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Mechanism of the Pyrene-Sensitized Photolysis of *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine

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The title hydroxylamine (NT) undergoes pyrene-sensitized photodecomposition to give rearrangement and fragmentation products. An analysis of linear Stern–Volmer plots, both for the sensitized photolysis of NT and for the fluorescence quenching of pyrene by NT, indicates the involvement of singlet pyrene in this photolysis. The observation of negligible effects of 1,3-cyclohexadiene and *trans*-stilbene as a triplet quencher on the reaction provides further supporting evidence for a singlet-pathway mechanism. A comparison of the relative state energies of NT and the sensitizer suggests the existence of a reactive singlet-exciplex intermediate formed between the singlet-state sensitizer and the ground-state NT. The results of solvent and micellar effects on the sensitized photolysis establish that electron transfer in the exciplex predominates in a polar solvent, and that in a nonpolar solvent energy transfer in this exciplex plays a major role in the reaction.

Our recent observation that the triplet-sensitized photolysis of *N*-(1-naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT) and related *N,O*-diacylhydroxylamines gives no rearranged products provided additional supporting evidence for the suggestion that "photoacyloxyl" migration proceeds mainly through the excited singlet state.[1,2] Furthermore, the results of micellar and solvent viscosity effects on the quantum yields for the direct photolysis of NT allowed us to conclude that the "in-cage" products are not derived from the reaction that occurs within the identical solvent cage but from recombination of two distinct spin-correlated radical pairs.[2] On the other hand, diaroyl peroxides have been known to undergo aromatic hydrocarbon-sensitized decompositions whose mechanism involves a reactive and nonemissive singlet-exciplex intermediate.[3–5] These works of Tokumaru and his co-workers on the mechanism of sensitized photolyses of the peroxides stimulated mechanistic investigation of the singlet-sensitized photolysis of our *N,O*-diacylhydroxylamines. NT was selected for the present study because we have already obtained detailed information regarding the mechanism of the direct and triplet-sensitized photolysis of this hydroxylamine.[2] We chose pyrene as a singlet sensitizer and investigated solvent and micellar effects on the pyrene-sensitized photolysis of NT in order to gain more definitive evidence for the reactive state (singlet or triplet state) from which "photoacyloxyl" migration takes place. We also hoped to clarify the mechanism of this sensitized photolysis.

Results

Pyrene-Sensitized Photolysis of NT (1). Irradiation of a N_2-purged benzene solution of NT (2.50—10.0$\times10^{-3}$ M, 1 M=1 mol dm^{-3}) in the presence of pyrene (3.00$\times10^{-3}$ M) with 366-nm light resulted in the sensitized decomposition of NT giving rearrangement (**2** and **3**) and fragmentation (**4** and **5**) products along with small amounts of unknown products.[6] These photoproducts undergo no sensitized decomposition under the same conditions as above. Pyrene

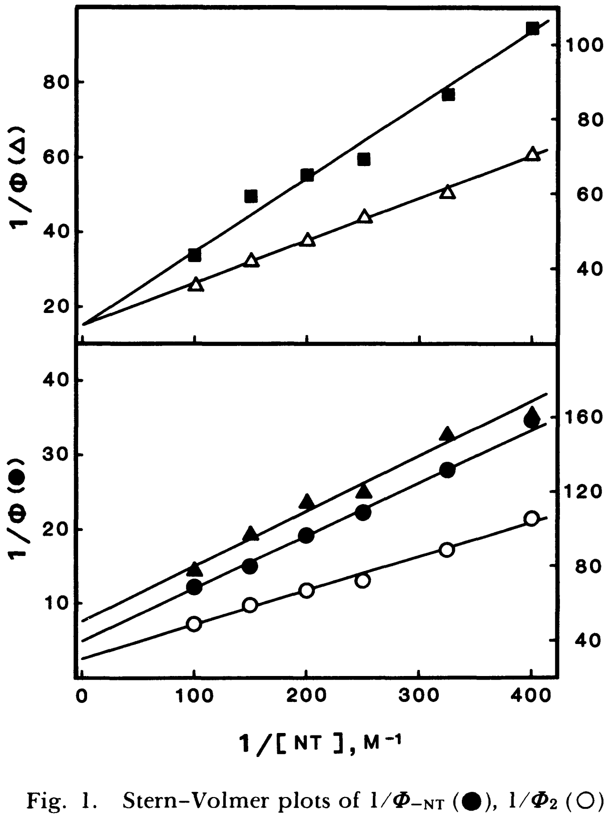


Fig. 1. Stern–Volmer plots of $1/\Phi_{-\mathrm{NT}}$ (●), $1/\Phi_2$ (○), $1/\Phi_3$ (▲), $1/\Phi_4$ (△), and $1/\Phi_5$ (■) vs. 1/[NT] for pyrene (3.00$\times10^{-3}$ M)-sensitized photolysis of NT with 366-nm light in benzene under nitrogen at room temperature (25±3 °C).

was found to decompose to a negligible extent during the irradiation within the experimental errors of HPLC analysis. In addition, no NT was photolyzed to yield these products without the sensitizer. On the other hand, NT is not subjected to the sensitized decomposition to a measurable extent in the presence of relatively low concentrations of pyrene (less than 10^{-4} M).

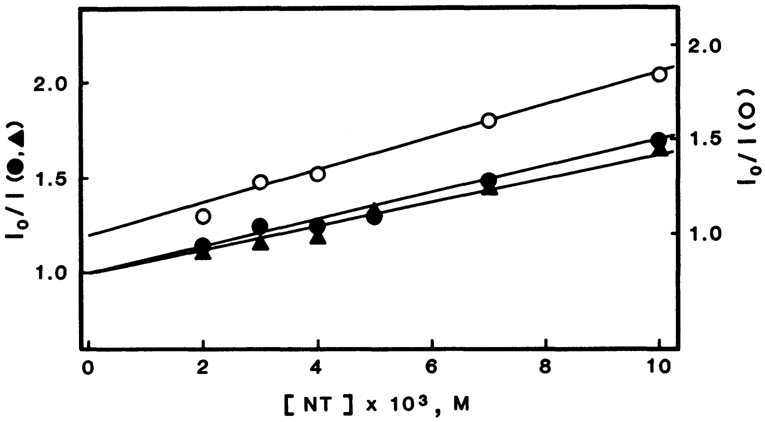
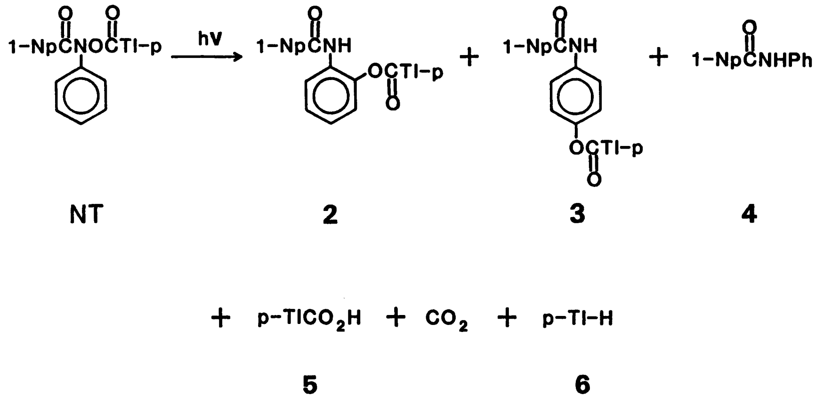


Fig. 2. Stern–Volmer plots for monomer-fluorescence quenching of pyrene (3.00×10^{-3} M) by NT in benzene (●), 1,2-dichloroethane (▲), and acetonitrile (O) under nitrogen at room temperature (23±1 °C). Excitation wavelength=366 nm. I and I_0 refer to fluorescence intensity at 390 nm of pyrene with and without NT, respectively.

Table 1. Solvent Effects on the Pyrene-Sensitized Photolysis of NT with 366-nm Light at 25±3 °C

Solvent (ε)[a]	$\Phi_{-\mathrm{NT,lim}}$	$\Phi_{2,\mathrm{lim}}$	$\Phi_{3,\mathrm{lim}}$	$\Phi_{4,\mathrm{lim}}$	$\Phi_{5,\mathrm{lim}}$	(k_d/k_r+C[b])	$k_t\tau_S$[c] / M^{-1}	$k_t\tau_S$[d] / M^{-1}	τ_S[e] / ns
Benzene (2.275)	0.233	0.034	0.019	0.068	0.038	3.3	136	70 (88)[f]	67 (90)[g]
CH_2ClCH_2Cl (10.36)	0.196	0.029	0.007[h]	0.066	0.064	4.1	94	62 (66)[f]	75 (98)[g]
CH_3CN (37.5)	0.211	0.004[h]	0.003[h]	0.009[h,i]	0.147	3.8	93	86 (90)[f]	52 (64)[g]
CH_3CN	0.150[j]	0.044[j]	0.032[j]	0.012[i,j]	0.041[j]	—	—	—	—

a) Dielectric constant. Ref. 17, p. 108 (benzene), p. 356 (CH_2ClCH_2Cl), and p. 400 (CH_3CN). b) $C=k_R(1+k_d/k_r)/(k_s+k_2)$. c) Average of the $k_t\tau_S$ values determined from quantum yield ($\Phi_{-\mathrm{NT}}$ and Φ_{2-5}) measurements. d) From quenching of pyrene-monomer fluorescence. e) Pyrene-monomer fluorescence lifetime. f) From quenching of pyrene-excimer fluorescence. g) Pyrene-excimer fluorescence lifetime. h) Because of fairly small quantum yield which gives less accurate intercept and intercept/slope ratio we could only determine approximate value. i) Due to side reactions of the amido radical taking place in competition with its hydrogen abstraction to form 4.[1] j) Quantum yield for the direct photolysis with 313-nm light.[2]



1-Np = 1-naphthyl, p-Tl = p-tolyl

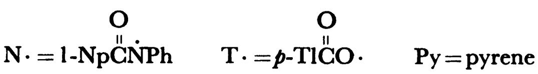
A potassium trioxalatoferrate(III) actinometry was applied to determine quantum yields for the disappearance of NT ($\Phi_{-\mathrm{NT}}$) and for the appearance of photoproducts (Φ_{2-5}) at low conversions (5—10%) of starting NT.[7] Stern–Volmer plots of the reciprocal of NT concentration against the reciprocal of quantum yields for the sensitized photolysis measured in the presence of a constant concentration of pyrene (3.00×10^{-3} M) gave a straight line for any plot from which we are able to obtain the limiting quantum yields ($\Phi_{\lim}$), i.e., the quantum yields extrapolated to the infinite concentration of NT. Typical double reciprocal plots are shown in Fig. 1. Similar linear plots are observed also in 1,2-dichloroethane and acetonitrile.

Quenching of the Fluorescence of Pyrene by NT. Pyrene (3.00×10^{-3} M) in any solvent employed for the sensitization experiments exhibits a monomer fluorescence at 390 nm and an excimer one at 470 nm under nitrogen at room temperature (23±1 °C). The intensity ratio of monomer- to excimer-fluorescence is in the range of 0.6 to 0.9. These fluorescences were quenched by NT following linear Stern–Volmer relationships, as shown in Fig. 2. The quenching constants ($k_t\tau_S$ where k_t and τ_S refer to the rate constant for singlet energy transfer and the lifetime of singlet pyrene without NT, respectively) for the monomer and excimer fluorescences of this sensitizer have not much different values as seen from Table 1, indicating that the monomer and excimer species are in dynamic equilibrium with each other at photostationary state. A consideration of the relative state energies of pyrene-monomer (77 kcal mol^{-1}) and -excimer ($\approx$60 kcal mol^{-1}) species responsible for the dual fluorescence allows us to assume that NT quenches the monomer fluorescence under our experimental conditions.[8] Measurements of monomer-fluorescence lifetimes under the same conditions as those for the sensitized photolysis permit estimations of the k_t values as 1.0×10^9, 0.8×10^9, and 1.7×10^9 M^{-1} s^{-1} in benzene, 1,2-dichloroethane, and acetonitrile, respectively (Table 1). These k_t values reveal that the pyrene fluorescence is quenched by NT at a rate which is close to the diffusion-controlled one.

Discussion

Solvent Effects on the Pyrene-Sensitization. Much higher singlet and triplet states of NT (the first singlet excitation energy, $E_{S_1}=90$; the first triplet excitation energy, $E_{T_1}=59$ kcal mol^{-1}; 1 kcal=4.184 kJ) in comparison with those of pyrene ($E_{S_1}=77$, $E_{T_1}=48$ kcal mol^{-1})[9] make singlet–singlet energy transfer from pyrene to NT endothermic and, hence, it very unlikely. It is known that dibenzoyl peroxide, whose structure is similar to that of NT, quenches the

	Process (rate constant)
$\mathrm{Py(S_0)} \xrightarrow{h\nu} \mathrm{Py(S_1)}$	Absorption of light
$\mathrm{Py(S_1)} \xrightarrow{k_d'=1/\tau_s} \mathrm{Py(S_0)}$	Deactivation of pyrene (k_d')
$\mathrm{Py(S_1) + NT(S_0)} \xrightarrow{k_t} \mathrm{Py\cdot NT(S_1)}$	Exciplex formation and energy transfer (k_t)
$\mathrm{Py\cdot NT(S_1)} \xrightarrow{k_r} {}^1\overline{\mathrm{N\cdot\quad\cdot T}} + \mathrm{Py(S_0)}$	Formation of primary cage (k_r)
$\mathrm{Py\cdot NT(S_1)} \xrightarrow{k_d} \mathrm{Py(S_0) + NT(S_0)}$	Deactivation of exciplex (k_d)
${}^1\overline{\mathrm{N\cdot\quad\cdot T}} \xrightarrow{k_s} {}^1\overline{\mathrm{N\cdot \Vert \cdot T}}$	Formation of secondary cage (k_s)
${}^1\overline{\mathrm{N\cdot\quad\cdot T}} \xrightarrow{k_2} \mathbf{2}$	Primary cage reaction (k_2)
${}^1\overline{\mathrm{N\cdot\quad\cdot T}} \xrightarrow{k_R} \mathrm{NT(S_0)}$	Recombination (k_R)
${}^1\overline{\mathrm{N\cdot \Vert \cdot T}} \xrightarrow{k_3} \mathbf{3}$	Secondary cage reaction (k_3)
${}^1\overline{\mathrm{N\cdot \Vert \cdot T}} \xrightarrow{k_{-s}} {}^1\overline{\mathrm{N\cdot\quad\cdot T}}$	Regeneration of primary cage (k_{-s})
${}^1\overline{\mathrm{N\cdot \Vert \cdot T}} \xrightarrow{k_D} \mathrm{N\cdot + T\cdot}$	Cage escape (k_D)
$\mathrm{N\cdot} \xrightarrow{k_4} \mathbf{4}$	Hydrogen abstraction (k_4)
$\mathrm{N\cdot} \xrightarrow{k_u^N}$ Unknown product(s)	Side reaction(s) (k_u^N)
$\mathrm{T\cdot} \xrightarrow{k_5} \mathbf{5}$	Hydrogen abstraction (k_5)
$\mathrm{T\cdot} \xrightarrow{k_6} \mathbf{6}$	Decarboxylation and hydrogen abstraction (k_6)
$\mathrm{T\cdot} \xrightarrow{k_u^T}$ Unknown product(s)	Side reaction(s) (k_u^T)


$\mathrm{N\cdot = 1\text{-}Np\overset{\overset{O}{\Vert}}{C}\dot{N}Ph}$ $\quad$ $\mathrm{T\cdot = }p\text{-}\mathrm{Tl\overset{\overset{O}{\Vert}}{C}O\cdot}$ $\quad$ Py = pyrene

Scheme 1.

fluorescence of pyrene through the formation of an nonemissive exciplex with a charge-transfer character.[4] This fact suggests the existence of a similar exciplex produced between the singlet-state pyrene monomer and the ground-state NT. The fluorescence from such an exciplex intermediate could not be detected under the present experimental conditions.

If the pyrene-sensitized decomposition of NT proceeds according to Scheme 1, then the following linear Stern–Volmer relationships can be derived between the reciprocals of quantum yields ($1/\Phi_{-\mathrm{NT}}$ and $1/\Phi_{2-5}$) and the reciprocals of varying concentrations of NT (1/[NT]) under the steady-state approximation:

$$1/\Phi_{-\mathrm{NT}} = C_1(1+k_\mathrm{R}/(k_\mathrm{s}+k_2))(1+1/k_\mathrm{t}\tau_\mathrm{S}[\mathrm{NT}]), \tag{1}$$

$$1/\Phi_2 = C_1(1+(k_\mathrm{s}+k_\mathrm{R})/k_2)(1+1/k_\mathrm{t}\tau_\mathrm{S}[\mathrm{NT}]), \tag{2}$$

$$1/\Phi_3 = C_1C_2(1+(k_{-\mathrm{s}}+k_\mathrm{D})/k_3)(1+1/k_\mathrm{t}\tau_\mathrm{S}[\mathrm{NT}]), \tag{3}$$

$$1/\Phi_4 = C_1C_2C_3(1+k_\mathrm{u}{}^\mathrm{N}/k_4)(1+1/k_\mathrm{t}\tau_\mathrm{S}[\mathrm{NT}]), \tag{4}$$

and

$$1/\Phi_5 = C_1C_2C_3(1+(k_6+k_\mathrm{u}{}^\mathrm{T})/k_5)(1+1/k_\mathrm{t}\tau_\mathrm{S}[\mathrm{NT}]), \tag{5}$$

where $C_1=1+k_\mathrm{d}/k_\mathrm{r}$, $C_2=1+(k_2+k_\mathrm{R})/k_\mathrm{s}$, and $C_3=1+(k_3+k_{-\mathrm{s}})/k_\mathrm{D}$. In this Scheme processes for the formation and deactivation of the pyrene excimer were omitted because we presumed no participation of this excimer in the sensitized photolysis. As shown typically in Fig. 2 the observation of linear plots of $1/\Phi$ against 1/[NT] provides a supporting evidence for the mechanism given in Scheme 1. These linear plots allow for the estimation of the values of Φ_lim, $k_t\tau_\mathrm{S}$, and $k_\mathrm{d}/k_\mathrm{r}+k_\mathrm{R}(1+k_\mathrm{d}/k_\mathrm{r})/(k_\mathrm{s}+k_2)$ summarized in Table 1. The $k_\mathrm{t}\tau_\mathrm{S}$ values, thus evaluated, correspond well to those determined from the fluorescence quenching in any solvent employed, giving an additional evidence in support of Scheme 1.

To confirm that the pyrene-sensitized photolysis of NT occurs undoubtedly from the excited singlet state, we tried to quench the reaction by 1,3-cyclohexadiene (E_{S_1}=97, E_{T_1}=52.4 kcal mol^{-1})[9] and *trans*-stilbene (E_{S_1}=94, E_{T_1}<50 kcal mol^{-1})[9]. 1,3-Cyclohexadiene has previously been found to quench the NT phosphorescence efficiently,[1] while triplet pyrene sensitizes the isomerization of *trans*-stilbene.[10] These facts indicate that 1,3-cyclohexadiene and *trans*-stilbene become good quenchers for the NT and pyrene triplets, respectively. We assume here that intersystem crossing of the singlet exciplex Py·NT(S_1) produces these two triplets, NT(T_1) and Py(T_1), but not the triplet exciplex Py·NT(T_1). Triplet pyrene is also formed by intersystem crossing of the singlet pyrene-monomer and -excimer.[8] This assumption allows us to predict that both the compounds quench the triplet-derived reaction. Figure 3 clearly shows that neither 1,3-cyclohexadiene nor *trans*-stilbene exerts their quenching effects on the disappearance of NT and the appearance of any product **2**—**5**.[11] This finding provides a strong piece of evidence for a singlet-pathway mechanism depicted in Scheme 1. The fact that "photoacyloxyl" migration is also observed by the singlet sensitization, therefore, demonstrates that the rearrangement products **2** and **3** come from the singlet-state reaction but not from the triplet-state one.

As evident from Table 1, the singlet-sensitized photolysis gives the same product distribution as that derived from direct photolysis. Interestingly, the quantum yields for the formation of **2** and **3** (Φ_2 and Φ_3) are fairly small, especially in acetonitrile, compared with those for the direct photolysis. On the contrary, the quantum yield for the formation of **5** (Φ_5) in acetonitrile becomes larger in the sensitized photolysis than in the direct photolysis. In addition, Φ_5 decreases with decreasing the polarity of solvents. Although the sum of Φ_2 and Φ_5 for the direct photolysis undergoes negligible solvent polarity effects,[2] the decreased polarity of solvents increases this sum for the sensitized photolysis. Quantum yields Φ_2, Φ_3, and Φ_5 in benzene are comparable to Φ_2,

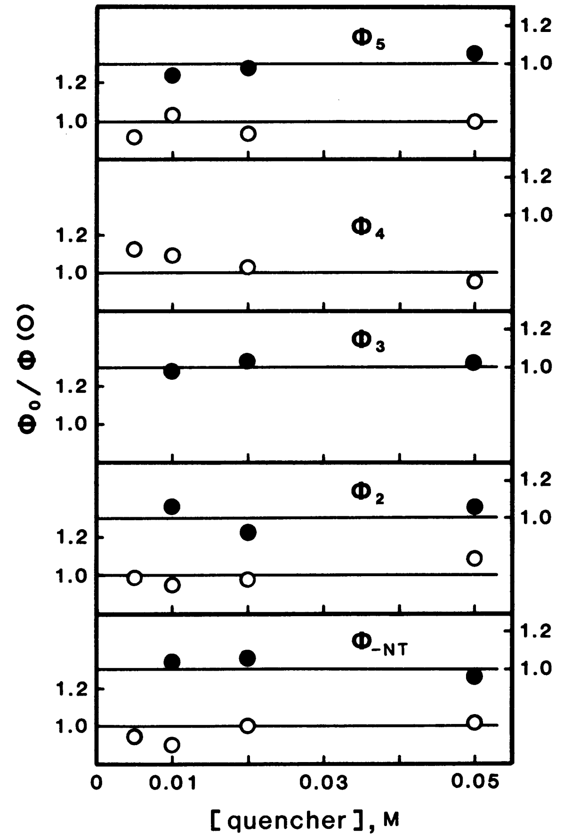
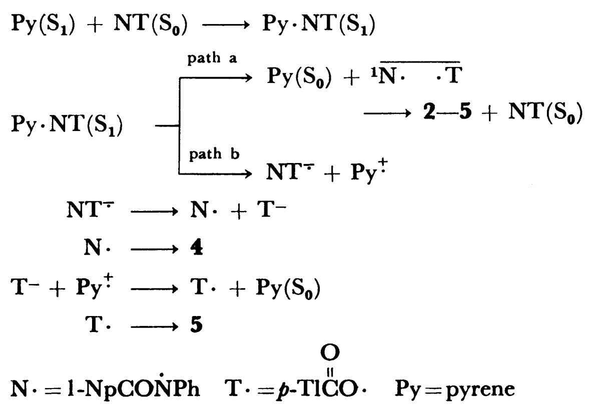


Fig. 3. Stern–Volmer plots for quenching of pyrene (3.00×10^{-3} M)-sensitized reaction of NT (6.67×10^{-3} M) with 366-nm light by 1,3-cyclohexadiene (●) and *trans*-stilbene (○) in 1,2-dichloroethane under nitrogen at room temperature (25±3 °C). Φ and Φ_0 are quantum yield for the reaction of NT with and without the quencher, respectively.



Scheme 2.

Φ_3, and Φ_5 for the direct photolysis, respectively. As previously discussed we used here Φ_5 as a measure of the extent of an "out-of-cage" reaction, owing both to a complicated fragmentation of the amido radical and to a minor decarboxylation process of the toluoyloxyl radical.[2]

As shown in Scheme 1, an energy transfer in the singlet exciplex intermediate causes a homolytic cleavage of the N–O bond in a NT molecule and the reactivities of the resulting geminate-radical pair should be affected to a lesser extent by the polarity of solvents based on our previous results.[1,2] Accordingly, Scheme 1 cannot explain the observed solvent polarity effects on $\Phi_2+\Phi_3$ and Φ_5 for the sensitized reaction. Because exciplexes with a charge-transfer character are well known to have a tendency to dissociate into radical ion pairs in polar solvents,[5,12] solvent polarity effects on the quantum yields ($\Phi_2+\Phi_3$ and Φ_5) for the reaction can be accounted for in terms of Scheme 2. In this Scheme an energy transfer in the singlet exciplex (path a) competes with electron transfer in this exciplex (path b). Path a gives the singlet geminate-radical pair from which the products **2**—**5** and starting NT are derived as already indicated in Scheme 1. On the other hand, electron transfer from pyrene to NT in the exciplex intermediate (path b) generates a NT anion radical and a pyrene cation radical. Polar solvents stabilize this radical ion pair but nonpolar solvents do not.[12] A NT anion radical, thus formed, may readily decompose to afford the amido radical and *p*-methylbenzoate which is oxidized by a pyrene cation radical to give the toluoyloxyl radical and pyrene. The amido and toluoyloxyl radicals abstract hydrogen atom from solvent molecules to yield the fragmentation products **4** and **5**. The exclusive participation of path b in the reaction makes the value of $\Phi_2+\Phi_3$ negligibly small. If path a predominates, then the quantum yields for the sensitized photolysis are expected to be comparable to those for the direct photolysis. Therefore the polar solvent, acetonitrile, prefers electron transfer to energy transfer in the exciplex intermediate to reduce $\Phi_2+\Phi_3$ accompanied by an increase in Φ_5, whereas energy transfer predominates in the nonpolar solvent, benzene. Both energy- and electron-transfer pathways may be important in 1,2-dichloroethane.

In order to examine whether or not electron transfer in the exciplex intermediate is thermodynamically possible, the free energy change ΔG in electron transfer was calculated by using the simplified Weller equation[13]

$$\Delta G\ (\text{kcal mol}^{-1}) = 23.06[E(\text{Py}^{\dot{+}}/\text{Py}) - E(\text{NT}/\text{NT}^{\bar{\cdot}})] - E_{S_1},$$

where $E(\text{Py}^{\dot{+}}/\text{Py})$ is the oxidation potential of pyrene (1.16 V vs. SCE in acetonitrile),[14] $E(\text{NT}/\text{NT}^{\bar{\cdot}})$ is the reduction potential of NT (−1.86 V vs. SCE in acetonitrile), and E_{S_1} is the first singlet excitation energy of pyrene (77 kcal mol^{-1}). The calculation of the free energy change gives $\Delta G=-7.4$ kcal mol^{-1}, strongly indicating electron transfer from the singlet-state pyrene to the ground-state NT to be thermodynamically very favorable process. Although the participation of both energy- and electron-transfer mechanisms in the singlet-sensitized photolysis modifies Eqs. 1—5 slightly, a linear relationship between $1/\Phi$ and $1/[\text{NT}]$ remains unaltered and the intercept/slope ratio of double reciprocal plots still give the same $k_t\tau_S$ values.

Micellar Effects on the Singlet Sensitization. Our previous study of micellar effects on the direct photolysis of NT provided us two interesting findings.[2] One is that diffusive separation of the singlet radical pair generated in hexadecyltrimethylammonium chloride (HTAC) micelles must be slow enough to allow efficient micellar cage reaction to yield exclusively **2**, **3**, and starting NT accompanying negligible formation of **4** and **5**. The other is that the appearance of the secondary cage-reaction product **3** is suppressed within the micelles owing to the high intramicellar viscosity. Based on these findings we expect that the micelle cage of HTAC can be used to distinguish between an energy- and an electron-transfer mechanisms both of which work in the pyrene-sensitized photolysis of NT depending on the polarity of solvents employed.

If the singlet-sensitized photolysis in HTAC micelles proceeds by an energy-transfer mechanism to result in the homolytic cleavage of the N–O bond in a NT molecule, then we expect negligibly small quantum yields for the formation of **4** and **5** compared to those of **2** and **3**. Thus the appearance of **4** and **5** in the micelles can be taken as indication for an electron-transfer mechanism. The sensitized decomposition of NT (3.00×10^{-3} M) by pyrene (1.00×10^{-3} M) in HTAC micelles (1.30×10^{-3} M) under nitrogen at room temperature (23±1 °C) gave the following results: $\Phi_{-\text{NT}}=0.051$, $\Phi_2=0.005$, $\Phi_3<0.001$, $\Phi_4=0.012$, and $\Phi_5=0.045$. These results strongly suggest a dominant electron-transfer mechanism for the reaction in HTAC micelles. Since hydrophobic nature of the amido and toluoyloxyl radicals should retard escape of these radicals from the micelle cage into the water phase,[15] we cannot offer a clear answer to the question of whether the rearranged products **2** is derived from recombination of the singlet geminate-radical pair or from recombination of the radical pair reencountered within the micelles after a NT anion radical decomposed to give the amido and toluoyloxyl radicals. The fact that the micelle surface has a polarity corresponding to that of alcohols seems to indicate minor contribution of an energy-transfer mechanism.[16,17]

Experimental

General Methods. Hitachi 638-50 HPLC apparatus with a 2.6×500-mm ODS (Hitachi gel #3050) column was used to accurately determine the concentrations of the starting materials that disappeared and of the photoproducts that appeared from linear calibration curves for each compound. Fluorescence spectra of pyrene with and without a quencher were taken under nitrogen on a Shimadzu RF-500 spectrophotofluorimeter. UV spectra were obtained with a Shimadzu UV-210A spectrophotometer. Fluorescence lifetimes of pyrene were measured under nitrogen on a Horiba NAES-1100 time-resolved spectrophotofluorimeter.

Materials and Solvents. *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT) and independently prepared authentic compounds **2**—**5** were the same as in previous studies.[2] Benzene and 1,2-dichloroethane (spectrograde from Dojin Chemical Co.) were used as received. Highly-purified acetonitrile was obtained by the modified procedure of Walden and Birr.[18] 1,3-Cyclohexadiene (Aldrich) was fractionally distilled just before its use and stored under nitrogen in a refrigerator. *trans*-Stilbene (reagent grade, Wako) was recrystallized twice from ethanol. Pyrene (reagent grade, Wako) was purified by repeated recrystallization from ethanol followed by sublimation at reduced pressure. Mobile phase for HPLC analysis consisted of acetonitrile (62 vol%) and water (38 vol%) (HPLC grade from Wako). Hexadecyltrimethylammonium chloride (HTAC, Wako) was recrystallized twice from acetone–methanol and sodium dodecyl sulfate (SDS, specially pure from Wako) was used as supplied.

Quantum Yields. The same methods as before was applied to determine the quantum yields for the pyrene-sensitized photolysis of NT.[2] The 366-nm light from a 450W high-pressure Hg lamp was isolated with Corning 0-52, Corning 7-37, and Toshiba IRA-25S glass filters (Transmittance=19% at 366 nm). Molar absorption coefficients of pyrene were determined to be 220, 190, and 130 ($M^{-1}\,cm^{-1}$) in benzene, 1,2-dichloroethane, and acetonitrile, respectively, so that more than 95% of the incident light is absorbed by pyrene in the sensitized decomposition of NT. All the quantum yields are average of more than three determinations. Quantum yields for the sensitized photolysis in HTAC micelles were measured at a pyrene concentration such that the [pyrene]/[micelle] ratio nearly equals unity. The micelle concentration was estimated based on the equation [micelle]=([HTAC surfactant]−cmc)/N, where [HTAC surfactant]=0.15 M, critical micelle concentration, cmc=1.3×10^{-3} M, and aggregation number, N=113.[19]

Fluorescence Lifetimes and Reduction Potential. Prior to fluorescence lifetime measurements, solutions were purged with oxygen-free nitrogen for about 10 min for deoxygenation. Fluorescence decay was traced by the use of a single photon counting technique for deconvolution of the data obtained with a computer attached to the apparatus. The reduction potential of NT was measured by cyclic voltametry in acetonitrile. For this purpose we used saturated calomel electrode (SCE) as a reference electrode and tetrabutylammonium bromide (0.1 M) as a supporting electrolyte.

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6) In the sensitized photolysis of NT in benzene there is a possibility of the formation of biphenyl whose chemical yield may be comparable to that of **4** and **5**. But it was impossible to check this possibility because we could not detect HPLC peak of biphenyl whose concentration was adjusted so as to become the same as that of **4** and **5** obtained by the photolysis under our analytical conditions. Additionally HPLC peak of any unknown product observed was not consistent with that of biphenyl.

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