From consideration of a molecular model for the trans species we conclude that D_4 is the highest symmetry possible. One can therefore argue for the appropriateness of a simple spin–orbit-coupling model to rationalize intensities. The states which mix under spin–orbit coupling are not easy to identify, however. Conceivably charge-transfer or very high-energy excited states are involved in the mechanism.

Kinetics and Mechanism of the Photocyclization of Diphenylamines. I. The Photochemical Primary Processes of Diphenylamines

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Abstract: A kinetic study of the direct, sensitized, and quenched photocyclization of diphenylamines in solution has been carried out. The quantum yields for carbazole formation have been measured in various solvents at 20° spectrophotometrically. On the basis of triplet–triplet energy transfer studied through triplet quenching by the acceptors piperylene and biphenyl and triplet sensitization by the aromatic ketone donors propiophenone, acetophenone, benzaldehyde, etc., photochemical evidence has been presented that photocyclization of diphenylamines occurs through the lowest triplet states of diphenylamines which lead to the formation of an intermediate. The quenching of the quantum yields for product formation by the biacetyl acceptor involved singlet–singlet and triplet–triplet energy transfers. The excess energy requirements, ΔE_T, in these triplet energy transfers were also observed. By means of the steady-state approximation, the photochemical primary processes of *N*-methyldiphenylamine have been revealed in some detail.

Recently, the photocyclizations of *cis*-stilbenes, diphenylamines, and similar organic compounds have been extensively studied. It is well known that the reversible cis–trans photoisomerization of stilbene is accompanied by a photocyclization.[2–8] Mallory and coworkers[9–11] have proposed that the photocyclization of *cis*-stilbene proceeds *via* the 4a,4b-dihydrophenanthrene intermediate whose two central hydrogens are in the trans configuration. Moore, *et al.*,[12] have shown that the intermediate, which has the first absorption band $\lambda_{max} \sim 450$ nm,[13] is transformed into phenanthrene by its oxidation in the presence of oxygen, and back into the ground state of *cis*-stilbene by its thermal decomposition in the degassed solution. Hammond and coworkers[14] have presented photochemical evidence that the intermediate formation occurs from the excited singlet state of *cis*-stilbene. Fischer, *et al.*,[15,16] have reported that the processes of the ring closure and the ring opening in the photocyclization of *cis*-stilbene represent the simplest photochromic system, such as those of spiropyrans and bianthrone-like compounds.[17–20]

The photocyclization of diphenylamines has been reported by several workers in preliminary papers. It was noted by Parker and Barnes that carbazole is a photoproduct of diphenylamine in solution.[21] Bowen and Eland[22] have reported that the photocyclization of diphenylamine involves a different state from the original excited state (but not the triplet, because there is no inhibition by butadiene) and further have found mass spectrometrically that the amount of molecular hydrogen produced is comparable to that of carbazole formed. These results would make us distinguish the status of photocyclization of diphenylamine from that of *cis*-stilbene. However, Linschitz, *et al.*,[23,24] have proposed that, on the basis of flash-excitation studies on N-substituted diphenylamines, the photocyclization of diphenylamines occurs through the triplet state, and the triplet transient converts to another transient, having an

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absorption maximum at 610 nm which is the intermediate (a closed-ring, polar structure) in the reaction. Similar results have been reported by Grellmann, *et al.*[25] Hinohara[26] has reported the possibility that the ring closure of diphenylamine occurs from the triplet state, but those of *N*-methyl- and *N*-phenyldiphenylamines take place from the excited singlet state or the triplet state in short lifetime. There are still some ambiguities concerning the reactive state and the intermediate in the photocyclization of diphenylamines. As for the reaction intermediate (11,12-dihydrocarbazole, hereafter M), whose two central hydrogens are in the cis configuration as has been suggested by Linschitz, *et al.*,[24] one of the papers from our laboratory has reported that the decay rate constants of the "610" transient formed by the flash excitation of diphenylamines apparently differ from the rate constants of product formation (corresponding carbazoles).[27] Furthermore, it seems most reasonable to conclude that the 610 transient cannot be assigned to the intermediate for carbazole formation from theoretical considerations by the SCF–MO–CI approximation method.[28] From these points of view, more extensive research should be performed. The present paper will report the photochemical primary processes, especially the reactive state in the photocyclization of diphenylamines.

Experimental Section

Materials. *N*-Methyldiphenylamine (N-MeDA) and triphenylamine (TPA) were Tokyo Kasei Co. G. R. grade products. Diphenylamine (DA) was a Takeda Yakuhin Co. reagent grade product, and was purified by repeated recrystallizations from the mixture of ethanol and water. Cyclohexane, methylcyclohexane, and ethanol used as the solvents were Tokyo Kasei Co. G. R. grade products, while cyclohexane and methylcyclohexane were purified by passing them through silica gel columns and by distillation. Benzene, which was used as a solvent in the photosensitization by aromatic ketones, was a Wako Pure Chemicals Industry reagent washed with concentrated sulfuric acid, dried over calcium chloride, and purified by distillation. *n*-Hexane was a Wako Pure Chemicals Industry reagent, purified in the same way as was benzene, passed through a silica gel column, and fractionally separated by distillation. Propiophenone, acetophenone, benzaldehyde, benzophenone, biphenyl, piperylene, and biacetyl were G. R. grade products of Tokyo Kasei Co. and were used as sensitizers or quenchers without further purification.

Light Source and Actinometry. A low-pressure mercury resonance lamp was used as the 2537-Å radiation source with a Vycor glass filter, while a xenon lamp (a Hitachi 150-W xenon lamp) with a diffraction grating admits only a narrow band of light wavelengths (±70 Å).

Actinometry was carried out using a ferric oxalate solution.[29]

Analysis. The amounts of photoproducts (carbazoles) were determined spectrophotometrically. Ultraviolet absorption spectra were taken with Hitachi 139 and EPS-2 spectrophotometers. Fluorescence and phosphorescence spectra were measured by a Hitachi MPF-2A fluorescence spectrophotometer.

Degassed System. The solution was thoroughly degassed on a high-vacuum line by the freeze–pump–thaw technique.

Results

(i) Absorption and Emission Spectra. In order to study the behavior of diphenylamines in electronically excited states, the absorption and emission spectra were measured. Figure 1 shows absorption and emission spectra of *N*-methyldiphenylamine (N-MeDA). Similar spectra of diphenylamine (DA) and triphenylamine (TPA) were measured. The large oscillator strengths, $f_{S_1 \leftarrow S_0}$, of diphenylamines (see below) are associated with the extensive charge-transfer character of the $S_1(\pi\pi^*) \leftarrow S_0$ transition, as has been reported by Lamola and Hammond.[30] The fluorescence quantum yields of derivatives of diphenylamine in degassed and aerated cyclohexane solutions[31] at 20° were approximately obtained by comparison with the relative fluorescence intensity of diphenylamine whose fluorescence quantum yield is 0.05.[22] Dissolved oxygen quenched slightly the fluorescence of diphenylamines, as has been reported by Bowen and Eland.[22] Each ratio of the fluorescence intensities of diphenylamines in the aerated cyclohexane against those in the degassed was about 0.9.

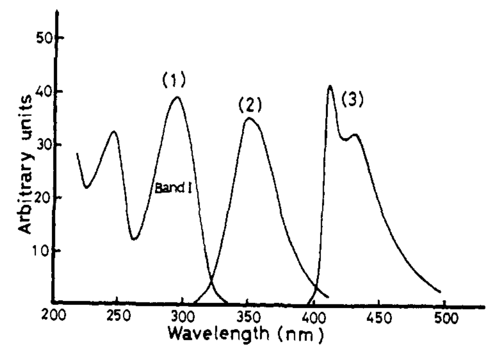

Figure 1. Absorption and emission spectra of N-MeDA: (1) absorption spectrum in cyclohexane at 20°, (2) fluorescence spectrum by the excitation of the 2537-Å light in cyclohexane at 20°, (3) phosphorescence spectrum by the excitation of the 2537-Å light in methylcyclohexane at 77°K.

Lamola and Hammond[30] have also reported values of the intersystem crossing probabilities for the $T_1 \leftarrow S_1$ process, ϕ_{ic}, of DA and TPA by means of the triplet-photosensitized cis–trans isomerization of selected olefins. The value of ϕ_{ic} of N-MeDA was obtained kinetically as will be discussed later. Several quantities including ϕ_{ic} for the electronically excited states of diphenylamines are summarized in Table I.

(ii) Quantum Yields for Product Formation and Decrease Quantum Yields of Diphenylamines. Spectral change of the cyclohexane solution of N-MeDA during photocyclization at 2537 Å was the same as that reported by Linschitz, *et al.*[23] The spectral changes of DA and TPA upon uv irradiation were similar to that of N-MeDA. These spectral changes indicated that the photoproducts are the corresponding carbazoles.[23] Quantum yields for carbazole formation and decrease quantum yields of diphenylamines were measured by means of spectrophotometry.[32]

Quantum yields for product formation from N-MeDA at 20° were measured under various conditions; the results are shown in Figure 2.

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[25] K. H. Grellmann, W. Kuhnle, and E. Tauer, *Ber. Bunsenges. Phys. Chem.*, 72, 321 (1968).

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[30] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[31] The excitation wavelength used in these measurements was 2537-Å light, and the concentrations of the solutions were adjusted so that the value of the optical density was 0.600 at 2537 Å.

[32] Molecular extinction coefficients, ϵ, for diphenylamines (original substances) are given in Table I; for carbazoles (photoproducts) in cyclohexane, they are as follows [λ, nm ($\epsilon \times 10^4$ l. mol^{-1} cm^{-1})]: *N*-methylcarbazole (N-MeCA), 343 (0.39); *N*-phenylcarbazole (N-PhCA), 339 (0.51); carbazole (CA), 331 (0.42).

Table I. Data for Several Measurements on the Electronically Excited States of Diphenylamines

Diphenylamines	Absorption band I λ_{max}, nm	$\epsilon \times 10^{-4}$ l. mol^{-1} cm^{-1}	$f_{S_1 \leftarrow S_0}$[a]	Q_{F_0}[b]	Q_F[b]	E_{S_1},[c] cm^{-1}	E_{T_1},[d] cm^{-1}	ϕ_{ic}
N-MeDA	292	1.25	0.259	0.042	0.037	31570	24600	0.89
TPA	300	2.37	0.5[e] 0.48	0.072	0.065	29140	24500[g] 24500	0.88[e]
DA	282	1.74	0.4[e] 0.39	0.05[f]	0.045	32790	25200[g] 25200	0.38[e]

[a] Estimated from absorption spectra using $f_{S_1 \leftarrow S_0} = (4.32 \times 10^{-9})\int \epsilon d\bar{\nu}$. [b] The fluorescence quantum yields, Q_{F_0} and Q_F, are those for degassed and aerated cyclohexane solutions, respectively. [c] $E_{S_1} \approx (\bar{\nu}_{max} + \bar{\nu}_F)/2$, where $\bar{\nu}_{max}$ is the wave number at λ_{max} of absorption band I and $\bar{\nu}_F$ is the wave number at λ_{max} of the fluorescence spectrum. [d] E_{T_1} obtained from phosphorescence spectra. [e] Data of Lamola and Hammond.[30] [f] Data of Bowen and Eland.[22] [g] Data of G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2100 (1944).

Quantum yields for product formation in cyclohexane at 2537 Å and 20° did not change with variation in the irradiation time, the concentration of N-MeDA (5 × 10^{-5}–3 × 10^{-3} *M*), or the light intensity (2 × 10^{14}–8 × 10^{15} photons sec^{-1}). The effect of oxygen dissolved in the solution was very apparent: the quantum yields for N-MeCA formation in aerated and degassed cyclohexane at 2537 Å and 20° were 0.67 and 0.06, respectively. Dependence of the quantum yields on excitation wavelength was absent, as is shown in Figure 2c. Quantum yields for carbazole formation from diphenylamines, Φ, and the decrease quantum yields of diphenylamines, Φ_{dec}, are listed in Table II.

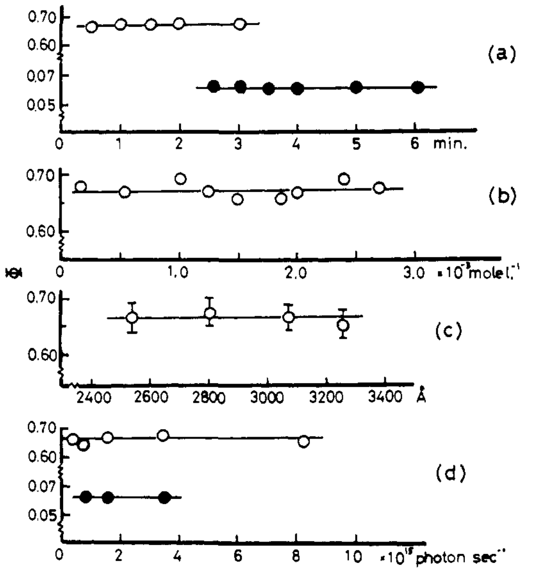

Figure 2. Dependence of quantum yields for N-MeDA in cyclohexane solutions at 20°: (a) on irradiation time with initial concentration of 1.2 × 10^{-3} *M;* (b) on concentration; (c) on excitation wavelength; (d) on light intensity; ○, in aerated cyclohexane; ●, in degassed cyclohexane.

(iii) Photosensitization and Quenching in the Photocyclization of Diphenylamines. Photosensitization and quenching during the photocyclization of diphenylamines have been studied quantitatively in cyclohexane or benzene at 20° through measurements of the quantum yields for carbazole formation and of both fluorescence and phosphorescence intensities.

Piperylene ($E_T \cong$ 20000 cm^{-1}),[33] biphenyl (E_T = 22800 cm^{-1}),[34] and biacetyl (E_T = 19700 cm^{-1})[34] were used as triplet quenchers of diphenylamines. Biacetyl is also expected to act as a singlet quencher because the lowest excited transition energies, E_{S_1}, in diphenylamines are larger than that in biacetyl (E_{S_1} = 22,400 cm^{-1}).[35] The excitation wavelengths (piperylene, 3000 ± 70; biphenyl, 3300 ± 50; and biacetyl, 2537 and 3000 ± 70 Å) were selected so that not the quenchers but the diphenylamines (energy donors) absorbed the irradiation light. However, biacetyl slightly absorbs light at 2537 or 3000 Å. The data in the case of biacetyl were corrected by the Beer–Lambert absorption law.

Table II. Quantum Yields for Product Formations, Φ, and Decrease Quantum Yields of Diphenylamines, Φ_{dec}, at 2537 Å and 20° [c]

Diphenyl-amines	Solvent	Φ	Φ_{dec}
N-MeDA	CH aerated	0.67	0.67
	degassed	0.06	0.06
	MeCH aerated	0.67	0.67
	degassed	0.06	
	n-H aerated	0.62	0.62
	degassed	0.06	
	degassed	0.01[a]	
	[O$_2$] 6 × 10^{-4} *M*	0.30 (Φ_{max})[a]	
	EtOH aerated	0.57	
TPA	CH aerated	0.12	0.12
	degassed	0.003	
DA	CH aerated	0.06	0.07
	degassed	0.10	
	MeCH aerated	0.06	
	n-H degassed	0.05[a]	
	degassed	0.10[b]	
	[O$_2$] 2 × 10^{-5} *M*	0.08[a]	
	MeOH degassed	0.10[b]	

[a] Data of Linschitz, *et al.*[24] [b] Data of Bowen and Eland.[22] [c] CH, cyclohexane; MeCH, methylcyclohexane; *n*-H, *n*-hexane; EtOH, ethanol; MeOH, methanol.

The quenching of the N-MeDA donor (E_{T_1} = 24,600 cm^{-1}) by the piperylene acceptor was performed using fixed concentrations of N-MeDA (3.5 × 10^{-4} and 2.1 × 10^{-3} *M*) and varying the piperylene concentration over approximately a tenfold range. These quenching data are presented in Figure 3, where Φ_0/Φ, in aerated cyclohexane, or $(\Phi_0/\Phi)_0$, in degassed cyclohexane, is plotted *vs.* the piperylene concentration. The quantities Φ and Φ_0 are the quantum yields for N-MeCA formation with and without the piperylene quencher, respectively. The phosphorescence intensity of N-MeDA in MP

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(33) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2396 (1961).

(34) G. N. Lewis and M. Kasha, *ibid.*, **66**, 2100 (1944).

(35) The value of E_{S_1} is obtained from the absorption spectrum of a cyclohexane solution of biacetyl.

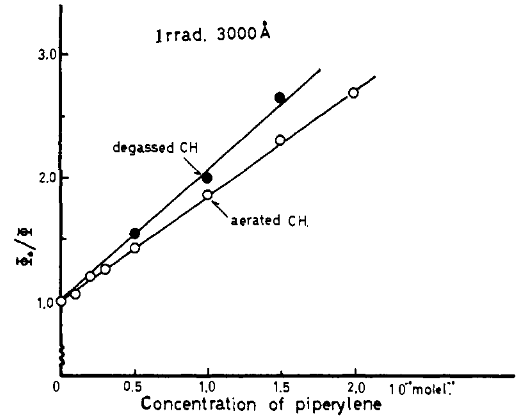

Figure 3. Quenching plot of the N-MeDA donor by the piperylene acceptor in cyclohexane at 20°.

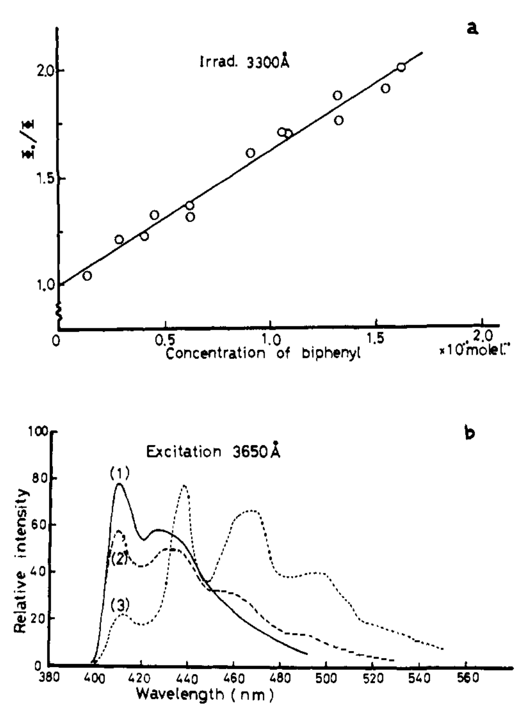

Figure 4. (a) Quenching plot of the N-MeDA donor by the biphenyl acceptor in cyclohexane at 20°. (b) Sensitized phosphorescence of the biphenyl acceptor by the N-MeDA donor in methylcyclohexane at 3300 Å and 77°K: (1) N-MeDA 1.4×10^{-3} M, (2) N-MeDA 1.4×10^{-3} M + biphenyl 1.0×10^{-2} M, (3) N-MeDA 1.4×10^{-3} M + biphenyl 5.1×10^{-2} M.

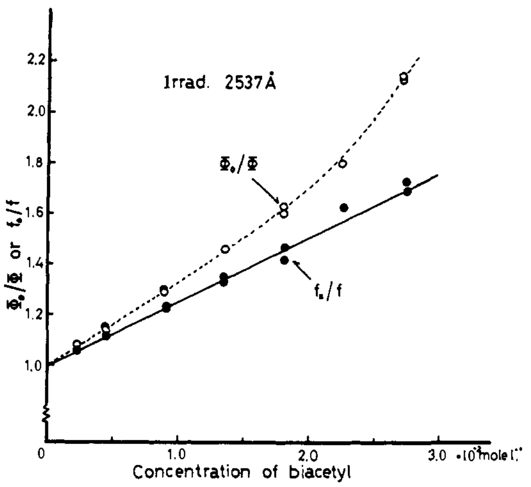

Figure 5. Quenching plot of the N-MeDA donor by the biacetyl acceptor in cyclohexane at 2537 Å and 20°.

glass[36] at 77°K was reduced in the presence of piperylene quencher. It was also confirmed that the addition of piperylene did not affect the fluorescence intensity of N-MeDA in cyclohexane at 20°.

Quenching experiments for N-MeDA (donor) by biphenyl (acceptor) were carried out and the result is shown in Figure 4a, where Φ_0/Φ is plotted *vs.* the biphenyl concentration. The quantities Φ and Φ_0 are the quantum yields for product formation in aerated cyclohexane with and without the biphenyl quencher, respectively. No dependence of the fluorescence intensity of N-MeDA on the addition of biphenyl was observed. When the concentration of the biphenyl acceptor was increased, the phosphorescence intensity of N-MeDA in MP glass at 77°K was reduced, and the sensitized phosphorescence of the biphenyl acceptor by the N-MeDA donor was observed as is shown in Figure 4b.[37] The quenching of the N-MeDA donor by the biacetyl acceptor is presented in Figure 5, where Φ_0/Φ or f_0/f is plotted as a function of biacetyl concentration. The quantities Φ and Φ_0 are the quantum yields for N-MeCA formation in aerated cyclohexane with and without the biacetyl quencher, respectively. The quantities f and f_0 are the fluorescence intensities in aerated cyclohexane with and without the biacetyl quencher, respectively. The quenching constant, k_Q, obtained from the Stern–Volmer plot (Φ_0/Φ *vs.* the biacetyl concentration) was larger than that of f_0/f. The plots of Φ_0/Φ *vs.* the biacetyl concentration gradually deviated from a straight line as the biacetyl concentration was increased.

The quenching of the TPA donor by the acceptors was also carried out, except in the degassed system, since the quantum yield for the *N*-phenylcarbazole formation in a degassed solution was very low as is shown in Table II. Unfortunately, the quenchings of the diphenylamine donor (E_{T_1} = 25200 cm^{-1})[34] by the quenchers described above, even in a degassed solution, were performed unsuccessfully because the absorption band of carbazole (331 nm) produced was masked by the tail of a broad band which appeared during the quenching process.[38] All of the data, except for cases in which the biacetyl acceptor was used, give a single straight line for the Stern–Volmer plot. The quenching constants, k_Q, are the slopes of the Stern–Volmer diagrams for diphenylamines. A summary of experimental conditions and the results for the quenching during the photocyclization of diphenylamines are given in Table III.

Propiophenone (E_T = 26,150 cm^{-1}),[39] acetophenone (E_T = 25,750 cm^{-1}),[39] benzaldehyde (E_T = 25,200 cm^{-1}),[34,39] and benzophenone (E_T = 24,000 cm^{-1})[39] were used as the triplet sensitizers of diphenylamines. The excitation wavelength used in these photosensi-

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(36) MP means a 2:1 mixture of methylcyclohexane and isopentane.

(37) When the concentration of biphenyl was increased to the extent of 10^{-2} M, the transparency of MP glass was considerably decreased.

(38) These phenomena were also observed in the photosensitization of diphenylamine by aromatic ketones. It seems that diphenylamine photosensitization is accompanied by a photochemical side reaction to produce unstable species which react with the added quencher.

(39) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, 86, 4537 (1964).

Table III. Results of the Quenching Experiments for Diphenylamines by Several Quenchers at 20°

Donor	Acceptor	Solvent	[Donor] × 10^3 *M*	Excitation wavelength, Å	ΔE_T,[a] cm^{-1}	Quenching constant K_Q^{Σ} [b]	K_Q^T	K_Q^S
N-MeDA	Piperylene	Aerated CH	0.35, 2.1	3000 ± 70	4550	8.4	8.4	0
		Degassed CH	0.35	3000 ± 70	4550	10.6	10.6	0
	Biphenyl	Aerated CH	2.5	3300 ± 50	1750	6.5	6.5	0
	Biacetyl	Aerated CH	0.95	2537	4850	33	8.0	25[c]
TPA	Piperylene	Aerated CH	0.25, 1.4	3000 ± 70	4500	53	53	0
	Biphenyl	Aerated CH	1.4	3300 ± 50	1700	33	33	0
	Biacetyl	Aerated CH	0.10	3000 ± 70		21	0	21[c]
DA	Biacetyl	Aerated CH	0.13	2537		21	0	21[c]

[a] Energy difference between the lowest triplet levels of donor and acceptor. [b] $K_Q^{\Sigma} = K_Q^T + K_Q^S$; K_Q^T and K_Q^S denote the quenching constants for triplet and singlet states of diphenylamines, respectively. [c] Obtained from the data of fluorescence quenching.

tizations was 3650 ± 50 Å, which was absorbed only by the sensitizers. Benzene was used as a solvent, since the decrease quantum yield of benzophenone in benzene is nearly zero, as has been reported by Beckett and Porter.[40] Indeed, the disappearance of aromatic ketones by irradiation with 3650-Å light was scarcely observed.

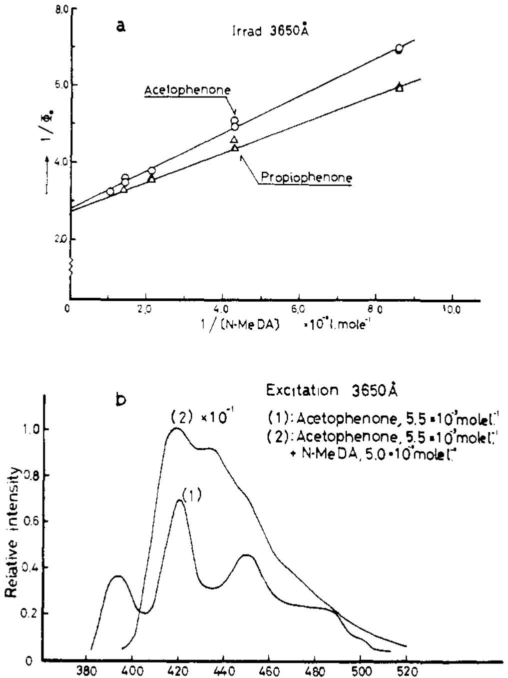

Figure 6. (a) Photosensitization of the N-MeDA acceptor by the propiophenone and acetophenone donors in benzene at 3650 Å and 20°. (b) Sensitized phosphorescence of the N-MeDA acceptor by the acetophenone donor in methylcyclohexane at 3650 Å and 77°K.

The absorption band of N-MeCA (photosensitized product) appeared at 346 nm (ϵ 3900) in benzene. The 346-nm band overlapped with the absorption spectra of the sensitizers. Therefore, the concentrations of the sensitizers were adjusted so that their optical densities at 346 nm were 0.6–0.9.

The sensitizations of the N-MeDA acceptor by the propiophenone and acetophenone donors are presented in Figure 6a, where $1/\Phi_S$ is plotted against the reciprocal of N-MeDA concentration. The quantity Φ_S is the quantum yield for the N-MeCA formation by triplet photosensitization in the aerated benzene solution. The rate of triplet energy transfer from benzaldehyde to N-MeDA was very low compared with those in the cases of propiophenone and acetophenone. Photosensitization of N-MeDA by benzophenone (E_T = 24,600 cm^{-1}) was scarce. The sensitized phosphorescence of N-MeDA by the acetophenone donor was observed as is shown in Figure 6b. The sensitized phosphorescence was also measured in the case of the propiophenone donor.

The sensitization of TPA by the propiophenone and the acetophenone donors has been measured, and similar results to those of N-MeDA were obtained. Unfortunately, the sensitization of diphenylamine could not be measured for the same reasons as those in the triplet quenching described above. All of the sensitization data can be represented by a single straight line. The constants, α, are the slopes of $1/\Phi_S$ *vs.* the reciprocal of N-MeDA concentration. A summary of the results for the triplet sensitization during the photocyclization of diphenylamines is shown in Table IV.

Table IV. Results of the Photosensitization of Diphenylamines by Some Triplet Sensitizers in Aerated Benzene at 3650 Å and at 20°

Acceptor	Donor	[Donor] × 10^2 *M*	ΔE_T,[a] cm^{-1}	$\alpha \times 10^3$ *M*$^{-1}$
N-MeDA	Propiophenone	5.2	1550	3.9
	Acetophenone	2.2	1150	5.5
	Benzaldehyde	8.3	600	~200[b]
	Benzophenone	1.4	−600	
TPA	Propiophenone	5.2	1600	6.0
	Acetophenone	2.2	1250	6.5

[a] Energy difference between the lowest triplet energy levels of donor and acceptor. [b] The approximate value.

Discussion

The results of the triplet photosensitization and quenching of diphenylamines, as are described above, support "the triplet mechanism" proposed by Linschitz, *et al.*[23,24] The photocyclization of diphenylamines originates from the lowest triplet state, which is formed by the process of $^3D_1 \leftarrow {}^3D_n \leftarrow {}^1D_n$ or $^3D_1 \leftarrow {}^1D_1 \leftarrow {}^1D_n$, and subsequently the triplet transient leads to the formation of an intermediate, M (which is different from the 610 transient),[27,28] competing with the triplet deactivation process, where $^3D_1$, ^3D_n, $^1D_1$, and ^1D_n are the lowest triplet state, the excited triplet state, the lowest excited singlet state, and the upper excited singlet

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(40) A. Beckett and G. Porter, *Trans. Faraday Soc.*, 59, 2038 (1963). The C–H (sp^2) bond energy in the benzene molecule is quite high (~103 kcal/mol), and the energy is presumably high enough to prevent hydrogen-atom abstraction by the triplet aromatic ketones.

state of diphenylamines, respectively. Then M converts to the corresponding carbazoles with and without oxygen or to the ground state of the original substance.

The results of Figures 3 and 4 and of Table III can be accounted for by the following mechanism, which is simplified in the processes of internal conversion and intersystem crossing

$$D + h\nu \longrightarrow {}^1D \tag{0}$$

$${}^1D \longrightarrow D \tag{1}$$

$${}^1D \longrightarrow D + h\nu_{D_F} \tag{2}$$

$${}^1D \longrightarrow {}^3D \tag{3}$$

$${}^1D + O_2 \longrightarrow D + O_2 \tag{4}$$

$${}^3D \longrightarrow D \tag{5}$$

$${}^3D \longrightarrow D + h\nu_{D_P} \tag{6}$$

$${}^3D \longrightarrow M \tag{7}$$

$${}^3D + O_2 \longrightarrow D + O_2 \tag{8}$$

$${}^3D + Q \longrightarrow D + {}^3Q \tag{8q}$$

$$M \longrightarrow D \tag{9}$$

$$M \longrightarrow C + (H_2) \tag{10}$$[22]

$$M + O_2 \longrightarrow C + (HO_2,\ H_2O_2) \tag{11}$$

where D is the ground state of diphenylamines, Q and ^{3}Q are the ground state and the triplet state of the quenchers, respectively, C is the ground state of the photoproduct (CA), and F and P denote fluorescence and phosphorescence, respectively. In process 11, H_2O_2 produced during photocyclization with O_2 was identified by iodometry. Then, using a steady-state approximation, the following equation is obtained.

$$\Phi = \frac{k_3}{k_1 + k_2 + k_3 + k_4[O_2]} \times \frac{k_7}{k_5 + k_6 + k_7 + k_8[O_2] + k_{8q}[Q]} \times \frac{k_{10} + k_{11}[O_2]}{k_9 + k_{10} + k_{11}[O_2]} \tag{12}$$

The ratios of the quantum yields for the product formation in the absence and the presence of quencher, Φ_0/Φ, are therefore

$$\Phi_0/\Phi = 1 + k_{8q}{}^3\tau[Q] = 1 + K_Q{}^T[Q] \tag{13}$$

for the aerated solution, and

$$(\Phi_0/\Phi)_0 = 1 + k_{8q}{}^3\tau_0[Q] = 1 + K_{Q_0}{}^T[Q] \tag{13$'$}$$

for the degassed solution, where $^3\tau$ and $^3\tau_0$ are the triplet lifetimes of the donors (diphenylamines) in aerated and degassed cyclohexane, respectively, $K_Q{}^T = k_{8q}{}^3\tau$, and $K_{Q_0}{}^T = k_{8q}{}^3\tau_0$. The quenching plot Φ_0/Φ *vs.* [Q] should be independent of donor concentration.[41,42] Table III also shows this to be the case, and from the slopes of straight lines in Figure 3, $K_Q{}^T = 8.4$ and $K_{Q_0}{}^T = 10.6$ l./mol. Thus, the ratio $K_{Q_0}{}^T/K_Q{}^T$ is obtained

$$\begin{aligned} K_{Q_0}{}^T/K_Q{}^T &= 1.26 \\ &= {}^3\tau_0/{}^3\tau = 1 + {}^3\tau_0 k_8[O_2] \end{aligned} \tag{14}$$

where $[O_2] = 2.3 \times 10^{-3}$ *M*.[43] If the rate constant k_8 is the diffusion-controlled rate constant, k_D, which is obtained from the modified Debye equation,[44] the triplet lifetime of N-MeDA in degassed cyclohexane and in the absence of quencher at 20°, $^3\tau_0$, is evaluated from eq 14.

$$\begin{aligned} {}^3\tau_0 &= 1.71 \times 10^{-8}\ \text{sec} \\ k_5 + k_6 + k_7 &= 5.85 \times 10^7\ \text{sec}^{-1} \end{aligned} \tag{15}$$

From eq 14, the triplet lifetime of N-MeDA in aerated cyclohexane at 20° is also obtained

$${}^3\tau = \frac{1}{k_5 + k_6 + k_7 + k_8[O_2]} = 1.36 \times 10^{-8}\ \text{sec} \tag{16}$$

where $k_8[O_2] = 1.52 \times 10^7$ sec^{-1}, and therefore $k_5 + k_6 + k_7 + k_8[O_2] = 7.37 \times 10^7$ sec^{-1}. The triplet lifetime of TPA seems to be longer by about a factor of 6 than that of N-MeDA, considering the $K_Q{}^T$ of TPA, as is shown in Table III.

The direct lifetime measurements for the excited singlet states of aromatic compounds have been reported by Dubois, *et al.*[41,45,46] They have shown that, under certain conditions, electronic energy transfer from the excited singlet state of a donor resulting in the excitation of a singlet level of an acceptor molecule is diffusion controlled, and in particular, with an acceptor having a low extinction coefficient, such as biacetyl, the long-range singlet–singlet energy transfer due to dipole–dipole interaction of the transferring species may be avoided. Therefore, the lifetimes of the lowest excited singlet states of diphenylamines can be estimated from the method of Dubois, *et al.*

The fluorescence quenching of the N-MeDA donor by the biacetyl acceptor (see Figure 5 and Table III) shows the singlet–singlet energy transfer, which may be diffusion controlled. The plot of Φ_0/Φ *vs.* the concentration of biacetyl in Figure 5 shows that singlet–singlet energy transfer from the excited singlet state of N-MeDA to biacetyl occurs together with triplet–triplet energy transfer from the triplet N-MeDA to biacetyl, which is similar to the energy transfer from the electronically excited benzene to biacetyl in the gas phase, as has been studied by Ishikawa and Noyes.[47] In the case of the quenching of diphenylamines by the biacetyl acceptor, eq 4q should be added to eq 0–11.

$${}^1D + Q \longrightarrow D + {}^1Q \tag{4q}$$

The ratio f_0/f is represented by

$$\begin{aligned} f_0/f &= 1 + \frac{k_{4q}[Q]}{k_1 + k_2 + k_3 + k_4[O_2]} \\ &= 1 + k_D{}^1\tau[Q] \\ &= 1 + K_Q{}^S[Q] \end{aligned} \tag{17}$$

where $k_{4q} = k_D$, $K_Q{}^S = k_D{}^1\tau$, and $^1\tau$ is the lifetime of the

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(41) J. T. Dubois and M. Cox, *J. Chem. Phys.*, **38**, 2536 (1963).

(42) H. H. Richtol and A. Belorit, *ibid.*, **45**, 35 (1966).

(43) The concentration of dissolved oxygen in aerated cyclohexane was determined by the measurement of the contact CT band between cyclohexane and oxygen as has been proposed by A. U. Munck and J. F. Scott, *Nature (London)*, **177**, 587 (1956).

(44) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942). The modified Debye equation is given by $k_D = 8RT/3000\eta$, where k_D is in units of l. mol^{-1} sec^{-1} when η, the viscosity of the solvent, is in units of P. The value of k_D for cyclohexane at 20° is 6.6×10^9 l. mol^{-1} sec^{-1}, which is taken from the data of J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

(45) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, **39**, 377 (1963).

(46) J. T. Dubois and R. L. V. Hemert, *ibid.*, **40**, 923 (1964).

(47) H. Ishikawa and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **84**, 1502 (1962).

excited singlet state of the donor in aerated cyclohexane. Therefore, the values of ${}^1\tau$ for diphenylamines in aerated cyclohexane at 20° are obtained from eq 17.

$$\begin{aligned} {}^1\tau(\text{N-MeDA}) &= 3.8 \times 10^{-9}\ \text{sec} \\ {}^1\tau(\text{TPA}) &= 3.2 \times 10^{-9}\ \text{sec} \qquad (18) \\ {}^1\tau(\text{DA}) &= 3.2 \times 10^{-9}\ \text{sec} \end{aligned}$$

If $k_4 = k_D$, the value of $k_4[O_2]$ in aerated cyclohexane is 1.52×10^7 sec^{-1}. From eq 18, eq 18′ is derived in the case of N-MeDA, where ${}^1\tau_0$ is the lifetime of the lowest excited singlet state of N-MeDA in degassed cyclohexane.

$$\begin{aligned} k_1 + k_2 + k_3 + k_4[O_2] &= 2.64 \times 10^8\ \text{sec}^{-1} \\ k_1 + k_2 + k_3 &= 2.49 \times 10^8\ \text{sec}^{-1} \qquad (18') \\ {}^1\tau_0 &= 4.02 \times 10^{-9}\ \text{sec} \end{aligned}$$

The ratio of the fluorescence quantum yields of diphenylamines in aerated and in degassed cyclohexane, Q_F/Q_{F_0}, is derived from eq 18′

$$\frac{Q_F}{Q_{F_0}} = \frac{k_1 + k_3 + k_3}{k_1 + k_2 + k_3 + k_4[O_2]} = 0.94 \qquad (19)$$

The ratio Q_F/Q_{F_0} obtained from the measurements of fluorescence intensity is also about 0.9, as is shown in Table I. Therefore, it is reasonable to estimate the lifetimes of the lowest excited singlet states of diphenylamines by the method of Dubois, *et al.*[41,45,46] The ratio of Φ_0/Φ is given by

$$\Phi_0/\Phi = 1 + (k_{4q}{}^1\tau + k_{8q}{}^3\tau)[Q] + k_{4q}k_{8q}{}^1\tau{}^3[Q]^2 \qquad (20)$$

In the low concentration of biacetyl, $[Q] \leq \sim 10^{-2}$ *M*, eq 20′ holds approximately.

$$\Phi_0/\Phi = 1 + (K_Q{}^S + K_Q{}^T)[Q] \qquad (20')$$

The value of $(K_Q{}^S + K_Q{}^T)$ is 33 l./mol, which is obtained from the slope of Φ_0/Φ *vs.* [Q] in Figure 5, and the value of $K_Q{}^S$ is 25 l./mol, which is obtained from the slope of f_0/f *vs.* [Q] in Figure 5. The triplet quenching constant of N-MeDA by the biacetyl acceptor, $K_Q{}^T$, is therefore 8 l./mol. When the concentration of biacetyl is increased, $[Q] \geq \sim 10^{-2}$ *M*, the value of Φ_0/Φ deviates from the straight line, as is shown in Figure 5, because the third term in eq 20 becomes nonnegligible.

On the other hand, in the cases of piperylene and biphenyl quenchers, triplet–triplet energy transfer occurs, since no effect of the addition of piperylene or biphenyl on the fluorescence intensity of N-MeDA was observed, and the phosphorescence intensity of N-MeDA was reduced by the addition of piperylene, or the photosensitized phosphorescence of biphenyl by the N-MeDA donor appeared as is shown in Figure 4b. When the quencher is absent, the quantum yields for the N-MeCA formation from N-MeDA in aerated and degassed cyclohexane at 20° were 0.67 and 0.06, respectively, as are shown in Figure 2 and in Table II. From eq 12, the ratio of 0.06/0.67 is given by

$$\frac{0.06}{0.67} = \frac{k_1 + k_2 + k_3 + k_4[O_2]}{k_1 + k_2 + k_3}(1 + {}^3\tau_0 k_8[O_2]) \times \left(\frac{k_{10}}{k_9 + k_{10}}\right)\left(1 + \frac{k_9}{k_{10} + k_{11}[O_2]}\right) \qquad (21)$$

where $(k_1 + k_2 + k_3 + k_4[O_2])/(k_1 + k_2 + k_3) = 1.06$, which is obtained from eq 19, $k_8[O_2] = 1.52 \times 10^7$ sec^{-1}, and ${}^3\tau_0 = 1.71 \times 10^{-8}$ sec. If the rate constant k_{11} is diffusion controlled and $k_{11}[O_2] \gg k_9$, eq 22 is derived from eq 21

$$(k_9 + k_{10})/k_{10} = 14.9 \quad \text{at } 20° \qquad (22)$$

and

$$k_9/k_{10} = 13.9$$

where k_9 is the rate constant from the intermediate, M, to the ground state of N-MeDA, and k_{10} is the rate constant of the dehydrogenation from M into N-MeCA. From eq 22, eq 22′ holds approximately.

$$\frac{k_{10} + k_{11}[O_2]}{k_9 + k_{10} + k_{11}[O_2]} \approx 1 \qquad (22')$$

Equation 23 is derived from eq 12, 16, and 22′.

$$\begin{aligned} 0.67 &= k_3{}^1\tau k_7{}^3\tau \\ \phi_{ic}{}'k_7 &= 4.93 \times 10^7\ \text{sec}^{-1} \end{aligned} \qquad (23)$$

Here $\phi_{ic}{}'$ is the intersystem crossing yield of N-MeDA in aerated cyclohexane and $\phi_{ic}{}' = k_3{}^1\tau$.

Judging from the large value 0.67 of Φ of N-MeDA in aerated cyclohexane the rate constant k_7 from T_1 to *M* at 20° is probably very high in comparison with the sum of the rate constants k_5 and k_6. Therefore, the value of k_7 is approximately obtained from eq 15.

$$k_7 \approx k_5 + k_6 + k_7 = 5.85 \times 10^7\ \text{sec}^{-1} \qquad (15')$$

From eq 15′ and 23, $\phi_{ic}{}'$ can be obtained.

$$\phi_{ic}{}' \approx 0.84 \qquad (24)$$

The intersystem crossing quantum yield of N-MeDA in degassed cyclohexane, ϕ_{ic}, is also obtained from eq 12, 15′, and 22.

$$\begin{aligned} 0.06 &= \phi_{ic}k_7{}^3\tau_0\frac{k_9}{k_9 + k_{10}} \\ \phi_{ic} &= 0.89 \end{aligned} \qquad (25)$$

The value of ϕ_{ic} is also derived from the following relation

$$\frac{\phi_{ic}}{\phi_{ic}{}'} = \frac{{}^1\tau_0}{{}^1\tau} = 1.06 \qquad (26)$$

where $\phi_{ic}{}' = 0.84$. The rate constant of the intersystem crossing in N-MeDA, k_3, is therefore

$$k_3 = \phi_{ic}/{}^1\tau_0 = 2.2 \times 10^8\ \text{sec}^{-1} \qquad (27)$$

The value of $(k_1 + k_2)$ is 2.7×10^7 sec^{-1}, which is obtained from eq 18′ and 27. The quenching rate constants, k_{8q}, of N-MeDA by the piperylene acceptor in degassed and aerated cyclohexane at 20° can be calculated as follows

$$k_{8q} = K_{Q_0}/{}^3\tau_0 = 6.2 \times 10^8\ \text{l. mol}^{-1}\ \text{sec}^{-1}$$

and (28)

$$k_{8q} = K_Q/{}^3\tau = 6.2 \times 10^8\ \text{l. mol}^{-1}\ \text{sec}^{-1}$$

As has been pointed out by Porter and Wilkinson,[48,49] when the triplet level of donor is considerably higher

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(48) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).

(49) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

than that of acceptor, the triplet–triplet energy transfer rate constants should be close to those expected from a diffusion-controlled process. However, the rate constant, k_{8q}, from the N-MeDA donor to the piperylene acceptor is about one-tenth of the predicted diffusion-controlled rate constant,[44] in spite of large ΔE_T a (see Table III). The quenching rate constant, k_{8q}, for the system of the N-MeDA donor and the biphenyl acceptor is also obtained.

$$k_{8q} = 4.8 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1} \qquad (29)$$

The photosensitization of diphenylamines by some triplet sensitizers is available to confirm the triplet path in the photocyclization of diphenylamines. The results of the triplet sensitization by aromatic ketones, as are shown in Figure 6 and Table IV, indicate that the photocyclization of diphenylamines involves the triplet path, as has been proposed by Linschitz, *et al.*[23,24]

The photosensitized reactions can be accounted for by the following scheme

$$\mathrm{R} + h\nu \longrightarrow {}^1\mathrm{R} \qquad (30)$$

$${}^1\mathrm{R} \longrightarrow \mathrm{R} \qquad (31)$$

$${}^1\mathrm{R} \longrightarrow \mathrm{R} + h\nu_{\mathrm{R_F}} \qquad (32)$$

$${}^1\mathrm{R} \longrightarrow {}^3\mathrm{R} \qquad (33)$$

$${}^1\mathrm{R} + \mathrm{O_2} \longrightarrow \mathrm{R} + \mathrm{O_2} \qquad (34)$$

$${}^3\mathrm{R} \longrightarrow \mathrm{R} \qquad (35)$$

$${}^3\mathrm{R} \longrightarrow \mathrm{R} + h\nu_{\mathrm{R_P}} \qquad (36)$$

$${}^3\mathrm{R} + \mathrm{D} \longrightarrow \mathrm{R} + {}^3\mathrm{D} \qquad (37)$$

$${}^3\mathrm{R} + \mathrm{D} \longrightarrow \mathrm{R} + \mathrm{D} \qquad (38)$$

$${}^3\mathrm{R} + \mathrm{O_2} \longrightarrow \mathrm{R} + \mathrm{O_2} \qquad (39)$$

$${}^3\mathrm{D} \longrightarrow \mathrm{D} \qquad (5)$$

$${}^3\mathrm{D} \longrightarrow \mathrm{D} + h\nu_{\mathrm{D_P}} \qquad (6)$$

$${}^3\mathrm{D} \longrightarrow \mathrm{M} \qquad (7)$$

$${}^3\mathrm{D} + \mathrm{O_2} \longrightarrow \mathrm{D} + \mathrm{O_2} \qquad (8)$$

$$\mathrm{M} \longrightarrow \mathrm{D} \qquad (9)$$

$$\mathrm{M} \longrightarrow \mathrm{C} + (\mathrm{H_2}) \qquad (10)$$

$$\mathrm{M} + \mathrm{O_2} \longrightarrow \mathrm{C} + (\mathrm{H_2O}, \mathrm{H_2O_2}) \qquad (11)$$

where R, ^{1}R, and ^{3}R are the ground state, the lowest excited singlet state, and the lowest triplet state of the sensitizer (aromatic ketone). Then, using a steady-state treatment, the following equation is obtained

$$\Phi_S = \frac{\gamma_{ic} k_{37}[\mathrm{D}]\zeta}{k_{35} + k_{36} + (k_{37} + k_{38})[\mathrm{D}] + k_{39}[\mathrm{O_2}]} \qquad (40)$$

where Φ_S is the quantum yield for the product formation by the triplet sensitization, γ_{ic} is the intersystem crossing quantum yield of the sensitizer, which is equal to about unity in benzene, as has been reported by Lamola and Hammond,[30] and

$$\zeta = \frac{k_7}{k_5 + k_6 + k_7 + k_8[\mathrm{O_2}]} \frac{k_{10} + k_{11}[\mathrm{O_2}]}{k_9 + k_{10} + k_{11}[\mathrm{O_2}]}$$

The reciprocal of Φ_S is therefore

$$1/\Phi_S = \left(1 + \frac{k_{38}}{k_{37}} + \frac{k_{35} + k_{36} + k_{39}[\mathrm{O_2}]}{k_{38}[\mathrm{D}]}\right)\frac{1}{\zeta} \qquad (41)$$

The slopes (α) and intercepts (β) of the plots in Figure 6 are

$$\alpha = \frac{k_{35} + k_{36} + k_{39}[\mathrm{O_2}]}{k_{38}\zeta} \qquad (42)$$

equals 3.9 l./mol for the propiophenone donor and 5.5 l./mol for the acetophenone donor, and

$$\beta = \left(1 + \frac{k_{38}}{k_{37}}\right)\frac{1}{\zeta} \qquad (43)$$

equals 2.7 for the propiophenone donor and 2.8 for the acetophenone donor, where $\zeta = 0.80$.[50] From eq 43, the ratio of the triplet energy transfer rate constant, k_{37}, to the deactivation rate constant, k_{38}, which is caused by the collision with the acceptor, can be obtained

$$k_{37}/k_{38} = 0.86_2 \qquad (44a)$$

for the propiophenone donor, and

$$k_{37}/k_{38} = 0.80_6 \qquad (44b)$$

for the acetophenone donor. It is well known that the triplet–triplet energy-transfer rate constant is considerably dependent on the triplet energy difference between donor and acceptor, ΔE_T: when the triplet energy levels become closer the transfer efficiency is decreased and no transfer is observed.[49] This tendency is also observed in the present work. The efficiency of the triplet energy transfer from the benzaldehyde donor to the N-MeDA ($\Delta E_T = 600$ cm^{-1}) is significantly decreased. The transfer in the case of the benzophenone donor ($\Delta E_T = -600$ cm^{-1}) is scarcely observed. It would be of interest to understand what the excess energy requirements are in a triplet energy-transfer system occurring by an exchange mechanism. From the data of Herkstroeter and Hammond,[51] the efficiency of the transfer between the stilbene acceptor and various sensitizers is constant for $\Delta E_T > \sim 1750$ cm^{-1}. From the data of Porter and Wilkinson,[49] the triplet–triplet energy-transfer rate constants between various donors and acceptors are also constant for $\Delta E_T > \sim 1900$ cm^{-1}, and the transfer becomes inefficient for $\Delta E_T < \sim 900$ cm^{-1}. The results given in eq 44 show that the deactivation process by the acceptor (eq 38) is significant for $\Delta E_T \sim 1150$–1550 cm^{-1}.

Disagreement in the quantum yields for the carbazole formation and for the disappearance of diphenylamine, as is shown in Table II, and the failures of sensitization and quenching indicate that diphenylamine has a photochemical side reaction. Photochemical cleavage of the N–H bond may occur in the solvents, as has been reported by Bowen and Eland.[22]

Finally, on the basis of the photosensitization and quenching of diphenylamines, it can be said that the primary processes in the photocyclization of diphenylamines occur through the lowest triplet state.

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(50) The value of ζ is obtained from the following relation: $\zeta = \Phi/\Phi_{ic}' = 0.67/0.84 = 0.80$ (see eq 12 and 24).

(51) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).