Mechanism of the Direct and Triplet-sensitized Photolysis of *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine

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Quantum yields (Φ) were determined for benzophenone-sensitized and direct photolysis of the title hydroxylamine (NT). Analysis of linear Stern-Volmer plots of the reciprocal of Φ against the reciprocal of NT concentration reveals that the sensitized decomposition of NT takes place *via* its first triplet excited state (T_1) produced by triplet-triplet energy transfer from benzophenone to NT. The fact that the quantum yields for the direct photolysis are independent of NT concentration indicates no occurrence of both self-quenching and induced decomposition of NT by the photochemically generated radicals. Closer examination of the micellar and solvent viscosity effects on the quantum yields for the direct photolysis with 313-nm light shows the existence of at least two spin-correlated (singlet) radical pairs: One is a contact radical pair whose recombination eventually yields 1,3-toluoyloxyl-migrated product and the other a solvent-separated radical pair from which 1,5-toluoyloxyl-migrated product is derived in competition with diffusive escape from the solvent or micelle cage. Exclusive occurrence of the direct photolysis from the first singlet excited state (S_1) was explained on the basis of the large energy gap between S_1 and T_1 (31 kcal mol^{-1}) which is likely to make intersystem crossing from S_1 to T_1 very inefficient.

We have discussed qualitatively the mechanism of direct and triplet-sensitized photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines on the basis of the chemical yields of photoproducts, and concluded that photoreactions under direct irradiations proceed exclusively through the singlet excited state affording 1,3- and 1,5-aroyloxyl-migrated products ("in-cage" products) along with the fragmentation products ("out-of-cage" products).[1] On the other hand, triplet-sensitized photolysis gives only the fragmentation products. These intriguing effects of spin multiplicity of the excited states that is responsible for the reaction on the product distribution gave an impetus to more quantitative investigation on the photolysis of *N*,*O*-diacylhydroxylamines. It has been also one of the important problems encountered in our previous work whether or not the "in-cage" products come from the reaction that takes place within the identical solvent cage. Thus the title hydroxylamine (NT) was chosen for the present study and quantum yields for the direct and sensitized photolysis of NT were determined in order to solve this problem and then shed more light on the mechanism of the photolysis under conditions where geminate radicals with different spin multiplicity are produced.

Results

Quenching of the Phosphorescence of Benzophenone by NT. To ensure the occurrence of triplet-triplet energy transfer from benzophenone (the first singlet excitation energy, E_{S_1}=74.4; the first triplet excitation energy, E_{T_1}=69.2 kcal mol^{-1}; 1 kcal=4.18 kJ)[2] to NT (E_{S_1}=90, E_{T_1}=59 kcal mol^{-1}),[1] phosphorescence quenching experiments were conducted under argon at room temperature (24±1 °C). This energy transfer can be clearly seen in the efficient quenching of sensitizer's emission that follows linear Stern-Volmer relationships with the slopes ($k_t\tau_T$ where k_t and τ_T are the rate constant for triplet energy transfer and the lifetime of triplet benzophenone without NT, respectively) of 1600 M^{-1} (1 M^{-1}=1 dm^3 mol^{-1}) in 1,2-dichloroethane and 2500 M^{-1} in acetonitrile (Fig. 1). These $k_t\tau_T$ values are collected in Table 1. From the reported lifetimes of triplet benzophenone in the absence of any quencher (τ_T=14 μs in carbon tetrachloride[3] and 26 μs in acetonitrile[4]), we obtain k_t=1.1×10^8 and 0.96×10^8 M^{-1} s^{-1} in 1,2-dichloroethane and acetonitrile, respectively. Under the present experimental conditions neither fluorescence nor phosphorescence of NT could be detected.

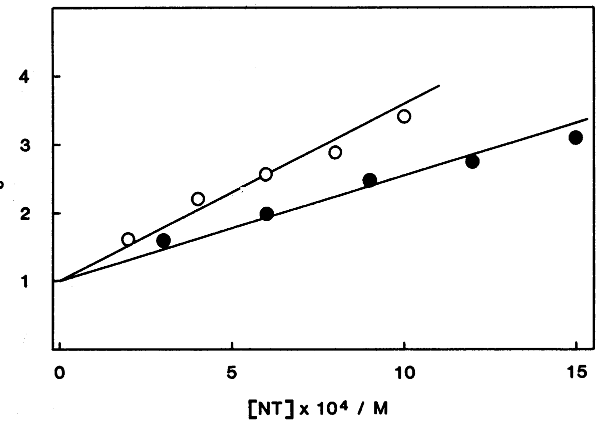


Fig. 1. Stern-Volmer plots of quenching of benzophenone (0.03 M) phosphorescence by NT in acetonitrile (○) and 1,2-dichloroethane (●) under argon at room temperature (24±1 °C). Excitation wavelength=366 nm. I and I_0 refer to the phosphorescence intensity of benzophenone with and without NT, respectively.

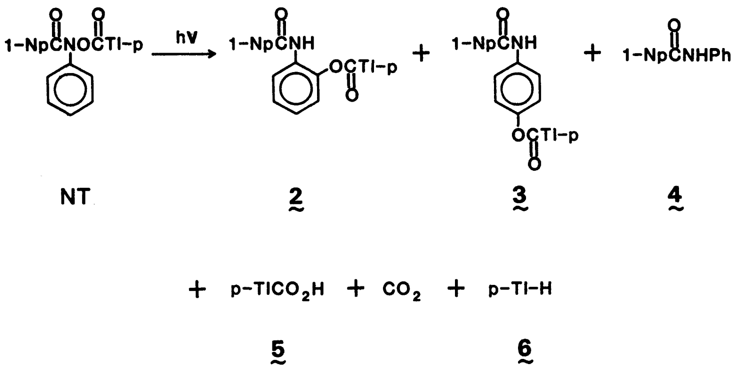
Quantum Yields for Triplet-sensitized Photolysis. As expected, irradiation of an N_2-saturated solution of NT (1.00—6.60 mM, 1 mM=10^{-3} mol dm^{-3}) in the presence of benzophenone (0.03 M) with 366-nm light led to only the fragmentation products **4**—**6**, as determined by HPLC analysis. Even trace amounts of

TABLE 1. QUANTUM YIELDS FOR THE TRIPLET-SENSITIZED PHOTOLYSIS OF NT (1.00—6.60 mM) BY BENZOPHENONE (0.03 M) AT 23±2°C

1 M=1 mol dm^{-3}

Solvent	Φ_{lim}[a)			Φ_6[b)	Φ_2[c)	Φ_3[c)	k_d/k_r	$k_t\tau_T$[d) M^{-1}	$k_t\tau_T$[e) M^{-1}
	$\Phi_{\text{-NT,lim}}$	$\Phi_{4,\mathrm{lim}}$	$\Phi_{5,\mathrm{lim}}$						
CH_2ClCH_2Cl	0.820	0.570	0.244	0.36	≈0	≈0	0.22	2700[f) 740[g) 1400[h) mean 1600	1600
CH_3CN	0.578	0.088	0.077	0.30	≈0	≈0	0.73	5500[f) 1300[g) 1600[h) mean 2800	2500

a) $\Phi_{\text{-NT,lim}}$, $\Phi_{4,\mathrm{lim}}$, and $\Phi_{5,\mathrm{lim}}$ are the limiting quantum yields (Φ_{lim}), *i.e.*, the quantum yields extrapolated to the infinite concentration of NT, for disappearance of NT and formation of **4** and **5**, respectively. b) Quantum yield for formation of **6** (GLC analysis) determined for 6.60 mM NT. c) Φ_2 and Φ_3 represent quantum yields for appearance of **2** and **3**, respectively. d) From quantum yield measurements. e) From quenching of sensitizer's phosphorescence by NT. f) From linear plot of $1/\Phi_{\text{-NT}}$ *vs.* 1/[NT]. g) From linear plot of $1/\Phi_5$ *vs.* 1/[NT]. h) From linear plot of $1/\Phi_4$ *vs.* 1/[NT].



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

the rearrangement products **2** and **3** could not be detected in this benzophenone-sensitized photolysis. The quantum yields (Φ) for the disappearance of NT and for the appearance of the products were determined by using a potassium trioxalatoferrate(III) actinometer. The large values of quantum yields indicate very efficient sensitized decomposition to take place (Table 1).

Control experiments demonstrate that no photolysis of NT occurs without the sensitizer and that the photoproducts **4**—**6** undergo negligible sensitized decomposition. One can see, however, some unknown HPLC peaks on the chromatograms in both solvents, which may be responsible for a little poor mass balance of the sensitized photolysis. No attempt to separate and identify these unknown products was made because this inevitable side reaction appears to make no serious trouble in discussing the reaction mechanism based on the quantum yields of the photoproducts in which we are interested. In addition, HPLC analysis of a 1,2-dichloroethane or an acetonitrile solution of benzophenone before and after the irradiation reveals that hydrogen abstraction from the solvent by the benzophenone triplet takes place to a negligible extent during the irradiation with 366-nm light.

If the triplet-sensitized reaction of NT with benzophenone (B) proceeds according to Scheme 1 in which Φ_{isc} refers to the quantum yield of intersystem crossing and is known to be unity, we expect a linear relation between $1/\Phi$ and 1/[NT] under the steady-state approximation as evident from Eqs. 1—3 even though reactions giving unknown products are taken into consideration. From the linear Stern-Volmer plots of $1/\Phi_{-\mathrm{NT}}$,

$$1/\Phi_{-\mathrm{NT}} = (1+k_d/k_r)(1+1/k_t\tau_T[\mathrm{NT}]) \tag{1}$$

$$1/\Phi_4 = (1+k_d/k_r)(1+k_u{}^{\mathrm{N}}/k_4)(1+1/k_t\tau_T[\mathrm{NT}]) \tag{2}$$

$$1/\Phi_5 = (1+k_d/k_r)(1+(k_6+k_u{}^{\mathrm{T}})/k_5)(1+1/k_t\tau_T[\mathrm{NT}]) \tag{3}$$

$1/\Phi_4$, and $1/\Phi_5$ *vs.* 1/[NT] (Fig. 2), we obtain the limiting quantum yields (Φ_{lim}) for both the disappearance of NT and the formation of **4** and **5**, which are collected in Table 1. The intercept/slope ratios of these linear plots give the $k_t\tau_T$ values, while the values of k_d/k_r can be estimated by using Eq. 1.

Quantum Yields for Direct Photolysis. In order

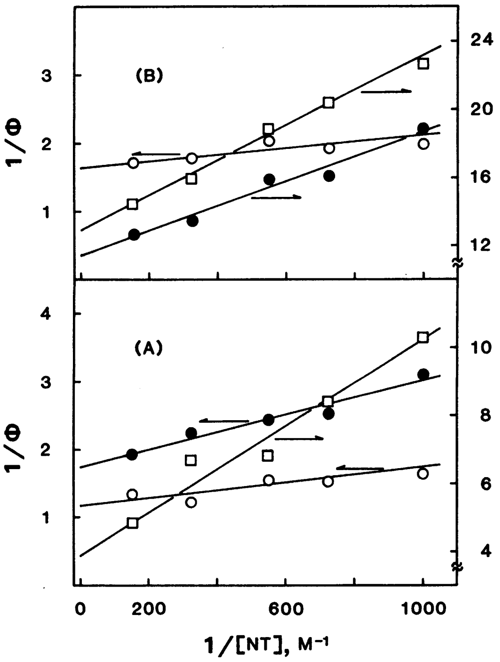


Fig. 2. Stern-Volmer plots of $1/\Phi_{-NT}$ (○), $1/\Phi_4$ (●), and $1/\Phi_5$ (□) *vs.* 1/[NT] for benzophenone (0.03 M)-sensitized photolysis with 366-nm light in 1,2-dichloroethane (A) and in acetonitrile (B).

to minimize undesired secondary photodecompositions of the products **2**—**5**, quantum yields for the direct photolysis with 313-nm light were determined at low conversions (5—10%) of starting NT. From Table 2 we see that the mass balance of the photolysis is fairly good. Direct irradiations of **2**—**5** indicate their very slight decomposition (less than 5%) to take place under conditions in which quantum yields shown in Table 2 were estimated.

Effects of solvents and hexadecyltrimethylammonium chloride (HTAC) micelle on the quantum yields for the disappearance of NT and for the formation of **2**—**5** were examined and results obtained are summarized in Table 2. In addition, quantum yield measurements were made on a 1,2-dichloroethane solution of NT whose initial concentration varied from 1.00×10^{-3} to 6.60×10^{-3} M (Fig. 3).

Discussion

Triplet Sensitization. The observation of a linear plot of $1/\Phi$ against the reciprocal of NT concentration is in accord with our suggested scheme for the sensitized photolysis (Scheme 1). Involvement of the benzophenone triplet in this sensitization is clearly seen in the finding that the $k_t\tau_T$ values (2500 M^{-1} in acetonitrile and 1600 M^{-1} in 1,2-dichloroethane), determined from the phosphorescence quenching experiments, are in satisfactory agreement with the average values of $k_t\tau_T$ (2800 M^{-1} in acetonitrile and 1600 M^{-1} in 1,2-dichloroethane), obtained from the linear plots of $1/\Phi$ *vs.* 1/[NT]. Because the rates of hydrogen abstraction from various compounds by the benzophenone triplet has been known to lie in the range 10^3—10^5 $M^{-1}s^{-1}$,[10] the estimated k_t values (0.96×10^8 and 1.1×10^8 $M^{-1}s^{-1}$ in acetonitrile and 1,2-dichloroethane, respectively) also show that benzophenone acts merely as an agent for energy transfer during the reaction, accompanying its negligible decomposition, and thus that NT undergoes sensitized decomposition

	process (rate constant)
$B(S_0) \xrightarrow{h\nu} B^*(S_1) \xrightarrow{\Phi_{isc} = 1} B^*(T_1)$	absorption and intersysten crossing
$B^*(T_1) \xrightarrow{k_d^B = 1/\tau_T} B(S_0)$	deactivation to the ground state (k_d^B)
$B^*(T_1) + NT(S_0) \xrightarrow{k_t} B(S_0) + NT^*(T_1)$	energy transfer (k_t)
$NT^*(T_1) \xrightarrow{k_d} NT(S_0)$	deactivation (k_d)
$NT^*(T_1) \xrightarrow{k_r} N\bullet + T\bullet$	homolysis of the N-O bond (k_r)
$N\bullet \xrightarrow{k_4}$ 1-naphthanilide (**4**)	hydrogen abstraction (k_4)
$N\bullet \xrightarrow{k_u^N}$ unknown product(s)	side reaction(s) (k_u^N)
$T\bullet \xrightarrow{k_5}$ p-toluic acid (**5**)	hydrogen abstraction (k_5)
$T\bullet \xrightarrow{k_6}$ toluene (**6**)	decarboxylation and hydrogen abstraction (k_6)
$T\bullet \xrightarrow{k_u^T}$ unknown product(s)	side reaction(s) (k_u^T)

$N\bullet = 1\text{-}Np\overset{O}{\overset{\|}{C}}\overset{\bullet}{N}Ph,\quad T\bullet = p\text{-}Tl\overset{O}{\overset{\|}{C}}O\bullet$

Scheme 1.

TABLE 2. QUANTUM YIELDS FOR THE DIRECT PHOTOLYSIS OF NT WITH 313-nm LIGHT AT 28±3°C

Solvent[a] (η)[b]	Dielectric constant	$\Phi_{\text{-NT}}$	Φ_2	Φ_3	Φ_4	Φ_5
CH_3CN (0.326)[c]	37.5[c]	0.150±0.030	0.044±0.005	0.032±0.005	0.012±0.002[d]	0.041±0.005
CH_2ClCH_2Cl (0.730)[c]	10.36[c]	0.140±0.022	0.048±0.007	0.029±0.005	0.044±0.004	0.045±0.008
Sulfolane (10.286)[c]	43.3[c]	0.104±0.020	0.061±0.003	0.013±0.001	0.011±0.001	0.015±0.002
HTAC(0.1 M) (18)[e]	18[f]	0.127±0.040	0.094±0.015	0.016±0.001	≈0	≈0

a) [NT]=5.00×10^{-3} M in organic solvents and 3.00×10^{-3} M in HTAC micelle. The critical micelle concentration of HTAC has been reported to be 1.5×10^{-3} M.[5] b) Viscosity in centipoise (cP) at 30°C. c) Ref. 6. d) This decrease in Φ_4 in acetonitrile is due to side reactions of the amido radical taking place in competition with its hydrogen abstraction giving **4** as previously discussed.[1] e) The intramicellar viscosity of HTAC has been estimated to be ≤21 cP at 20°C[7] and 18 cP at 30°C.[8] f) Ref. 9.

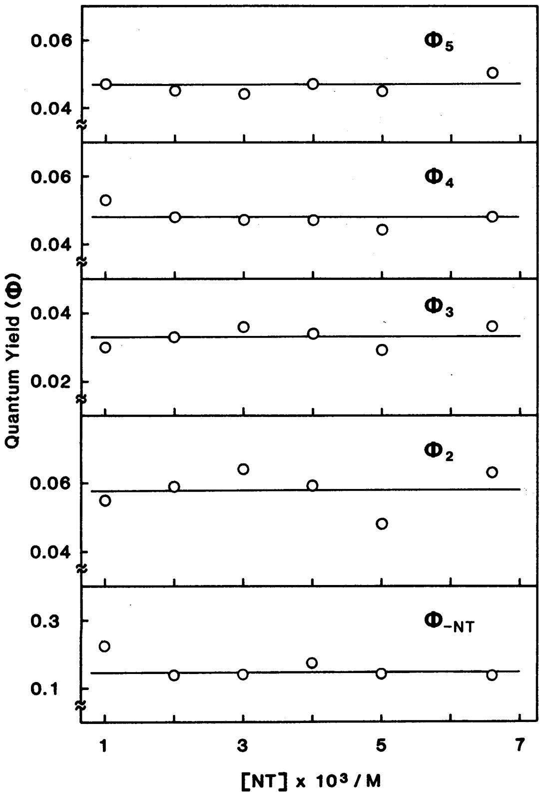
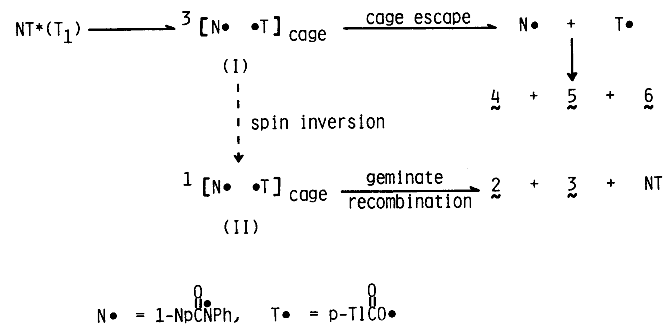


Fig. 3. Quantum yields for the direct photolysis with 313-nm light as a function of NT concentration in 1,2-dichloroethane.

through triplet-triplet energy transfer from the sensitizer to NT.

On the other hand, our values of k_d/k_r require that the resulting NT triplet dissipates its energy in part without dissociating into the amido and aroyloxyl radicals. Comparison of these values in two solvents used establishes higher reactivity of the NT triplet in 1,2-dichloroethane than in acetonitrile. We can also estimate the values of k_u^N/k_4 and k_u^T/k_5 from Eqs. 2 and 3 with these k_d/k_r values: $k_u^N/k_4=6$ in acetonitrile and 0.4 in 1,2-dichloroethane; $k_u^T/k_5=2$ in the former and 0.6 in the latter on assuming $k_6/k_5=\Phi_6/\Phi_5$. The values of k_u^N/k_4 and k_u^T/k_5 thus evaluated show that a complicated fragmentation of the triplet-derived radicals takes place in acetonitrile, while hydrogen abstraction and decarboxylation constitute a major fragmentation process in 1,2-dichloroethane.

Similar decreased efficiency of geminate recombination of radical pairs has been observed in the triplet-sensitized photodecompositions of peroxides,[11] azo compounds,[12] and allyl phenyl ether.[13] The most reasonable explanation for these observations was that there is a barrier to recombination of a caged radical pair produced as a triplet because spin inversion of a triplet radical pair must precede its coupling in the cage. The presence of the barrier results in preferential diffusive separation of radicals from the cage. This concept of triplet→singlet spin inversion in a radical pair has been critically scrutinized and then verified to have a wide applicability to reactions of spin-correlated radical pairs.[14] No formation of **2** and **3** in our triplet-sensitized photolysis of NT can be nicely explained in terms of the idea mentioned above. An illustration of the sensitized photolysis of NT appears in Scheme 2. The observation that Φ_2 and Φ_3 are negligibly small compared to Φ_4, Φ_5, and Φ_6 suggests that in our system the rate of spin inversion from the triplet pair (I) to the singlet pair (II) should be slow enough to allow the exclusive escape of the radical pair from the cage.



Scheme 2.

Direct Irradiation. Our previous results of the direct photolysis of NT that occurs through the singlet excited state provided us some interesting problems to be solved:[1] (1) Is there self-quenching or induced decomposition of starting NT brought about by radicals produced? and (2) Are the rearrangement products **2** and **3** derived from recombination within the identical solvent cage?

Figure 3 shows that neither $\Phi_{-\mathrm{NT}}$ nor Φ_{2-5} varies over the concentration range of NT investigated, allowing us to conclude that no starting NT meets with self-quenching and induced decomposition under conditions examined.

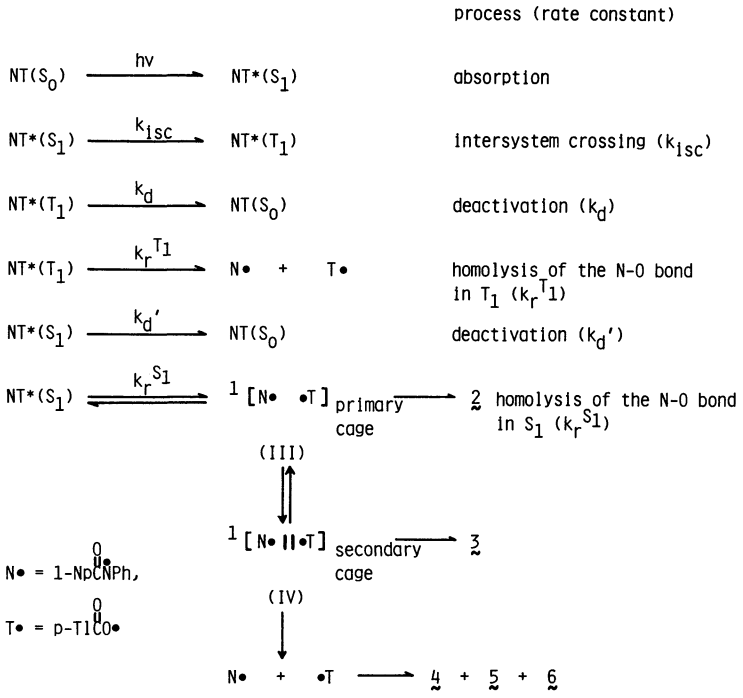
To answer the next question, we have studied solvent effects on the quantum yields for the photolysis with 313-nm light. It was suggested in the previous work[1] that the chemical yields of **2**, **3**, and **5** are not sensitive to both the polarity of solvents of comparable viscosity and the ease with which hydrogen atoms of solvents are abstracted by the photochemically generated toluoyloxyl radical, whereas the yield of **4** is very sensitive to this ease of solvents. Despite the secondary hydrogens of sulfolane and HTAC are very likely to be much more reactive toward hydrogen abstraction by free radicals compared with the primary hydrogens of acetonitrile,[15] the quantum yields of the fragmentation products (especially Φ_5) are much smaller in sulfolane and HTAC than in acetonitrile, indicating that the quantum yields shown in Table 2 correlate neither with the solvent polarity nor with the reactivity of a solvent hydrogen atom. This finding provides further support for the suggestion mentioned above. Thus the quantum yields for the direct photolysis seem to nicely correlate with the solvent viscosity although the slightly smaller value of Φ_5 in acetonitrile than that in 1,2-dichloroethane indicates that the reactivity of solvents toward hydrogen abstraction also plays a some but minor role in determining the relative extent of "out-of-cage" and "in-cage" reactions. The facts that decarboxylation of the toluoyloxyl radical giving eventually toluene is a minor process in the direct photolysis and that a complicated fragmentation of the amido radical occurs in relatively inert solvents toward hydrogen abstraction allow us to use Φ_5 rather than Φ_4 as a measure of the extent of "out-of-cage" reaction. These considerations force us to discuss solvent effects on $\Phi_{-\mathrm{NT}}$, Φ_2, and Φ_5 solely from the standpoint of micellar and solvent viscosity effects on the efficiency of geminate recombination of radical pairs.

On the other hand, micelles are known to become a good device for causing an efficient cage reaction of radical pair produced photochemically or thermally.[14] The photolysis in aqueous HTAC micelle is, therefore, expected to significantly reduce the rate of escape of the radical pair from the micelle cage, causing more efficient geminate recombination and hence leading to a decrease in $\Phi_{-\mathrm{NT}}$ and Φ_5 and an increase in Φ_2 and Φ_3. An increase in the solvent viscosity will exert similar but less remarkable effects on these quantum yields.

Micellar effects on $\Phi_{-\mathrm{NT}}$, Φ_2, and Φ_5 are consistent with this expectation. However, a decrease in Φ_3 was observed in the photolysis in HTAC micelles. Almost no formation of the fragmentation products **4** and **5** is interpreted to mean that the recombination of the radical pair formed in the micelle is much faster than the exit of these hydrophobic radicals from the micelle. As expected the increased viscosity effects on the efficiency of geminate recombination are less remarkable compared to micellar effects on this efficiency, though both effects are similar, supporting the view that the hydrophobic micelle aggregate serves as a cage for causing more efficient cage reaction than that in homogeneous sulfolane solution whose macroscopic viscosity is comparable to the intramicellar microviscosity of HTAC.

Different dependence of Φ_2 and Φ_3 upon reaction environments indicates the existence of at least two spin-correlated radical pairs as originally inferred by Noyes:[16] One is a contact radical pair (III) whose recombination eventually yields 1,3-rearrangement product **2** and the other a solvent-separated radical pair (IV) from which 1,5-rearrangement product **3** is derived in competition with regeneration of (III) and diffusive escape out of the solvent or micelle cage as shown in Scheme 3.

According to Scheme 3, an increase in the solvent viscosity should impede primary cage reaction to a negligible extent whereas secondary cage and fragmentation reactions are suppressed to different extent by increasing the solvent viscosity.[17] Furthermore, this suppression of secondary cage and fragmentation reactions will result in an increase in Φ_2 and a decrease in $\Phi_{-\mathrm{NT}}$. These are consistent with the results obtained. The finding that the solubilized probe can move about within the micelle offers a good explanation for the formation of **3** in the photolysis in the micelle.[18] In micellar system hydrocarbon chain of the micelle-forming surfactant may serve as a solvent. Because the triplet radical pair generated selectively from the first triplet excited state (T_1) of NT results in the appearance of the cage coupling products **2** and **3** in a negligible quantum yield, the spin multiplicity of two caged radical pairs (III) and (IV) must be singlet. Exclusive occurrence of the direct photolysis from the first singlet excited state (S_1) should be due to the much slower rate of intersystem crossing relative to the rate of reaction which arises from S_1, namely, $k_{\mathrm{isc}} \ll k_r^{S_1}$ in Scheme 3. In view of the fact that a large singlet-triplet energy gap reduces Franck-Condon factor,[19] it is reasonable to believe that the large energy gap between S_1 and T_1 for NT ($\Delta E_{\mathrm{ST}}=$ 31 kcal mol^{-1}) renders the rate of intersystem crossing from S_1 to T_1 considerably slow.



Scheme 3.

Experimental

General Methods. HPLC analysis of the photoproducts was performed on a Hitachi 638-50 high-performance liquid chromatography apparatus with a 2.6×500-mm ODS (Hitachi gel #3050) column. Linear calibration curves for each compound, prepared under the same analytical conditions, were employed to quantify both disappearance of starting material and appearance of the products. GLC analysis was carried out on a Hitachi 663-50 gas chromatograph using 2-m column packed with 10% Silicone SE-30 on Uniport B (60/80 mesh, Gasukuro Kogyo Inc.). Phosphorescence of benzophenone with and without quencher was measured under argon with a Shimadzu RF-500 spectrophotofluorimeter. UV spectra were taken on a Shimadzu UV-210A spectrophotometer.

Materials and Solvents. *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT) and authentic compounds for the photoproducts **2**—**5** were prepared and purified according to the same procedure as previously described.[1] 1,2-Dichloroethane (spectrograde from Dojin Chemical Co.) and Sulfolane (Merck, Uvasol) were used without further purification. The same method as before[1] was employed to get highly-purified acetonitrile. Acetonitrile and water (HPLC grade from Wako Pure Chemical Industries, Ltd.) were used as received for HPLC analysis. Pure benzophenone was obtained by repeated recrystallization from aqueous ethanol. Hexadecyltrimethylammonium chloride (HTAC, Wako) was recrystallized twice from acetone–methanol and dried *in vacuo* at room temperature.

Quantum Yield Determinations. Quantum yields were determined according to the method of Hatchard and Parker[20] which employs a potassium trioxalatoferrate(III) actinometer solution. A 450 W high pressure Hg lamp was used as the light source from which 313-nm light for direct irradiation was isolated by means of a potassium chromate (0.002 M) in a 1% aqueous solution of potassium carbonate and Corning 7-54 filters. The 366-nm light from the same Hg lamp was selected with Corning 0-52, Corning 7-37, and Toshiba IRA-25S glass filters.

In the sensitized reaction, more than 99% of the incident light was absorbed by benzophenone because molar absorption coefficients of NT and benzophenone at 366 nm are 2.6 and 50 ($\mathrm{M^{-1}cm^{-1}}$) in acetonitrile, respectively, and 3.1 and 58 ($\mathrm{M^{-1}cm^{-1}}$) in 1,2-dichloroethane, respectively, at room temperature. All the quantum yields for the direct and sensitized photolysis are average of more than three determinations. Quantum yields for the photolysis in HTAC micelles were determined in the same manner as that used for homogeneous solutions.

On the other hand, the solubility of NT in water could not be determined accurately owing to turbidity of the solution. However, the saturated water solution gave no signs of the absorption of NT so that NT concentration in water should be less than 10^{-6} M. On solubilization of NT in HTAC micelles by ultrasonic dispersal the solution became clear and showed no turbidity. The possibility of hydrolysis of NT in this micellar solution before and after the photolysis can be ruled out because HPLC analysis of the micellar solution indicated no formation of *p*-toluic acid and *N*-(1-naphthoyl)-*N*-phenylhydroxylamine.

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