS$^\bullet$ appeared at 420 nm by homolytic photodissociation of the S–S bond of 4,4′-dipyridine disulfide (DPDS) in Ar-saturated THF [eqn. (1)],[15,16,24] which also confirms the generation of 4-PyS$^\bullet$ from 4-HOPyT (Scheme 2). Since the decay rate of the 4-PyS$^\bullet$ absorption (420-nm band) was not affected by O_2, this species shows a low reactivity towards O_2, which is one of the characteristics of such arylthiyl radicals.[15,16,24,25] The

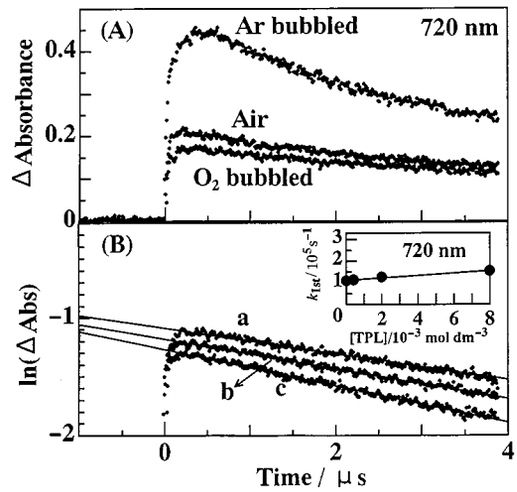
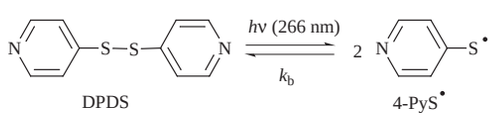


Fig. 3 (A) Time profiles of the 720-nm absorption band of 4-HOPyT (0.4×10^{-3} mol dm^{-3}) in 355-nm laser photolysis in Ar-saturated THF and (B) first-order rate plots in the presence of tocopherol; [tocopherol] (a) 0.0, (b) 2.0×10^{-3} and (c) 8.0×10^{-3} mol dm^{-3} (detector, PMT). Inset: pseudo-first-order plot for the hydrogen-abstraction reaction.

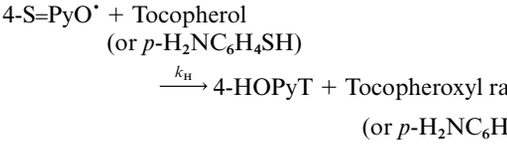


(1)

decay of 4-PyS$^\bullet$ is attributed to recombination to the disulfide, as presumed from the second-order plot.[15,16,24]

In contrast, the absorption bands at 720 and 680 nm appeared immediately after the laser pulse; afterwards their absorption intensities rose for *ca.* 1 μs and then decayed (Fig. 2). The rise in the intensity was quenched by O_2 (Fig. 3A) and other triplet quenchers, which suggests that the secondary reaction of ^{3}(4-HOPyT)* with 4-HOPyT (Scheme 2) is responsible for this slow rise. The initial main absorption intensities of the 720- and 680-nm bands, which appeared immediately after the laser pulse, were not affected by triplet quenchers such as O_2 and β-carotene. Thus, the 720- and 680-nm bands may be assigned to an O-centered radical (4-S=PyO$^\bullet$), which is produced by direct O–H bond cleavage as well as by H-abstraction from the ground state 4-HOPyT by the reactive ^{3}(4-HOPyT)* and by $^\bullet$OH (Scheme 2). The absorption maxima of 4-S=PyO$^\bullet$ in the longer wavelength region support the assigned quinoid structure.

Slow hydrogen abstraction by the 720- and 680-nm species (Fig. 3B) from α-tocopherol (or aminobenzenethiol) to generate the tocopheroxyl radical at 420 nm[18] (or the aminobenzenethiyl radical at 480 nm)[18] was observed [eqn. (2)] with

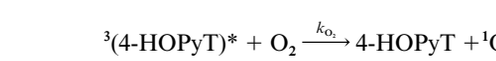


(2)

the rate constant $k_H = 5.6 \pm 0.8 \times 10^6$ mol^{-1} dm^3 s^{-1} (or $5.8 \pm 0.8 \times 10^7$ mol^{-1} dm^3 s^{-1}). These H-abstraction reactions are expected for 4-S=PyO$^\bullet$. The $^\bullet$OH may also be important for H-abstraction from α-tocopherol.

Triplet quenching rate constants

From the increase in the decay rates of ^{3}(4-HOPyT)* at 420 nm in the presence of O_2, the second-order triplet-quenching rate constant [k_{O_2} in eqn. 3)] was evaluated as $2.7 \pm 0.14 \times 10^9$ mol^{-1}



(3)

Table 1 Rate constants for the energy transfer (k_{ent}) of ^{3}(4-HOPyT)* to triplet quenchers at 23 °C in Ar-saturated THF

Quenchers	E_{T_1}/kcal mol^{-1}	k_{ent}/mol^{-1} dm^3 s^{-1} [a]
β-Carotene	19.4 [b]	3.9×10^9
O_2	22.5 [c]	2.7×10^9
Ferrocene	42.9 [d]	2.5×10^9
Anthracene	42.7 [c]	3.1×10^9
1,3-CHD [e]	52.4 [c]	1.1×10^9
Benzil	54.3 [c]	9.6×10^7

[a] Estimated error is ±5% of the stated values. [b] Ref. 27(*c*). [c] Refs. 18 and 27(*a*). [d] Ref. 27(*b*). [e] CHD is cyclohexa-1,3-diene.

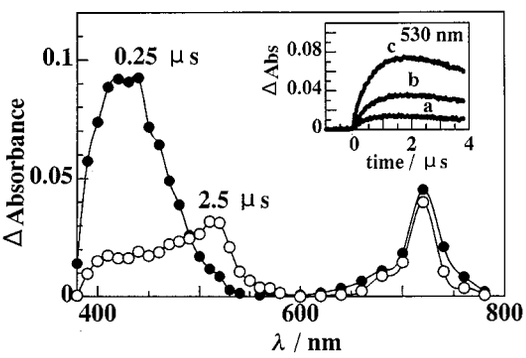


Fig. 4 Transient spectra of the laser photolysis of 4-HOPyT (0.2×10^{-3} mol dm^{-3}) in the presence of β-carotene (0.05×10^{-3} mol dm^{-3}) at 355-nm excitation in Ar-saturated THF (detector, PMT). Inset: rise of ^{3}(β-carotene)* at 530 nm; [β-carotene] (a) 0.025, (b) 0.05 and (c) 0.075×10^{-3} mol dm^{-3}.

dm^3 s^{-1} in THF. The formation of singlet oxygen was confirmed by the consumption of 1,3-diphenylisobenzofuran (DPBF).[18,26]

Fig. 4 shows the transient spectra of ^{3}(4-HOPyT)* in the presence of β-carotene in Ar-saturated THF. A new absorption band was observed at 530 nm, while the 420-nm absorption of ^{3}(4-HOPyT)* decreased. The absorption band at 530 nm (see inset in Fig. 4) is attributed to the T–T absorption band of β-carotene [^{3}(β-carotene)*],[18] which indicates energy transfer from ^{3}(4-HOPyT)* to β-carotene [eqn. (4a)].[18] The competitive addition reactions of $^{\bullet}$OH, ^{3}(4-HOPyT)* and 4-PyS$^{\bullet}$ to the double bonds of β-carotene [(eqn. (4b–4d)][16,24] may cause the

$$^3\text{(4-HOPyT)*} + \text{β-carotene} \xrightarrow{k_{ent}} \text{4-HOPyT} + {}^3\text{(β-carotene)*} \quad (4a)$$

$$^3\text{(4-HOPyT)*} + \text{β-carotene} \xrightarrow{k_{ad}} \text{Addition reaction} \quad (4b)$$

$$\text{4-PyS}^{\bullet} + \text{β-carotene} \xrightarrow{k_{ad}} \text{(4-PyS—β-carotene)}^{\bullet} \quad (4c)$$

$$\text{HO}^{\bullet} + \text{β-carotene} \xrightarrow{k_{ad}} \text{(HO—β-carotene)}^{\bullet} \quad (4d)$$

low intensities of the absorption bands of ^{3}(β-carotene)* and 4-S=PyO$^{\bullet}$ at 530 and 720 nm, respectively.

The rate constant [k_{ent} in eqn. (4a), Table 1] for energy transfer from ^{3}(4-HOPyT)* to β-carotene was evaluated from the slopes of the pseudo-first-order plots of the first-order rate constants (k_{1st}) obtained by curve fitting with a single exponential of the rise curve of ^{3}(β-carotene)* at 530 nm. For other triplet quenchers, the k_{ent} values are summarized in Table 1. Although the k_{ent} value for cyclohexa-1,3-diene (1.1×10^9 mol^{-1} dm^3 s^{-1}; $E_{T_1} = 52.4$ kcal mol^{-1})[18,27] is close to the diffusion controlled limit ($k_d = 1.2 \times 10^{10}$ mol^{-1} dm^3 s^{-1} in THF),[24] the k_{ent} value for benzil (9.6×10^7 mol^{-1} dm^3 s^{-1}; $E_{T_1} = 54.3$ kcal mol^{-1})[18,27] is about 1/100 of k_d, which indicates that E_{T_1} of ^{3}(4-HOPyT)* is *ca.* 57.3 kcal mol^{-1}, as calculated from the Sandros equation.[28]

The lowest triplet energy (E_{T_1}) of ^{3}(4-HOPyT)* was also calculated from the 0–0 transition of the phosphorescence band at 475 nm, which was measured in glassy Me-THF at 77 K (Fig. 1)

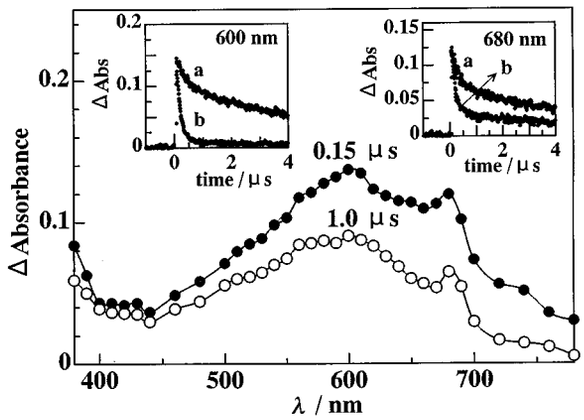


Fig. 5 Transient absorption spectra in the laser photolysis of 4-HOPyT (0.2×10^{-3} mol dm^{-3}) at 355-nm excitation in Ar-saturated aqueous alkaline (pH 12) solution (detector, PMT). Inset: decay time profiles in (a) Ar-saturated and (b) O_2-saturated solutions.

to be 60.1 ± 0.2 kcal mol^{-1}. This is in agreement within *ca.* 2.5 kcal mol^{-1} with the E_{T_1} value determined by quenching experiments of ^{3}(4-HOPyT)*. In ethanol glass at 77 K, the phosphorescence peak is shifted to shorter wavelength comparing the peak in Me-THF (a blue shift of about 5 nm), which indicates that the lowest triplet state (T_1) of ^{3}(4-HOPyT)* has ^{3}(n,π*) character.[18,20–23] In contrast, solvent polarity does not affect the nonpolar ^{3}(π,π*) electronic configuration of T_1.[18,20–23]

Transient spectra in aqueous media

In Ar-saturated buffer solution at pH 7, a transient absorption spectrum similar to Fig. 2 was observed for the 355-nm laser excitation of 4-HOPyT, suggestive of the formation of ^{3}(4-HOPyT)*, 4-PyS$^{\bullet}$ and 4-S=PyO$^{\bullet}$, which are the transient species assigned in organic solvents. To prove that the homolytic cleavage of the N–O bond of 4-HOPyT is the photoprocess that gives rise to 4-PyS$^{\bullet}$, evidence for the concomitant formation of $^{\bullet}$OH was sought. Indeed, the formation of $^{\bullet}$OH was confirmed by an indirect method. Thus, the laser photolysis of 4-HOPyT in the presence of KSCN in Ar-saturated buffer solution at pH 7 resulted a transient absorption band with a maximum at 480 nm, which is attributed to $(SCN)_2^{\bullet -}$.[16,29] The formation of $(SCN)_2^{\bullet -}$ is proposed to derive from the reaction between thiocyanate ion (SCN^-) and $^{\bullet}$OH according to eqn. (5a) and (5b).[16] When DMSO and phenol (known as efficient

$$SCN^- + {}^{\bullet}OH \longrightarrow SCN^{\bullet} + OH^- \quad (5a)$$

$$SCN^- + SCN^{\bullet} \rightleftharpoons (SCN)_2^{\bullet -} \quad (5b)$$

$^{\bullet}$OH scavengers) are added, the transient absorption band of $(SCN)_2^{\bullet -}$ at 480 nm disappears.[16]

These observations corroborate that $^{\bullet}$OH is generated by the homolytic scission of the N–O bond of 4-HOPyT (Scheme 2), as previously demonstrated by spin-trapping experiments with 5,5′-dimethylpyrroline-*N*-oxide (DMPO) and subsequent EPR spectroscopy.[14] In acidic buffer solution at pH 4.02, photochemical processes of 4-HOPyT similar to those at pH 7 were observed.

Fig. 5 shows the transient absorption spectra recorded by the laser photolysis ($\lambda_{exc} = 355$ nm) of 4-HOPyT in Ar-saturated alkaline buffer solution at pH 12, in which 4-HOPyT exists as an anionic form [eqn. (6)].[19] The broad band around 600 nm, which is efficiently quenched by O_2 (see inset in Fig. 5) or N_2O and decays within 10 μs in Ar-saturated solution, is assigned to solvated electron (e_{aq}^-).[15,16,30] The absorption intensity at 680 nm did not decay completely in the presence of O_2 (see inset in Fig. 5) or N_2O due to the overlap with the absorption of 4-S=PyO$^{\bullet}$ derived from 4-HOPyT (assigned in Fig. 2 and 3) by photoionization as shown in eqn. (6).[15,16]

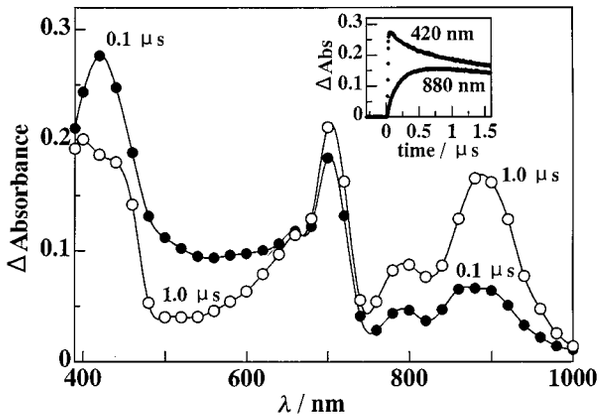
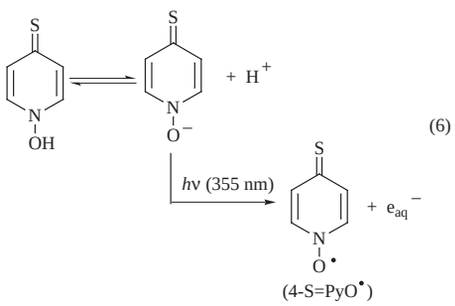


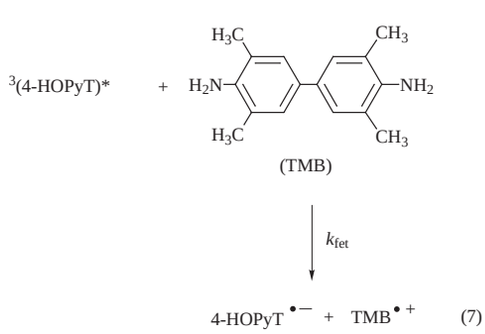
Fig. 6 Transient absorption spectra in the visible/near-IR regions of the laser photolysis of 4-HOPyT (0.2×10^{-3} mol dm^{-3}) at 355-nm excitation in the presence of TMB (0.6×10^{-3} mol dm^{-3}) in Ar-saturated acetonitrile (detector, Si-PIN). Inset: time profiles of the 420- and 880-nm absorption bands.



Photoinduced electron transfer

The transient absorption spectra of the laser photolysis (355 nm excitation light) of 4-HOPyT in the presence of tetramethylbenzidine (TMB) in Ar-saturated acetonitrile are shown in Fig. 6. The absorption maximum of ^{3}(4-HOPyT)* at 420 nm was observed immediately after the laser flash, along with the appearance of absorption bands at 800 and 880 nm due to TMB$^{\bullet+}$.[18,31] The time profiles of the decay and the rise in the absorption of ^{3}(4-HOPyT)* and TMB$^{\bullet+}$ at 420 and 880 nm, respectively, are shown in the inset of Fig. 6. The 420-nm band of ^{3}(4-HOPyT)* did not decay completely due to its overlap with the rising absorption band of TMB$^{\bullet+}$ in the region of 400–470 nm.[18,31]

In the presence of O_2, the absorption of the TMB$^{\bullet+}$ was suppressed due to the quenching of ^{3}(4-HOPyT)*. This finding indicates that electron transfer takes place from TMB to ^{3}(4-HOPyT)*, as shown in eqn. (7),[18,31] but not from TMB to



4-PyS$^{\bullet}$. From the rise of the TMB$^{\bullet+}$ absorption at 880 nm, the first-order rate constants (k_{1st}) were evaluated by curve-fitting with a single exponential as shown in Fig. 7. The second-order rate constant for electron transfer [k_{fet} in eqn. (7)] from TMB to ^{3}(4-HOPyT)* may be evaluated by the [TMB] dependence of

Table 2 Rate constants for forward-electron-transfer (k_{fet}) and back-electron-transfer (k_{bet}) reactions in Ar-saturated acetonitrile[a]

Substrate	k_{fet}/mol^{-1} dm^3 s^{-1}	($k_{bd}/\varepsilon_{radical\ ion}$)[b]/cm s^{-1}	k_{bd}/mol^{-1} dm^3 s^{-1}
TMB	5.5×10^9	4.9×10^5	9.9×10^9
p-DNB	6.6×10^9	6.9×10^5	4.1×10^9
o-DNB	6.1×10^9	[c]	[c]
m-DNB	5.9×10^9	[c]	[c]

[a] Estimated error is ±8% of the stated values. [b] $\varepsilon_{TMB^{\bullet+}} = 20\,200$ mol^{-1} dm^3 cm^{-1} at 880 nm (Refs. 18, 31) and $\varepsilon_{p\text{-}DNB^{\bullet-}} = 5900$ mol^{-1} dm^3 cm^{-1} at 910 nm (Refs. 18, 32) in acetonitrile. [c] The transient absorption bands of *o*-DNB$^{\bullet-}$ and *m*-DNB$^{\bullet-}$ overlapped with that of ^{3}(4-HOPyT)*.

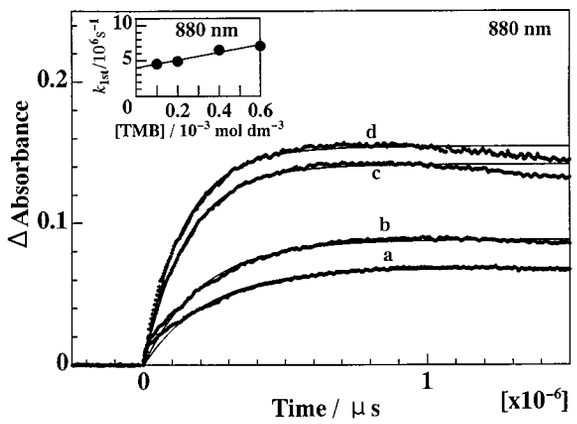


Fig. 7 Rise of the 880-nm absorption band of TMB$^{\bullet+}$ in Ar-saturated acetonitrile with [TMB]; (a) 0.1, (b) 0.2, (c) 0.4 and (d) 0.6×10^{-3} mol dm^{-3} (detector, Si-PIN). Inset: pseudo-first-order plot for electron transfer.

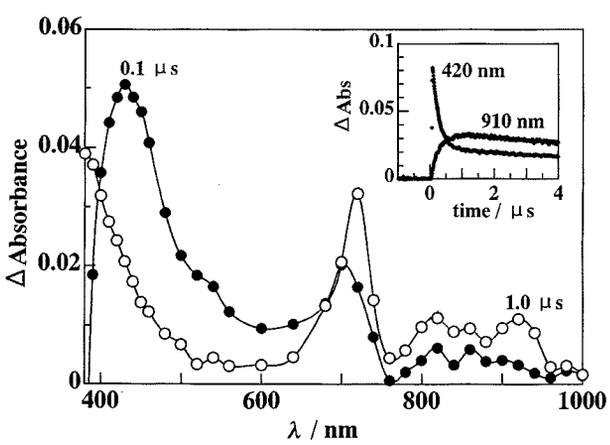


Fig. 8 Transient absorption spectra in the visible/near-IR regions of the 355-nm laser photolysis of 4-HOPyT (0.1×10^{-3} mol dm^{-3}) in the presence of *p*-DNB (0.4×10^{-3} mol dm^{-3}) in Ar-saturated acetonitrile (detector, Si-PIN). Inset: time profiles of the 420- and 910-nm absorption bands.

the first-order rate constant (see inset in Fig. 7), as listed in Table 2. The absorption band of 4-S=PyO$^{\bullet}$ at 700 nm (Fig. 6) was not enhanced in the presence of TMB, which indicates that electron transfer does not take place between 4-S=PyO$^{\bullet}$ and TMB.

With electron acceptors such as *p*-dinitrobenzene (*p*-DNB) in Ar-saturated acetonitrile, the absorption intensity of ^{3}(4-HOPyT)* at 420 nm decreased within a few hundred nanoseconds, new absorption bands appearing at 860 and 910 nm in the near-IR region (Fig. 8). The latter increasing absorption bands are attributed to the radical anion of *p*-DNB (*p*-DNB$^{\bullet-}$).[18,32] When O_2 gas was introduced, the absorption bands for *p*-DNB$^{\bullet-}$ at 860 and 910 nm were suppressed, which

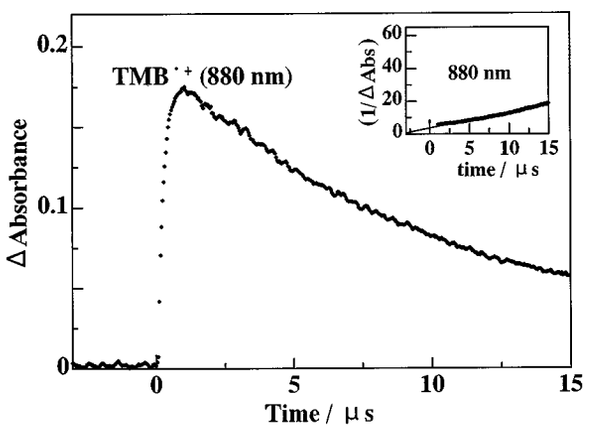
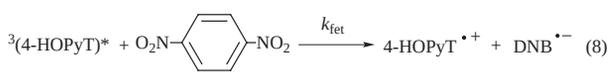


Fig. 9 Absorption–time profile at 880 nm for the decay of $TMB^{\bullet+}$ in the 355-nm laser photolysis of a mixture of TMB and 4-HOPyT in Ar-saturated acetonitrile (detector; Si-PIN). Inset: second-order plot.

indicates that ^{3}(4-HOPyT)* is the precursor for the reaction with *p*-DNB. The rate constants (k_{1st}) obtained from the decay profiles of ^{3}(4-HOPyT)* with *p*-DNB are in good agreement with those from the rise time profiles of *p*-$DNB^{\bullet-}$ absorption in acetonitrile. Thus, it is evident that the rate constants for the quenching of ^{3}(4-HOPyT)* by *p*-DNB and for the formation of *p*-$DNB^{\bullet-}$ in acetonitrile may be attributed to electron transfer (k_{fet} in Table 2) from ^{3}(4-HOPyT)* to *p*-DNB [eqn. (8)].[18,32]



(DNB)

Similar results were obtained for *m*- and *o*-DNB (Table 2). These findings coincide with our previous observations that the triplet states of pyridinethiones and purinethione act as electron donors to DNB.[18]

The absorption intensities of the radical ions $TMB^{\bullet+}$ and $DNB^{\bullet-}$ decay slowly after reaching their maxima in acetonitrile. These decays obey second-order kinetics, as shown in Fig. 9, and may be attributed to bimolecular decay processes (k_{bd}).[18,31,32] From the slopes of the second-order plots (see inset in Fig. 9), $k_{bd}/\varepsilon_{radical\ ion}$ may be obtained, as listed in Table 2. By substitution of the reported values of $\varepsilon_{radical\ ion}$,[18,31,32] the k_{bd} values were evaluated for $TMB^{\bullet+}$ and $DNB^{\bullet-}$ in acetonitrile (Table 2). Since k_{bd} is close to k_d, it can be considered that the bimolecular rate constants (k_{bd}) are due to back electron transfer.

MO calculations

The unpaired π-electron densities of the SOMO and the electronic transition energies of 4-PyS$^\bullet$ and 4-S=PyO$^\bullet$ were calculated by the unrestricted open-shell Hartree-Fock (ROHF) method on the geometries optimized at the MNDO/CI level by using the MOPAC program package.[33] The unpaired π-electron is mainly localized on the S atom in 4-PyS$^\bullet$. In the case of 4-S=PyO$^\bullet$, the unpaired π-electron density on the O atom is greater than on the other atoms. The first allowed electronic transitions of 4-PyS$^\bullet$ and 4-S=PyO$^\bullet$ were calculated to be 430 (oscillator strength = 0.54) and 725 (oscillator strength = 0.68) nm, respectively, which are in good agreement with the observed λ_{max} at 420 and 710 nm, respectively. Thus, the MO calculations substantiate the experimental assignments of the 4-PyS$^\bullet$ and 4-S=PyO$^\bullet$ radical species.

Concluding remarks

In the present study, it has been disclosed that the photochemistry of 4-HOPyT is rather complicated; 4-PyS$^\bullet$ and $^\bullet$OH were generated by homolytic N–OH bond cleavage concomitant with the formation of ^{3}(4-HOPyT)*. 4-S=PyO$^\bullet$ was produced by direct photodissociation of the O–H bond as well as by the reactions of ^{3}(4-HOPyT)* and $^\bullet$OH with 4-HOPyT. In aqueous alkaline solution, solvated electron (e_{aq}^-) and 4-S=PyO$^\bullet$ were produced by photoionization of the anionic form of 4-HOPyT. Thus, the change of pH allows control of the generation of $^\bullet$OH.

The lowest triplet-state energy (E_{T_1}) of ^{3}(4-HOPyT)* was evaluated as 60.1 kcal mol^{-1}. From the polar nature of ^{3}(4-HOPyT)*, the electronic configuration of T_1 is attributed to ^{3}(n,π*). The high triplet energy of ^{3}(4-HOPyT)* may be related to the electron donor–acceptor properties of ^{3}(4-HOPyT)* with the electron acceptor DNB and the electron donor TMB in polar solvents.

Experimental

Materials and methods

N-Hydroxypyridine-4-thione (4-HOPyT) was prepared by the method described elsewhere.[19,34] Commercially available 4,4′-dipyridine disulfide (DPDS), 3,3′,5,5′-tetramethylbenzidine (TMB), dinitrobenzenes (DNB's) and other reagents were used after recrystallization. 1,3-Diphenylisobenzofuran (DPBF) and β-carotene were purchased from the Aldrich Chemical Co. Solvents used for the transient absorption measurements were of spectroscopic grade. Absorption and fluorescence spectra were determined on UV–VIS (Jasco V-570) and fluorescence (Shimadzu RF-5300PC) spectrophotometers with an appropriate optical path. The phosphorescence spectrum was measured in frozen glassy media at 77 K.

The laser-flash-photolysis apparatus was a standard design equipped with Nd:YAG laser (fwhm 6 ns).[18,24] The solutions were photolyzed at 355 nm from a third-harmonic generator (THG). Transient spectra were recorded with a multichannel photodiode (MCPD) system. The time profiles in the visible region were followed by a photomultiplier tube (PMT) as a detector during continuous irradiation with a Xe lamp (150 W). In the visible and near-IR regions (350–1000 nm), an 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 processed by means of a personal computer.[18,24] The laser photolysis was performed at 23 °C for deaerated and O_2-saturated solutions, obtained by purging with Ar and O_2 gas, respectively, in a rectangular quartz cell with a 10-mm optical path.

MO calculations

The MO calculations were performed by the MNDO method by using MOPAC, available from the Japan Program Exchange Association.[33]

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