Kinetics and Mechanism of the Photocyclization of Diphenylamines. II. Photochemical Secondary Processes of Diphenylamines

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Abstract: Temperature and oxygen effects on quantum yields for carbazole formation have been studied in some detail. A kinetic study of photocyclization of diphenylamines has also been carried out using a flash technique. It has been shown that the intermediate M (11,12-dihydrocarbazole) differs from the "610-nm" transient produced by flashing solutions of diphenylamines, because the rate of product formation is much higher than that of the 610-nm transient, whose half-lives for *N*-methyldiphenylamine are 80 μsec in aerated cyclohexane and 670 μsec in degassed cyclohexane at 30°. The mechanism of the reaction has been studied kinetically. Rate constants and activation energies are also given for photochemical processes of *N*-methyldiphenylamine.

In a previous paper,[1] a kinetic study of the direct, sensitized, and quenched photocyclizations of diphenylamines was reported. The photocyclization of diphenylamines originates from the lowest triplet state, T_1, and subsequently the triplet transient leads to the formation of an intermediate, M (11,12-dihydrocarbazole, whose two central hydrogens are in the cis configuration), competing with the triplet deactivation processes. The intermediate M then is converted to the corresponding carbazole, with and without oxygen, or to the ground state of the original substance.

This paper reports a flash-excitation study of diphenylamines, the temperature and oxygen effects on quantum yields for carbazole formation, and a discussion of secondary processes in the photocyclization of diphenylamines.

Experimental Section

The solvents and the procedure for quantum-yield measurements were the same as those described in a previous paper.[1] In measurement of one temperature effect on the quantum yield, a quartz dewar flask designed for spectrometry was used as a reaction cell, and it provided control of the temperature to within ±2°. The concentration of dissolved oxygen was adjusted by flushing with nitrogen at room temperature, and was determined by the method of Munck and Scott.[2] The amounts of carbazole formation were measured by spectrophotometry at 20°.

The flash apparatus used was a Nakano Denshi Co. Ltd. product. An excitation flash lamp with xenon gas was made of quartz. Two flash lamps in series were used. The condenser charged up 11 kV with a capacitor of 2 μF whose energy corresponded to 121 J. The pulse had a half-width value of about 20 μsec. The monochromator and the synchroscope used were Shimazu GE-100 and Toshiba 3054 products, respectively.

Results

Flash Study of Diphenylamine Solutions. Figure 1 shows some typical synchroscopes obtained on flashing *N*-methyldiphenylamine (N-MeDA) solutions at 30°. Figure 2 shows the spectral changes following flash excitation of N-MeDA solution in cyclohexane at 30°. The transient species having an absorption at 610 nm, as reported by Linschitz, *et al.*,[3,4] was also observed. The absorption at 343 nm, which indicates *N*-methylcarbazole (N-MeCA) formation from N-MeDA appeared immediately after flashing (<20 μsec). However, the "610-nm" transient slowly decayed with first-order kinetics (half-life $\tau_{1/2} = 80$ μsec in aerated cyclohexane at 30°), as shown in Figure 3. The flash study of diphenylamines was carried out under various conditions. Some typical results are summarized in Table I.

The 610-nm transient formation decreased in the presence of oxygen or piperylene (triplet quencher). No 610-nm transient was observed in the flash excitations of N-MeDA in AcOH or of DA in CH. It is apparent that the decay rate constants for the 610-nm transient differ from the rate constant for product formation (carbazoles): the 610-nm transient is not the intermediate, M (11,12-dihydrocarbazole), in the photocyclization of diphenylamines, although the 610-nm transient produced by flashing has not yet been assigned.

Of course, the $T^* \leftarrow T$ absorption band (530 nm)[3,5] could not be observed at 30°, because the triplet lifetime of N-MeDA, $^3\tau_0$, is small (1.71×10^{-8} sec in degassed CH at 20°).[1] The absorption at 530 nm observed at 30° is the tail of the 610-nm absorption, since the half-lives are the same values, as shown in Table I and Figure 2.

Effect of Oxygen on the Quantum Yield of Carbazole Formation. Measurement of the quantum yield for carbazole formation from diphenylamines at 2537 Å and 20° was carried out under various concentrations of oxygen dissolved in cyclohexane. Oxygen dissolved in cyclohexane was adjusted by flushing with nitrogen at room temperature and was determined by the method of Munck and Scott.[2] Quantum yields in degassed and aerated solutions at 20° were reported in a previous paper.[1] Figure 4 shows the quantum yields for carbazole formation from diphenylamines as a function of oxygen concentration. The effect of oxygen on the quantum yield of N-MeDA (Figure 4a) is in accord with

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[1] H. Shizuka, Y. Takayama, I. Tanaka, and T. Morita, *J. Amer. Chem. Soc.*, **92**, 727 (1970).

[2] A. U. Munck and J. F. Scott, *Nature* (*London*), 177, 587 (1956). The molar extinction coefficient of the contact CT band between cyclohexane and oxygen was 109 l. mol^{-1} cm^{-1} at 220 nm.

[3] K. H. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1881 (1963).

[4] H. Linschitz and K. H. Grellmann, *ibid.*, 86, 303 (1964).

[5] G. C. Terry, V. E. Uffindell, and F. W. Willets, *Nature* (*London*), **223**, 1050 (1969).

Table I. Absorbance Changes and Kinetics in Flashed Diphenylamine Solutions at 30°

Substance[a]	Solvent[b]	Wavelength, Å	Sweep, sec/cm	Added perylene, M	$\tau_{1/2}$, μsec	Optical density,[c] D_t
N-MeDA	Aerated CH	6100	20	0	8.0×10	0.45
			20	0	8.5×10	0.43
			20	10^{-2}	1.7×10^2	0.25
	Degassed CH	6100	200	0	6.7×10^2	0.62[d]
			200	10^{-2}	1.6×10^2	0.24
	Aerated CH	5300	20	0	8.0×10	0.14
			20	0	7.0×10	0.13
	Aerated CH	3430	20	0		0.06 const
			20	0		0.06 const
	Degassed CH	3430	20	0		≃0.005 const
	Aerated EtOH	6100	20	0	9.0×10	0.29
		5300	20	0	9.0×10	0.09
		3430	20	0		0.05 const
	Aerated AcOH	6100	50	0		0
TPA	Aerated CH	6100	20	0	5.0×10	0.14
		5300	20	0	4.5×10	0.08
		3400	20	0		0.01 const
DA	Aerated CH	6100	20	0		0
		5300	20	0		0
		3310	20	0		≃0.006 const

[a] N-MeDA, *N*-methyldiphenylamine; TPA, triphenylamine; DA, diphenylamine. [b] CH, cyclohexane; EtOH, ethanol; AcOH, acetic acid. [c] D_t, optical density at time t after flashing, where t = 20 μsec, unless otherwise noted. [d] t = 40 μsec.

that obtained by kinetic studies, as will be discussed later. A summary of the optimum quantum yields (Φ_{max}) is listed in Table II.

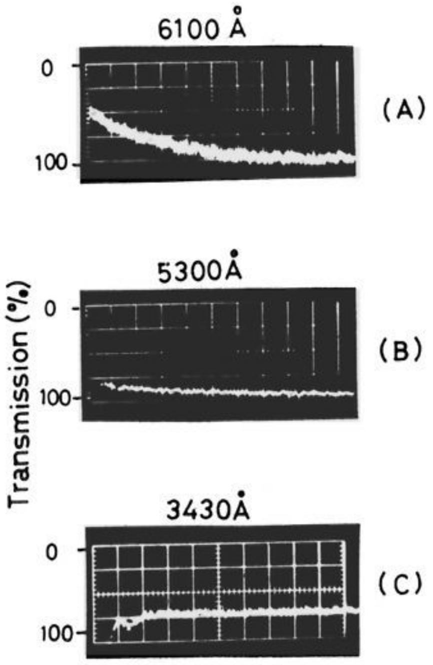

Figure 1. Typical flash synchroscopes of N-MeDA solutions (8×10^{-5} M) in aerated cyclohexane at 30°; absorption changes at (A) 6100, (B) 5300, and (C) 3430 Å; sweep = 20 μsec/cm (1 division = 1 cm); flash energy = 121 J; cell length = 7 cm.

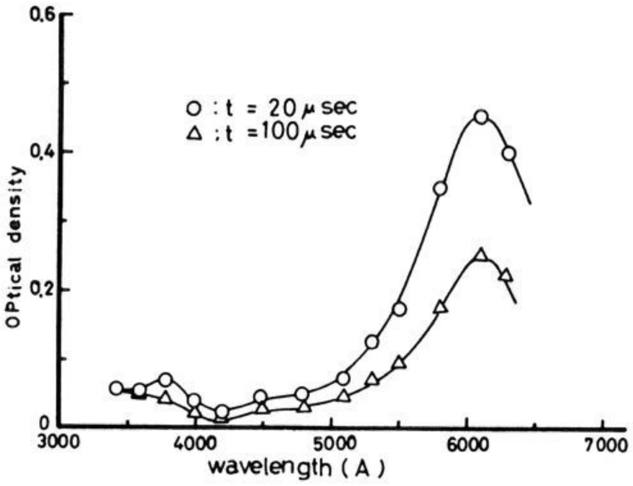

Figure 2. Spectral changes following flash excitation of N-MeDA solutions in cyclohexane at 30°: ○, t = 20 μsec; △, t = 100 μsec.

Temperature Effects on the Quantum Yield of Carbazole Formation. Temperature effects on the quantum yield in methylcyclohexane (MeCH) have been measured at 2537 Å. No difference in quantum yield is observed in CH and MeCH at 2537 Å and 293°K.[1]

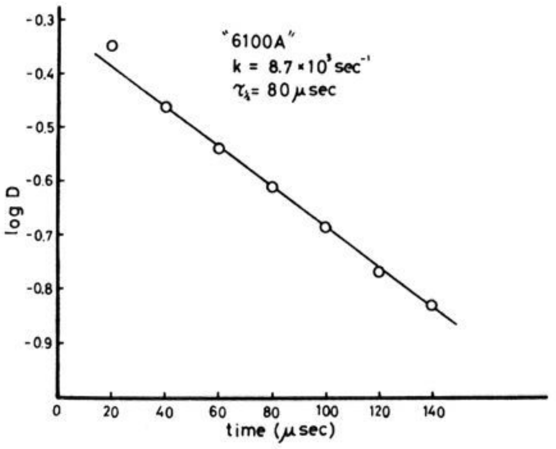

Figure 3. Kinetics of the decay process of the "610-nm" transient produced by flashing of N-MeDA in aerated cyclohexane at 30°.

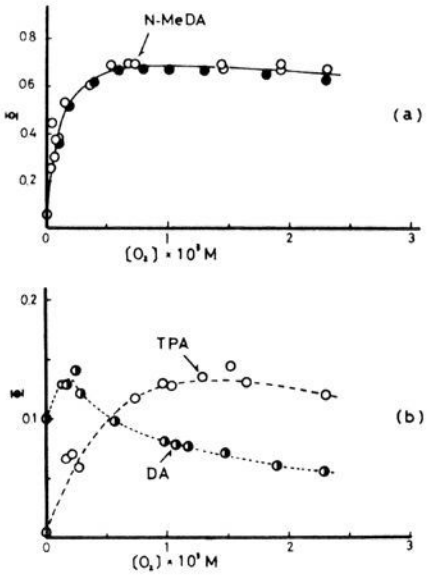

Figure 4. Quantum yields as a function of dissolved oxygen.

Figures 5, 6, and 7 show the dependence of the quantum yield on temperature. The quantum yield in degassed MeCH increased as temperature was lowered

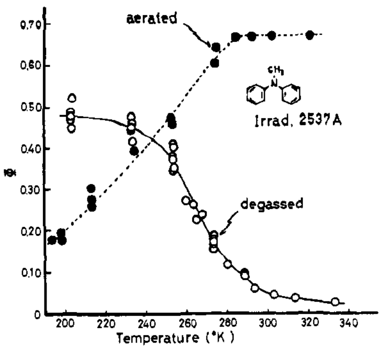

Figure 5. Quantum yields for *N*-methylcarbazole formation from N-MeDA *vs.* temperature: ○, degassed MeCH; ●, aerated MeCH.

(Figures 5–7). In regions of low temperature, the quantum yield in the degassed system showed the optimum value which was given by Bowen and Eland.[6] At liquid nitrogen temperature, no photocyclization took place, but photoionization, resulting in the formation of cation radicals of diphenylamine occurred, as was reported by Lewis and Lipkin.[7] The optimum quantum yields in degassed MeCH were: N-MeDA, 0.48 at ~200°K; TPA, ~0.08 at ~200°K; and DA, 0.10 at 260°K. In the aerated system, the quantum yields decreased as temperature was lowered (see Figures 5 and 6).

Table II. Quantum Yields (Φ) for Carbazole Formation from Diphenylamines in CH at 2537 Å and 20°

Substance	Solvent[a]	$[O_2]$, *M*	Φ	Ref
N-MeDA	CH degassed	0	0.06	1
	CH	7×10^{-4}	0.70 (Φ_{max})	This work
	CH aerated	2.3×10^{-3}	0.67	1
	n-H degassed	0	0.01	4
	n-H	6×10^{-4}	0.30 (Φ_{max})	4
TPA	CH degassed	0	0.003	1
	CH	1.3×10^{-3}	0.13 (Φ_{max})	This work
	CH aerated	2.3×10^{-3}	0.12	1
DA	CH degassed	0	0.10	1
	CH	1.5×10^{-4}	0.13 (Φ_{max})	This work
	CH aerated	2.3×10^{-3}	0.06	1
	n-H degassed	0	0.05	4
	n-H degassed	0	0.10	*b*
	n-H	2×10^{-5}	0.08 (Φ_{max})	4
	n-H aerated	3×10^{-3}	0.02	4

[a] CH, cyclohexane; *n*-H, *n*-hexane. [b] E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc., London*, 202 (1963).

Discussions

The temperature and oxygen effects on the quantum yield of the reaction can be accounted for by the scheme of eq 0–11, which is simplified in the processes of in-

$$D + h\nu \longrightarrow {}^1D \qquad (0)$$

$${}^1D \longrightarrow D \qquad (1)$$

$${}^1D \longrightarrow D + h\nu_f \qquad (2)$$

$${}^1D \longrightarrow {}^3D \qquad (3)$$

$${}^1D + O_2 \longrightarrow D + O_2 \qquad (4)$$

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

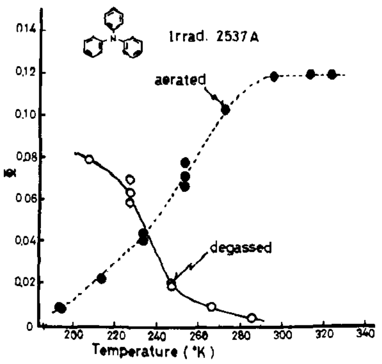

Figure 6. Quantum yields for *N*-phenylcarbazole formation from TPA *vs.* temperature: ○, degassed MeCH; ●, aerated MeCH.

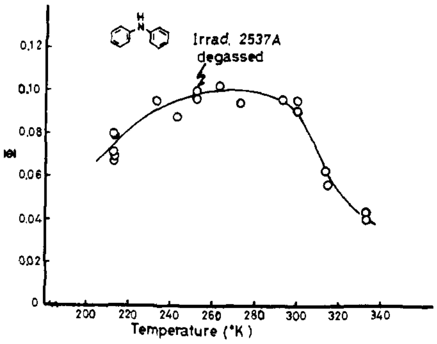

Figure 7. Quantum yields for carbazole formation from DA in degassed MeCH.

$${}^3D \longrightarrow D + h\nu_p \qquad (6)$$

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

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

$$M \longrightarrow D \qquad (9)$$

$$M \longrightarrow C + (H_2) \qquad (10)$$

$$M + O_2 \longrightarrow C + (HO_2, H_2O_2) \qquad (11)$$

ternal conversion and intersystem crossing; and where D, ^1D, and ^3D are the ground state, the lowest excited singlet state, and the lowest triplet state of diphenylamines, respectively; C represents carbazole, and f and p denote fluorescence and phosphorescence, respectively. From the steady-state approximation, eq 12 and 13 are obtained, where Φ and Φ_0 are the quantum yields

$$\Phi = \frac{k_3}{k_1 + k_2 + k_3 + k_4[O_2]} \times \frac{k_7}{k_5 + k_6 + k_7 + k_8[O_2]} \frac{k_{10} + k_{11}[O_2]}{k_9 + k_{10} + k_{11}[O_2]} \qquad (12)$$

$$\Phi_0 = \Phi_{ic} \frac{k_7}{k_5 + k_6 + k_7} \frac{k_{10}}{k_9 + k_{10}} \qquad (13)$$

for carbazole formation with and without oxygen, respectively. The rate constants for N-MeDA in CH at 20° were obtained in a previous paper.[1]

$$k_1 + k_2 = 2.9 \times 10^7 \text{ sec}^{-1}$$

$$k_3 = 2.2 \times 10^8 \text{ sec}^{-1}$$

$$k_4 \simeq k_8 \simeq k_{11} \simeq 6.6 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

$$k_7 \simeq k_5 + k_6 + k_7 = 5.85 \times 10^7 \text{ sec}^{-1}$$

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

$$\Phi_{ic} = k_3/(k_1 + k_2 + k_3) = 0.89$$

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(6) E. J. Bowen and J. H. D. Eland, *Proc. Chem. Soc., London*, 202 (1963).

(7) G. N. Lewis and D. Lipkin, *J. Amer. Chem. Soc.*, 64, 2801 (1942).

It has been reported[8-10] that intersystem crossing has a small activation energy (2.2–2.5 kcal/mol) if the energy level (E_{T_n}) of the excited triplet state T_n lies slightly above the level (E_{S_1}) of the lowest excited singlet state S_1. Intersystem crossing and internal conversion occur through $\mathrm{T}_1 \leftarrow \mathrm{T}_n \leftarrow \mathrm{S}_1$ ($n \geq 2$). When $E_{\mathrm{T}_n} \gg E_{\mathrm{S}_1}$ or $E_{\mathrm{S}_1} > E_{\mathrm{T}_n}$, no temperature effect on Φ_{ic} is observed.[8-10] These phenomena can be understood by considering that intersystem crossing from the vibrationally excited S_1 to T_n occurs when the final electronic state T_n has slightly higher energy than the initial electronic state S_1. In the case of N-MeDA, the temperature effect on Φ_{ic} is probably absent because the order of energy levels of the excited N-MeDA molecule is $E_{\mathrm{S}_1} > E_{\mathrm{T}_n}$ from theoretical considerations using the SCF–MO–CI approximation.[11] Therefore, $^3\mathrm{D}$ in eq 3 may be produced through the path $^3\mathrm{D} \leftarrow {}^3\mathrm{D}_n \leftarrow {}^1\mathrm{D}$, which results in a high value of Φ_{ic} (0.89).

Temperature effects on triplet decay have been extensively studied and indicate that the triplet lifetime of aromatic hydrocarbons in rigid matrices decreases slightly with increasing temperature.[12-21] For most systems investigated, the triplet lifetime at 77°K is about twice the triplet lifetime at 300°K. It is also well known that in fluid media triplet decay is very dependent on temperature. Of course, the rate constants k_5 and k_6 involve some activation energy. If k_5 and k_6 have some activation energy, the value of Φ_0 in eq 13 does not change in the temperature range 203–293°K because the sum of k_5 and k_6 is very small in comparison with k_7. Thus, the simulation of the temperature effect on the quantum yield Φ_0 for N-MeCA formation has been carried out assuming that the values of Φ_{ic} and $(k_5 + k_6)$ are approximately constant. If the rate constants k_7, k_9, and k_{10} have activation energies E_7, E_9, and E_{10}, and have frequency factors A_7, A_9, and A_{10}, respectively, eq 14 is derived from eq 13.

$$\frac{\Phi_{\mathrm{ic}} - \Phi_0}{\Phi_0} = \frac{k_5 + k_6}{A_7} \exp\left(\frac{E_7}{RT}\right) + \frac{A_9}{A_{10}} \exp\left(\frac{E_{10} - E_9}{RT}\right) + \frac{A_9(k_5 + k_6)}{A_7 A_{10}} \times \exp\left(\frac{E_7 - E_9 + E_{10}}{RT}\right) \quad (14)$$

Equation 14 is simplified as the following equation

$$\frac{\Phi_{\mathrm{ic}} - \Phi_0}{\Phi_0} = A \exp\left(\frac{E_7}{RT}\right) + B \exp\left(\frac{E_{10} - E_9}{RT}\right) + AB \exp\left(\frac{E_7 - E_9 + E_{10}}{RT}\right) \quad (14')$$

Table III. Simulation of the Temperature Effect on the Quantum Yield Φ_0 of N-MeDA in Degassed MeCH

Temp, °K	$(\Phi_0)_{\mathrm{obsd}}$	$(\Phi_0)_{\mathrm{calcd}}$	A	B	E_7, kcal/mol	$(E_9 - E_{10})$, kcal/mol
203	0.478	0.485	10^{-8}	10^7	7	7
233	0.460	0.467	10^{-7}	10^7	7	8
253	0.381	0.368	10^{-8}	10^7	7	8
263	0.265	0.253	10^{-8}	10^7	7	8
273	0.173	0.167	10^{-8}	10^7	7	8
293	0.060	0.064	10^{-7}	10^7	7	8

where $A = (k_5 + k_6)/A_7$ and $B = A_9/A_{10}$. The simulation of the temperature effect on Φ_0 in the degassed system was carried out by varying A from 10^{-3} to 10^{-10}, B from 10^3 to 10^{10}, E_7 from 1 to 10 kcal/mol, and $(E_9 - E_{10})$ from 1 to 15 kcal/mol. The results are summarized in Table III. Thus

$$A = (k_5 + k_6)/A_7 \simeq 10^{-8} \quad (15)$$

$$B = A_9/A_{10} = 10^7 \quad (16)$$

$$E_7 = 7 \text{ kcal/mol} \quad (17)$$

$$E_9 - E_{10} \simeq 8 \text{ kcal/mol} \quad (18)$$

From the value of k_7 (5.85×10^7 sec^{-1} at 293°K)[1] and eq 17, A_7 is derived.

$$A_7 = 9.7 \times 10^{12} \text{ sec}^{-1} \quad (19)$$

Muszkat and Fisher[22] also estimated that the frequency factor in the process from the S_1 state of diphenylcyclopentene (DCP) to the cyclopentenodihydrophenanthrene (C-DHP) intermediate is about 10^{12} sec^{-1}. Therefore, the frequency factor in the process from the initial state (S_1 or T_1) to the ring-closed intermediate (C-DHP or M) is of the order of magnitude of vibrational frequency (10^{12}–10^{13} sec^{-1}). The activation energy E_7 (7 kcal/mol) for the process $\mathrm{M} \leftarrow {}^3\mathrm{D}$ is large in comparison with that (2.6 kcal/mol) for the process C-DHP $\leftarrow$ S_1. The difference in activation energy may be due to the energy difference of the potential barriers between the intermediates and the initial states. Thus, the rate constants k_7 and $(k_5 + k_6)$ are given by

$$k_7 = 9.7 \times 10^{12} \exp\left(\frac{-7 \times 10^3}{RT}\right) \text{sec}^{-1} \quad (20)$$

and

$$k_5 + k_6 = A \times A_7 \simeq 10^5 \text{ sec}^{-1} \quad (21)$$

The ratio k_9/k_{10} at 293°K is 13.9, as has been reported previously,[1] and eq 22 holds, where $A_9/A_{10} = 10^7$

$$k_9/k_{10} = (A_9/A_{10}) \exp[(E_{10} - E_9)/RT] = 13.9 \quad (22)$$

and T = 293°K. From eq 22, $(E_9 - E_{10})$ is also obtained, and the value 8 kcal/mol is in accord with that in eq 18. Therefore, the activation energy E_9 in the decay process from M to D is $(8 + E_{10})$ kcal/mol. The value of E_{10} in the dehydrogenation process[8] from M to N-MeCA (see eq 10) seems to be low, as was suggested by Linschitz, *et al.*[4] In spite of low activation energy (E_{10}), the value of k_{10} is much smaller than that of k_9, namely $k_{10} = k_9/13.9$ at 293°K, since the frequency factor A_{10} is very small ($A_{10} = A_9 \times 10^{-7}$).

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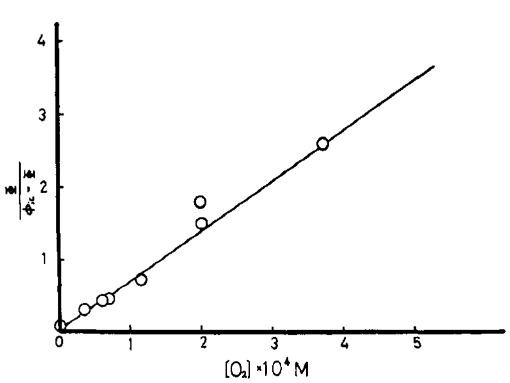

Figure 8. $\Phi/(\Phi_{ic} - \Phi)$ as a function of $[O_2]$.

In the presence of low concentration of dissolved oxygen, $[O_2] \leq 5 \times 10^{-4}$ *M*, eq 23 holds approximately.

$$\Phi/(\Phi_{ic} - \Phi) = (k_{10}/k_9) + (k_{11}/k_9)[O_2] \quad (23)$$

Figure 8 shows $\Phi(\Phi_{ic} - \Phi)$ *vs.* $[O_2]$. From the slope of the plot in Figure 8, the ratio k_{11}/k_9 is given by

$$k_{11}/k_9 = 6.8 \times 10^3 \text{ l. mol}^{-1} \quad (24)$$

If k_{11} is diffusion controlled (6.6×10^9 l. mol^{-1} sec^{-1}), the value of k_9 is therefore

$$k_9 = 9.7 \times 10^5 \text{ sec}^{-1} \text{ at } 293°\text{K} \quad (25)$$

From eq 22 and 25, k_{10} is obtained.

$$k_{10} = 7.0 \times 10^4 \text{ sec}^{-1} \text{ at } 293°\text{K} \quad (26)$$

The lifetimes of the intermediate M of N-MeDA are therefore

$$\tau_M{}^0 = 1/(k_9 + k_{10}) = 9.6 \times 10^{-7} \text{ sec} \quad (27)$$

in the absence of oxygen at 293°K, and

$$\tau_M = 1/(k_9 + k_{10} + k_{11}[O_2]) = 6.2 \times 10^{-8} \text{ sec} \quad (28)$$

in aerated CH at 293°K, where $k_{11}[O_2] = 1.52 \times 10^7$ sec^{-1}. Therefore, the absorption of very short-lived M could not be observed at 30° by the flash method. The rate of carbazole formation is measured unsuccessfully at 30°, because the rate constant for product formation, k_{10} (see eq 26), has a large value even in a degassed solution.

Then, the quantum yield Φ for N-MeCA formation from N-MeDA at 20°C can be calculated from eq 12 using the rate constants k_1–k_{11}, as described above. Figure 4a shows Φ_{calcd} *vs.* $[O_2]$, which is in good agreement with Φ_{obsd} as a function of $[O_2]$.

The temperature effects on Φ_0 and Φ as shown in Figures 5–7 are mainly caused by the activation energies E_7 and E_9. Although the yield of intermediate M is very high (~0.89) in the degassed system at 20°, since k_7 is very large (5.85×10^7 sec^{-1} at 20°C), the decay rate constant k_9 from M to D is 13.9 times larger than k_{10}, and therefore the value of Φ_0 for N-MeDA becomes very low (0.06 at 20°C). As the temperature is lowered in degassed MeCH, the value of k_9 is decreased because k_9 has an activation energy of $(8 + E_{10})$ kcal/mol, and the value of $k_7/(k_5 + k_6 + k_7)$ in eq 13 is slightly changed because $k_7 \gg (k_5 + k_6)$. Thus, the value of Φ_0 in eq 13 is increased. However, as the temperature is lowered, Φ_0 is gradually decreased to the optimum value because k_7 becomes small, according to eq 20, and then the value of $k_7/(k_5 + k_6 + k_7)$ also becomes small. Carbazole formation at 77°K by uv light could not be observed, as was also reported by Bowen and Eland,[6] and cation radicals of diphenylamines were produced in EPA rigid matrices by irradiation with uv light, as was reported by Lewis and Lipkin.[7]

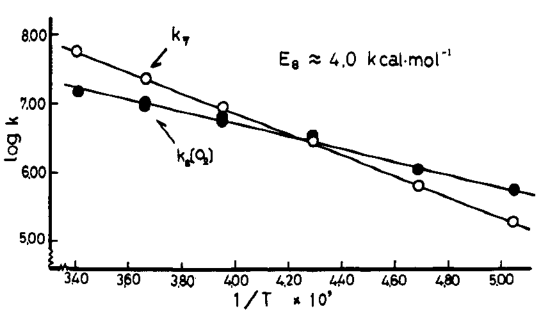

Figure 9. Plots of log $k_8[O_2]$ as a function of $1/T$.

The temperature effects on Φ of N-MeDA in aerated MeCH can be accounted for by the following equation

$$\Phi = \Phi_{ic}{}' \frac{k_7}{k_5 + k_6 + k_7 + k_8[O_2]} \frac{k_{10} + k_{11}[O_2]}{k_9 + k_{10} + k_{11}[O_2]} \quad (12')$$

where $\Phi_{ic}{}'$ is the intersystem crossing yield of N-MeDA in aerated CH ($\phi_{ic}{}' = 0.84$),[1] and $(k_{10} + k_{11}[O_2])/(k_9 + k_{10} + k_{11}[O_2]) \simeq 1$. It is assumed that the value of $\Phi_{ic}{}'$ in aerated MeCH is approximately the same as in aerated CH, because Φ_0 and Φ have been observed to be the same in these solutions.[1] Equation 29 is derived from eq 12′

$$k_8[O_2] = [(\Phi_{ic}{}'/\Phi) - 1]k_7 - (k_5 + k_6) \quad (29)$$

where $k_7 = 9.7 \times 10^{12} \exp[(-7 \times 10^3)/RT]$ sec^{-1} and $k_5 + k_6 = 10^5$ sec^{-1}. From eq 29, the value of $k_8[O_2]$ can be calculated using the experimental data for Φ in aerated MeCH and in various temperatures. Figure 9 shows the linear relationship log $k_8[O_2]$ *vs.* $1/T$. Although the values of k_7 and $k_8[O_2]$ decrease as the temperature is lowered, the temperature effect on the rate constant k_7 shows a large activation energy, 7 kcal/mol, in comparison with that for $k_8[O_2]$ (4.0 kcal/mol). It seems that the activation energy 4.0 kcal/mol obtained from the straight line of log $k_8[O_2]$ *vs.* $1/T$ corresponds to that in the diffusion-controlled process. The two straight lines in Figure 9 cross at about 240°K. This means that, at ~240°K, the value of Φ for N-MeDA in aerated MeCH equals that in the degassed system. In fact, the observed data for Φ_0 and Φ for N-MeDA in aerated and degassed MeCH are equivalent at ~240°K, as shown in Figure 5. As the temperature becomes lower than the crossing point, 240°K, the value of Φ in the aerated system becomes smaller than that in the degassed solution because the triplet deactivation rate $k_8[O_2] > k_7$ as shown in Figures 5 and 9.

N-Substituted derivatives of diphenylamine formed by irradiation with uv light undergo photocyclization to yield the corresponding carbazoles, as has been described above. However, in the case of *N*-acetyldiphenylamine,[23] photocyclization does not occur, but a photo-Fries rearrangement take place. The rearrange-

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[23] H. Shizuka, M. Kato, T. Ochiai, K. Matsui, and T. Morita, *Bull. Chem. Soc. Jap.*, **43**, 67 (1970).

ment occurs through predissociation by intersystem crossing ${}^3\sigma_0$(N–C) $\leftarrow$ $S_1(\pi\pi^*)$ resulting in radical pairs. Subsequently, the radical pairs recombine efficiently in a solvent cage, as has been shown by Shizuka, *et al.*[23–28]

Finally, it can be said that the intermediate M (11,12-dihydrocarbazole) is different from the 610-nm transient on the basis of a flash study of diphenylamines. The rate constant k_7 for the process of from the formation of M from the triplet and the decay rate constant k_9 for conversion from M to the starting material have activation energies of 7 and (8 + E_{10}) kcal/mol, respectively, which result in a temperature effect on the quantum yield for carbazole formation. The mechanism for photocyclization of diphenylamine was shown in eq 0–11.

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Hydrogen–Deuterium Exchange of a Charged Poly(methacrylamide) and Its Monomeric Analog

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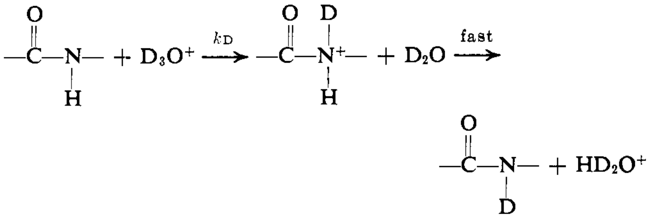
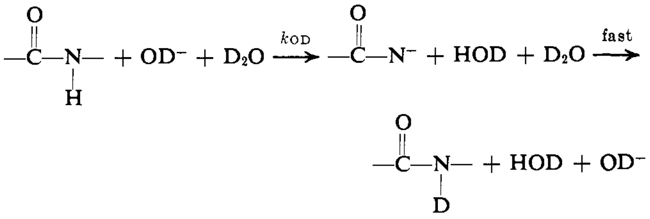
Abstract: The kinetics of hydrogen–deuterium exchange in a charged polymeric amide–poly(ϵ-aminomethacrylyl-L-lysine)—and its monomeric analog—ϵ-aminoisobutyryl-L-lysine—were measured in D_2O solutions. The polymer was selected as a model for charge effects on the exchange rates of proteins since its net charge will vary with pH as that of a protein. Both polymer and monomer showed parabolic rate *vs.* pD profiles characteristic of specific acid and base catalysis. The polymer, however, had a drastically reduced rate of minimum exchange, $K_{\min}$, compared with the monomer. The polymer also showed a slightly increased pD of minimum exchange, $\mathrm{pD}_{\min}$. The shift in $\mathrm{pD}_{\min}$ was interpreted as a decrease in K_W in the vicinity of the polymer backbone. Although a decrease in K_W also would decrease $k_{\min}$, the major factor contributing to slow exchange appeared to be steric inhibition inherent with each residue. That interpretation is supported by a possible 3-kcal/mol increase in $E_a{}^*$ for exchange in the polymer over that of the monomer. In addition, internal catalysis by the amino group of the lysine moiety was observed in the polymer. Its effect also showed a drastic reduction over that of small molecules. Interestingly, upon the acquisition of a net positive charge, the rates were *reduced*, despite evidence for some expansion of the molecule. The rate reductions were about twice those predicted by ΔG_{el} from potentiometric titration data. Possibly, the basicities of carboxylate anions and amide groups are affected differently by the proximity of a positive charge.

Hydrogen–deuterium exchange has been shown to be a sensitive method for detecting conformational changes in biological macromolecules.[2–5] Proper interpretation of H → D exchange data in those cases, however, frequently depends on information gained through model systems. To date, considerable data have been gathered on protein analogs. For example, the following facts are known. (i) Labile-side-chain hydrogens (such as $-OH$, $-NH_3{}^+$, and COOH) all exchange with half-life times well below 1 min under the usual experimental conditions.[6,7] (ii) H → D exchange of amides usually proceeds much slower (half-life time of several minutes) and shows specific, as well as general, acid and base catalysis.[8–10] (iii) The acid- and base-catalyzed steps shown below probably involve charged amide nitrogen intermediates.[8]



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}- + D_3O^+ \xrightarrow{k_D} -\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle D}{|}}{N^+}}- + D_2O \xrightarrow{\text{fast}} -\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle D}{|}}{N}- + HD_2O^+$$

acid catalysis



$$-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{N}- + OD^- + D_2O \xrightarrow{k_{OD}} -\overset{\overset{\displaystyle O}{\|}}{C}-N^- + HOD + D_2O \xrightarrow{\text{fast}} -\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle D}{|}}{N}- + HOD + OD^-$$

base catalysis

(iv) Exchange rates of an amide hydrogen reflect the local environment of that group.[11,12]

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