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Energy- and Electron-Transfer Pathways in the Triplet-Sensitized Photolysis of *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine with Substituted Benzophenones

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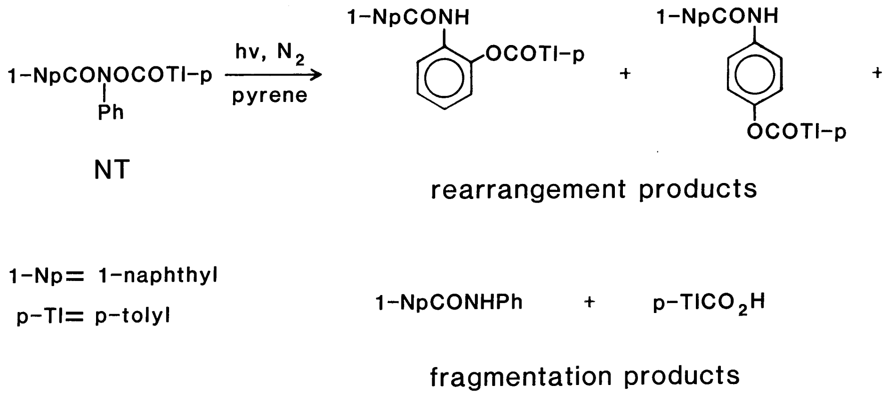
Quantum-yield and thermodynamic analyses of the triplet-sensitized photolysis of the title hydroxylamine (NT, **1**) with 4,4′-bis(dimethylamino)benzophenone (BAB), 4-dimethylaminobenzophenone (DAB), 4,4′-dimethoxybenzophenone (DMB), and 3,3′-bis(trifluoromethyl)benzophenone (BFB) suggest that the BAB- and DAB-sensitized reactions proceed by a preferential electron-transfer pathway within a triplet-exciplex intermediate, formed between the triplet-state sensitizer and the ground-state NT, to give *N*-phenyl-1-naphthalenecarboxamide (**2**) and *p*-toluic acid (**3**). On the other hand, the energy-transfer pathway in this exciplex intermediate, eventually forming **2** and **3**, as well as toluene (**4**), predominates for reactions sensitized with DMB and BFB having fewer electron-donating substituents than does the dimethylamino group of BAB and DAB. The finding that benzil, both excited singlet and triplet states of which lie below those of NT, brings about a sensitized photolysis to afford the same fragmentation products, provides strong evidence for the existence of a triplet-exciplex intermediate. In addition, evidence concerning the operation of an electron-transfer mechanism in our sensitized photolysis comes from an observation that the photolysis of NT sensitized with *N*,*N*,*N*′,*N*′-tetramethylbenzidine, the excited state of which is one of the most powerful one-electron reductants, gives the same product distribution as does that obtained by the BAB- and DAB-sensitized reactions.

An exciplex is undoubtedly one of the most important intermediates in a great number of photosensitized reactions. Strong evidence has been accumulated to support the existence of this exciplex intermediate.[1] In our previous study[2] we showed that the pyrene-sensitized photolysis of *N*-(1-naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT, **1**) proceeds through a singlet-exciplex intermediate to yield the rearrangement and fragmentation products shown in Scheme 1. An analysis of solvent and micellar effects on this sensitized photolysis established that both energy and electron transfers take place in the singlet-exciplex intermediate to affect the final product distribution. On the other hand, the triplet-sensitized photolysis of NT with benzophenone (BP) afforded only the fragmentation products, but no rearrangement products.[3] This finding was explained in terms of the idea that the rate of spin inversion from the triplet radical pair to the singlet one must be slow enough to allow the exclusive escape of radicals from the solvent cage.

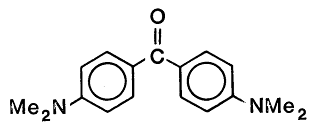
One important problem in which we are interested is whether or not the triplet-sensitized photolysis of our model compound, NT, occurs from a triplet-exciplex intermediate formed between the triplet-state sensitizer and the ground-state NT. We are particularly concerned with the potentiality of competitive energy and electron transfers in this triplet exciplex. To these ends we have investigated the effects of substituents of BP on the sensitized process of NT. We also hoped to clarify the mechanism of the triplet-sensitized photolysis of *N*,*O*-diacyl-*N*-phenylhydroxylamines in more detail by choosing NT for the present study.

Results

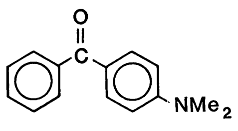
Structure Effects of Triplet Sensitizers on the Photolysis. In our previous study[3] we found that triplet NT has a higher reactivity in 1,2-dichloroethane than in



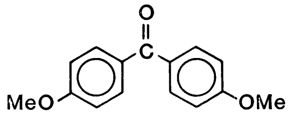
Scheme 1.



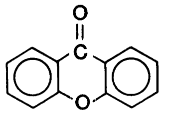
BAB



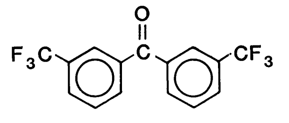
DAB



DMB

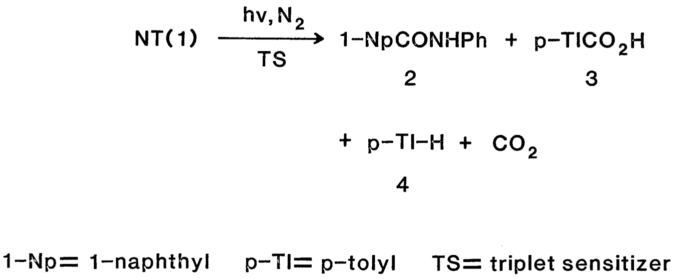


XT



BFB

acetonitrile, and that undesired side reactions of the triplet-derived radical, especially the amidyl radical, occur in a solvent of low reactivity toward hydrogen abstraction by this radical. We thus selected 1,2-dichloroethane as a solvent, and used 4,4′-bis(dimethylamino)benzophenone (BAB; the first singlet excitation energy, $E_{S_1}<90$; the first triplet excitation energy, $E_{T_1}=62$ kcal mol^{-1}; 1 kcal=4.184 kJ),[4,5] 4-dimethylaminobenzophenone (DAB; $E_{S_1}<90$; $E_{T_1}=62$ kcal mol^{-1}),[5] 4,4′-dimethoxybenzophenone (DMB; $E_{S_1}=77$; $E_{T_1}=71$ kcal mol^{-1}),[4,5] xanthone (XT; $E_{S_1}=78$; $E_{T_1}=74$ kcal mol^{-1}),[4] and 3,3′-bis(trifluoromethyl)benzophenone (BFB; $E_{S_1}<90$; $E_{T_1}=69$ kcal mol^{-1})[5] as triplet sensitizers. Irradiation of an oxygen-free 1,2-dichloroethane solution of NT (1.0—7.0×10^{-3} M, 1 M=1 mol dm^{-3}) containing each sensitizer (0.030 M) with 366-nm light gave fragmentation products **2** and **3** for BAB and DAB and **2**—**4** for DMB, XT, and BFB (Scheme 2). The quantum yields for the disappearance of NT and for the appearance of **2**—**4** were determined under nitrogen by using a potassium trioxalatoferrate(III) actinometer.[6] The finding that the phosphorescences of all sensitizers (0.030 M) were efficiently quenched by NT (7.0×10^{-3} M; $E_{S_1}=90$; $E_{T_1}=59$ kcal mol^{-1})[7] in 1,2-dichloroethane at 77 K indicates that all of these compounds are potent triplet sensitizers for NT photolysis. A comparison of the E_{S_1} of NT with that of each sensitizer makes a singlet-singlet energy transfer from any sensitizer to NT very unlikely.



$$\mathrm{NT(1)} \xrightarrow[\mathrm{TS}]{h\nu,\,\mathrm{N_2}} \underset{\mathbf{2}}{\text{1-NpCONHPh}} + \underset{\mathbf{3}}{p\text{-TlCO}_2\text{H}} + \underset{\mathbf{4}}{p\text{-Tl-H}} + \mathrm{CO_2}$$

1-Np= 1-naphthyl p-Tl= p-tolyl TS= triplet sensitizer

Scheme 2.

As shown typically in Fig. 1, the observation of a linear relationship between the reciprocal of quantum yields (Φ) for the sensitized photolysis and the reciprocal of NT concentration suggests that the sensitized decomposition of NT proceeds according to Scheme 3, in which the quantum yields (Φ_{isc}) of intersystem crossing in all of the triplet sensitizers used were assumed to be unity. Similar double reciprocal plots were also obtained for

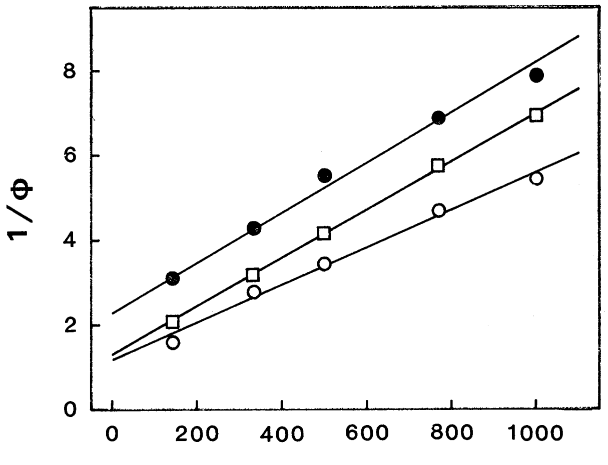
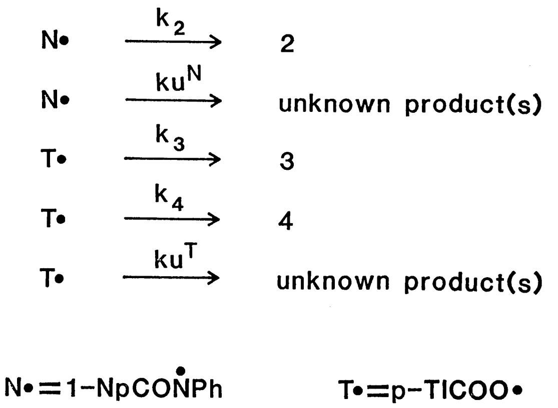


Fig. 1. Stern–Volmer plots of $1/\Phi_{\text{-NT}}$ (○), $1/\Phi_2$ (●), and $1/\Phi_3$ (□) versus 1/[NT] for the BAB (0.030 M)-sensitized photolysis of NT with 366-nm light in oxygen-free 1,2-dichloroethane.



$$\begin{aligned}
&\mathrm{TS(S_0)} \xrightarrow{h\nu} \mathrm{TS(S_1)} \xrightarrow{\Phi_{isc}\approx 1} \mathrm{TS(T_1)}\\
&\mathrm{TS(T_1)} \xrightarrow{1/\tau_T} \mathrm{TS(S_0)}\\
&\mathrm{TS(T_1)} + \mathrm{NT(S_0)} \xrightarrow{kt} \mathrm{NT(T_1)} + \mathrm{TS(S_0)}\\
&\mathrm{NT(T_1)} \xrightarrow{kd} \mathrm{NT(S_0)}\\
&\mathrm{NT(T_1)} \xrightarrow{kr} \mathrm{N\bullet} + \mathrm{T\bullet}\\
&\mathrm{N\bullet} \xrightarrow{k_2} \mathbf{2}\\
&\mathrm{N\bullet} \xrightarrow{ku^N} \text{unknown product(s)}\\
&\mathrm{T\bullet} \xrightarrow{k_3} \mathbf{3}\\
&\mathrm{T\bullet} \xrightarrow{k_4} \mathbf{4}\\
&\mathrm{T\bullet} \xrightarrow{ku^T} \text{unknown product(s)}
\end{aligned}$$

$\mathrm{N\bullet}=\text{1-NpCO}\overset{\bullet}{\mathrm{N}}\text{Ph}$ $\mathrm{T\bullet}=p\text{-TlCOO}\bullet$

Scheme 3.

Table 1. Quantum Yields for the Triplet-Sensitized Photolysis of NT (1.0—7.0×10^{-3} M) with 366-nm Light in 1,2-Dichloroethane at 23±2°C

Sensitizer (0.030 M)	E_{T_1}	k_d/k_r	Φ_{lim}			Φ_4[a]	$k_t\tau_T$[b]
	kcal mol^{-1}		$\Phi_{-\mathrm{NT}}$	Φ_2	Φ_3		M^{-1}
BAB	62	0.20	0.83	0.45	0.77	ca. 0	300
DAB	62	3.8	0.21	0.18	0.22	ca. 0	900
DMB	71	0.11	0.90	—[c]	0.14	0.59	2400
BP	69	0.22	0.82	0.57	0.24	0.36	1600
XT	74	0.39	0.72	0.32	0.08	0.28	400
BFB	69	0.11	0.90	ca. 0.7[a,d]	0.12	0.61	1600

a) Quantum yield determined at [NT]=7.0×10^{-3} M. b) Average of the $k_t\tau_T$ values obtained from linear plots of $1/\Phi_{-\mathrm{NT}}$, $1/\Phi_2$, and $1/\Phi_3$ versus 1/[NT]. c) Could not be determined because of overlapping with the HPLC peak of DMB. d) Could not be determined accurately because of overlapping with the HPLC peak of unknown product.

other sensitizers. By applying the steady-state approximation to Scheme 3, we obtain Eqs. 1—3:

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

$$1/\Phi_2 = (1 + k_d/k_r)(1 + k_u{}^{\mathrm{N}}/k_2)(1 + 1/k_t\tau_T[\mathrm{NT}]), \quad (2)$$

and

$$1/\Phi_3 = (1 + k_d/k_r)(1 + (k_4 + k_u{}^{\mathrm{T}})/k_3)(1 + 1/k_t\tau_T[\mathrm{NT}]). \quad (3)$$

We can thus estimate the limiting quantum yields for the disappearance of NT ($\Phi_{-\mathrm{NT,lim}}$) as well as for the appearance of **2** ($\Phi_{2,\mathrm{lim}}$) and **3** ($\Phi_{3,\mathrm{lim}}$), while the intercept/slope ratios of linear double reciprocal plots give the $k_t\tau_T$ values. In addition, the k_d/k_r values are easily obtained from the relationship $1/\Phi_{-\mathrm{NT,lim}}=1+k_d/k_r$. All of these values are collected in Table 1, along with those available from the BP-sensitized photolysis of NT.[3] NT was found to undergo a dark reaction in the presence of BAB, to some extent forming **2** and **3**. The apparent quantum yields were therefore corrected for this dark reaction. The decomposition of any sensitizers employed occurred to a negligible extent during irradiation, while some unknown HPLC peaks, which may be responsible for a slightly poor mass balance of the sensitized photolysis, were detected on the chromatograms. The observation that products **2**—**4** do not undergo a sensitized decomposition allows us to discuss the reaction mechanism based on the quantum yields of these products.

Table 1 shows that BAB- or DAB-sensitized photolysis affords only **2** and **3**, but not **4**, derived from the decarboxylation of the toluoyloxyl radical. Photolysis with other sensitizers, however, produces **4** in substantial quantum yield. These results suggest the participation of two different mechanisms in our sensitized photolyses.

Oxidation Potentials of Triplet Sensitizers. In order to examine the possibility of electron transfer from the triplet-state sensitizer to the ground-state NT, the oxidation potentials ($E_{\mathrm{ox}}{}^{\mathrm{S}}$) of the sensitizers were determined in acetonitrile at room temperature, and are collected in Table 2 along with the reduction potential ($E_{\mathrm{red}}{}^{\mathrm{NT}}$) of NT. From these potentials and the $E_{\mathrm{T}_1}{}^{\mathrm{S}}$ of sensitizers we calculated the free-energy change (ΔG) in the electron transfer by using the simplified Weller equation[8] (Table 2):

Table 2. Redox Potentials of NT ($E_{\mathrm{red}}{}^{\mathrm{NT}}$) and Sensitizers ($E_{\mathrm{ox}}{}^{\mathrm{S}}$) and Free Energy Changes (ΔG) for Electron Transfer in Acetonitrile at Room Temperature

Compound	$E_{\mathrm{red}}{}^{\mathrm{NT}}$	$E_{\mathrm{ox}}{}^{\mathrm{S}}$	ΔG
	V vs. SCE	V vs. SCE	kcal mol^{-1}
NT	−1.87		
BAB		0.87	1.2
DAB		0.97	3.5
DMB		1.82	14.1
BP		1.90	17.9
XT		2.04	16.2
BFB		—[a]	—
TMB		0.32[b]	−32.5[c] −12.5[d]

a) Could not be measured owing to interference from the electrolytic oxidation of trace amounts of water present in acetonitrile. b) Ref. 9. c) Value for electron transfer from the singlet-state TMB. d) Value for electron transfer from the triplet-state TMB.

$$\Delta G(\mathrm{kcal\ mol^{-1}}) = 23.06[E_{\mathrm{ox}}{}^{\mathrm{S}} - E_{\mathrm{red}}{}^{\mathrm{NT}}] - E_{\mathrm{T}_1}{}^{\mathrm{S}}.$$

On the other hand, the excited singlet and triplet states of *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB; E_{S_1}=83; E_{T_1}=63 kcal mol^{-1}) are both powerful electron donors, and easily reduce many electron acceptors.[9] The ΔG value for electron transfer from the TMB excited states to the NT ground state indicates this electron transfer to be thermodynamically a very favorable process. TMB can thus be employed to generate an NT anion radical, and to investigate products arising from this anion radical intermediate. Irradiation of a N_2-purged 1,2-dichloroethane solution of NT (5.0×10^{-3} M) containing TMB (1.0×10^{-2} M) with light of wavelengths longer than 330 nm resulted in the decomposition of NT, giving **2** and **3** in quantitative yields at conversions of up to 20% of the starting NT; no toluene (**4**) was detected in the photolyzate.

Benzil-Sensitized Photolysis. It was previously found that the pyrene-sensitized photolysis of NT proceeds through a singlet-exciplex intermediate in which energy and electron transfers compete with each other, depending on the solvent polarity.[2] In addition to a singlet exciplex, a triplet exciplex has also been demonstrated to play a significant role as an intermediate in photosensitized reactions.[10] We therefore attempted a benzil (BZ; $E_{S_1}=59$; $E_{T_1}=53$ kcal mol^{-1})[4]-sensitized photolysis of NT. Consideration of the relative singlet- and triplet-state energies of BZ and NT reveals that both singlet-singlet and triplet-triplet energy transfers from BZ to NT should be very unlikely. The finding that NT does not quench BZ fluorescence ($\Phi_{isc}=0.92$)[4] in 1,2-dichloroethane at room temperature, but does so regarding BZ phosphorescence in an alcohol glass at 77 K (Fig. 2A), suggests the potential involvement of a triplet-exciplex intermediate in this phosphorescence quenching process. The BZ (0.050 M)-sensitized photolysis of NT (2.5—10.0×10^{-3} M) produced *N*-phenyl-1-naphthalenecarboxamide (**2**, $\Phi_{2,\mathrm{lim}}=0.02$) and *p*-toluic acid (**3**), though the quantum yield for the formation of **3** could not be accurately determined, due to the overlap of its HPLC peak with that of unknown product(s).[11] Additionally, the quantum yield for the disappearance of NT could not be estimated, because of considerably low conversions (<1%) of the starting NT. As shown in Fig. 2B, there exists a linear relation between $1/\Phi_2$ and 1/[NT], suggesting that photolysis proceeds by a mechanism similar to that depicted in Scheme 2.

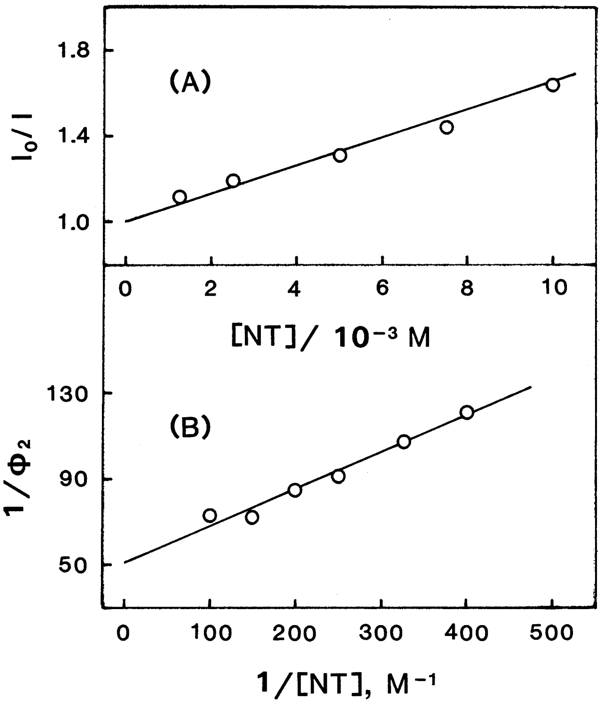


Fig. 2. Stern–Volmer plots (A) for the phosphorescence quenching of BZ (0.050 M) by NT in MeOH–EtOH (1:1 v/v) at 77 K and (B) of $1/\Phi_2$ versus 1/[NT] for the BZ (0.050 M)-sensitized photolysis of NT with 366-nm light under nitrogen in 1,2-dichloroethane. In Fig. 2A I and I_0 are the phosphorescence intensity of BZ with and without NT, respectively. Excitation wavelength=366 nm.

Discussion

Effects of Sensitizer's Structure on the Triplet Sensitization. As already mentioned in the preceding section, the studied sensitizers can be divided into two groups. One includes BAB and DAB, which give only **2** and **3** in comparable quantum yields. The other involves DMB, BP, XT, and BFB, which afford **4** in addition to **2** and **3**. The fact that the former group provides the same products as those derived from the TMB-sensitized photolysis suggests the involvement of an NT anion radical intermediate formed by electron transfer from the triplet sensitizer to NT in the ground state. This anion radical seems to decompose, giving the 1-naphthalenecarboxamidyl radical (N· in Scheme 3) and *p*-methylbenzoate (*p*-$\mathrm{TlCO_2^-}$), which must be oxidized by the sensitizer cation radical forming the *p*-toluoyloxyl radical (T· in Scheme 3) as well as the starting sensitizer, as was already discussed regarding the pyrene-sensitized photolysis in a polar solvent.[2] The toluoyloxyl radical, thus formed, may abstract a hydrogen atom from a solvent molecule much faster than does decarboxylation of this radical.

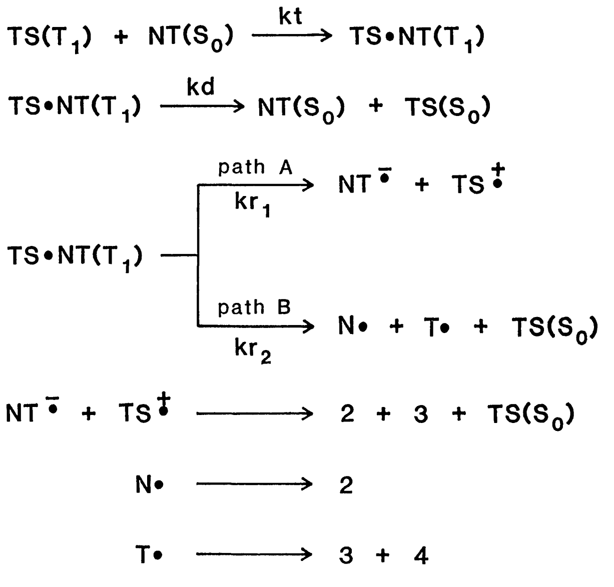
The recent development of laser flash spectroscopic studies of diaroyl peroxides has made it possible to detect directly transient aroyloxyl radicals and to analyze kinetically the reactivity of these radicals.[12a-d,13] Ingold and co-workers have determined the rate constants for hydrogen abstraction from cyclohexane and decarboxylation of the *p*-toluoyloxyl radical to be 2×10^6 M^{-1} s^{-1} and 1×10^6 s^{-1} at ambient temperature, respectively.[13] If we can assume a comparable reactivity of cyclohexane and 1,2-dichloroethane toward hydrogen abstraction, we can then estimate the rate for hydrogen abstraction of this radical from 1,2-dichloroethane as (2×10^6 M^{-1} s^{-1})(12.6 M)=3×10^7 s^{-1} at room temperature. Hence, hydrogen abstraction takes place more than 30 times as fast as does decarboxylation, which must be slower in the more polar 1,2-dichloroethane than in the less polar carbon tetrachloride,[12c] showing the predominant occurrence of hydrogen abstraction as observed for our BAB- or DAB-sensitized reaction in 1,2-dichloroethane.

The excited states of BP and related ketones work as electron acceptors in the presence of amines;[13] they were also recently shown to become good electron donors for diphenyliodonium salts ($\Delta G=-1$—0 kcal mol^{-1}) to initiate radical polymerization.[15] The magnitude of the ΔG for an electron transfer from the BAB (+1.2 kcal mol^{-1}) or the DAB (+3.5 kcal mol^{-1}) triplet to

NT makes this process thermodynamically possible, even in 1,2-dichloroethane, though it is not very favorable.[16] If a triplet-exciplex intermediate with a charge-transfer character is formed between the triplet-state BAB or DAB and the ground-state NT, electron transfer from these triplet-state sensitizers to NT should thus be accelerated to a greater extent than that expected from the magnitude of the ΔG, since the generation of exciplexes increases both the electron-donating and -accepting abilities of molecules constituting these exciplexes.[17] This means that exciplexes with a charge-transfer character make it possible to efficiently cause a somewhat endothermic electron transfer in polar or moderately polar solvents.[18]

On the other hand, the latter group (DMB, BP, XT, and BFB) affords **4**, arising from the decarboxylation of the toluoyloxyl radical, in substantial quantum yields (Table 1). A consideration of the ΔG values (>14 kcal mol^{-1}) for these sensitizers reveals that electron transfer should be a thermodynamically unfavorable process and, thus, that triplet-triplet energy transfer must be mainly responsible for the activation of NT. What is the driving force for accelerating decarboxylation of the toluoyloxyl radical generated from the NT triplet? It is conceivable that NT in the excited triplet state gives the vibrationally excited toluoyloxyl radical, decarboxylation of which should be much more rapid compared with that of the vibrationally relaxed toluoyloxyl radical. The electronic state of this radical (σ or π)[19] in the vibrationally excited state seems to play a role in determining the relative ease with which decarboxylation occurs in competition with hydrogen abstraction. It is beyond the scope of our present study to discuss this subject in detail; we must therefore await further studies.

We assume a triplet-exciplex intermediate shown in Scheme 4 in order to explain the large difference in magnitude of the k_d/k_r between BAB and DAB, as well as the negligible formation of **4** in the sensitized photolysis with these two sensitizers. Since the k_d/k_r value can be used as a measure of the reactivity of the assumed exciplex intermediate, the large difference in this value between BAB and DAB may be explained in terms of the much greater reactivity of the BAB-derived exciplex than the DAB-derived one. On the other hand, an inspection of the E_{T_1} and ΔG values for BAB and DAB suggests that a triplet-triplet energy transfer could compete with an electron transfer to produce some amounts of **4**. Thus, the negligible formation of **4** forces us to conclude that electron transfer (path A in Scheme 4) takes place exclusively in the exciplex, giving the NT anion and sensitizer cation radicals from which only **2** and **3** are obtained as final products, along with the starting sensitizer. As already suggested, the involvement of a triplet exciplex in the course of the sensitization process should result in a remarkable acceleration of electron transfer.



Scheme 4.

It is reasonable to propose that the sensitized photolyses with DMB, BP, XT, and BFB also proceed by way of triplet-exciplex intermediates (path B in Scheme 4). If so, the contribution of electron transfer (path A in Scheme 4) to the overall activation process of NT may not be neglected, even though the triplet-exciplex reactivity (k_d/k_r=0.11—0.39) is not so much different among these sensitizers. Singer and co-workers have reported that the triplet states of BP and its derivatives in the presence of substituted benzenes are deactivated via the formation of triplet exciplexes with a charge-transfer character.[20] Their result that triplet benzophenones have a marked tendency to form exciplexes during bimolecular quenching processes provides support for our interpretation of the sensitized photolysis of NT. The magnitude of the $k_t\tau_T$, which may be regarded as a measure of exciplex-formation efficiency, indicates only a modest variation (factor of about 8) between BAB and DMB. In addition, there is no good correlation between this efficiency and the E_{T_1} or E_{ox}^S of the sensitizers.

The finding that BZ brings about a decomposition of NT, which quenches the BZ phosphorescence, but not the BZ fluorescence, presents strong evidence in support of the participation of a triplet-exciplex intermediate in our sensitized reactions. Because the triplet excitation energy of the exciplex BZ·NT(T_1) must be lower than that of BZ (E_{T_1}=53 kcal mol^{-1}),[4] which is comparable to a N–O bond dissociation energy of about 53 kcal mol^{-1},[21] deactivation of this exciplex giving the ground-state NT and BZ is very likely to occur in preference to the sensitized N–O bond cleavage, which eventually affords fragmentation products **2** and **3**. The predominant occurrence of this deactivation may be responsible for the fairly low efficiency of the BZ-sensitized decomposition of NT.

Experimental

General Methods. The same HPLC instrument and column as mentioned before[2,3] were employed to quantitatively analyze the products arising from the sensitized photolysis (detection wavelength=230 nm; mobile phase, $CH_3CN : H_2O = 62 : 38$ v/v). The GLC analysis of toluene, one of the products, was carried out on a Shimadzu Model GC-8AP gas chromatography apparatus (FID, N_2 as carrier) using a 3.0×3000-mm glass column packed with 10% Silicone SE-30 on Uniport B (60/80 mesh, Gasukuro Kogyo). The phosphorescence spectra of sensitizers with and without quencher were measured at 77 K with a Shimadzu Model RF-500 spectrofluorimeter equipped with a cylindrical rotating sector.

Materials and Solvents. *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT, **1**), *N*-phenyl-1-naphthalenecarboxamide (**2**), *p*-toluic acid (**3**), and toluene (**4**) were the same as those used in our previous study.[2,3] 4,4′-bis(dimethylamino)-benzophenone (BAB), 4-dimethylaminobezophenone (DAB), 4,4′-dimethoxybenzophenone (DMB), xanthone (XT), 3,3′-bis(trifluoromethyl)benzophenone (BFB), benzil (BZ), and *N*,*N*,*N*′,*N*′-tetramethylbenzidine (TMB) were all recrystallized from ethanol at least twice. 1,2-Dichloroethane was of spectroscopic grade and was used as supplied. Methanol and ethanol were purified by fractional distillation from potassium hydroxide. Distilled acetonitrile and water were employed as a mobile phase for the HPLC analysis.

Quantum Yields and Redox Potentials. The quantum yields were determined by means of potassium trioxalatoferrate(III) actinometry,[6] and are the average of more than five determinations. The combination of Corning 0-52, Corning 7-37, and Toshiba IRA-25S glass filters made it possible to isolate the 366-nm light from a 450W high-pressure Hg lamp. The light of wavelengths longer than 330 nm was selected with Corning 4-70 and Toshiba IRA-25S glass filters, and irradiated for the TMB-sensitized photolysis of NT. A quantitative HPLC or GLC analysis of the photoproducts **2**—**4** was made by utilizing linear calibration curves for each product, which were obtained under the same analytical conditions.

The half-wave redox potentials of NT, BAB, DAB, DMB, XT, BFB, and benzophenone were measured in acetonitrile by cyclic voltammetry on a Hokuto Model HAB-151 potentiostat/galvanostat connected to a Yokokawa XY recorder. The electrode system comprised a platinum working electrode, a platinum auxiliary electrode, and a saturated calomel reference electrode (SCE). Solutions containing the substrates at 10^{-3} M were prepared in dry degassed acetonitrile with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. The scanning voltage was 50 mV s^{-1} and the current 5 μA cm^{-1}.

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5) It is evident from a comparison of the UV spectra of sensitizers with that of NT that the E_{S_1} of NT is much higher than that of the sensitizers. DAB shows a shoulder around 461 nm in its phosphorescence spectrum in 1,2-dichloroethane at 77 K. We assumed this shoulder to be the 0–0 band from which the E_{T_1} value was evaluated. On the other hand, both DMB and BFB give well defined 0–0 bands at 408 and 414 nm, respectively, the position of which allows us to calculate the E_{T_1} values of these sensitizers. The E_{T_1} for DMB (70 kcal mol^{-1}) is consistent with the literature value[4] of 71 kcal mol^{-1} within experimental error.

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11) The BZ-sensitized photolysis of NT was expected to give **4** along with **2** and **3**. But attempts to detect **4** by GLC were unsuccessful. It is likely that some of the tolyl and toluoyloxyl radicals were trapped by BZ, in competition with their hydrogen abstraction, to yield unknown products. The result of the BZ-sensitized photolysis of dibenzoyl peroxide under the same irradiation conditions as above supports this possibility. In addition, significantly low conversions of the starting NT (<1%) make the GLC detection of **4** very difficult.

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