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Hydrogen Atom Transfer in the Quenching of Pyrene Fluorescence by Amines

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The mechanism of the quenching of pyrene fluorescence by primary and secondary amines has been studied by means of fluorescence measurements and transient absorption measurements with the use of laser photolysis as well as conventional flash photolysis methods. It has been confirmed that 1-hydro-1-pyrenyl radicals and amino radicals are produced in the course of the fluorescence quenching reaction. The relative yields of 1-hydro-1-pyrenyl radicals for various amine quenchers were estimated.

It is well known that excited pyrene forms heteroexcimers with *N*,*N*-dimethylaniline (DMA) and *N*,*N*-dimethylnaphthylamines. However, when aniline, *N*-methylaniline and naphthylamines are used as electron donors for the heteroexcimer formation with excited aromatic hydrocarbons in solution at room temperature, no heteroexcimer fluorescence can be observed, quenching of the fluorescence of aromatic hydrocarbon occurring even in nonpolar solvents.[1,2] It seems plausible that the charge transfer interaction in the encounter complex followed by some efficient radiationless processes plays an important role in the case of the quenching by primary or secondary amines.

A possible mechanism for this fluorescence quenching by amines with free N–H group might be the charge transfer followed by a rapid proton transfer from the amine to the aromatic hydrocarbon in the encounter complex. In the case of hydrogen abstraction by excited ketones, especially for the ketone–amine systems, it is frequently assumed that the photoreduction proceeds *via* the charge transfer from the amine to the triplet ketone followed by proton transfer.[3,4] In contrast to the case of carbonyl compounds, only a few studies have been carried out concerning the hydrogen abstraction reaction of excited aromatic hydrocarbons. No attempt seems to have been made dealing with direct measurements on the hydrogen abstraction process of excited hydrocarbons.

In order to elucidate the mechanism of the quenching of the aromatic hydrocarbon fluorescence by amines with free N–H group, we have made detailed studies on excited pyrene–amine systems by means of fluorescence measurements as well as transient absorption measurements.

Exprimental

Fluorescence spectra were measured with an Aminco-Bowman spectrophotofluorometer equipped with an HTV-R446S photomultiplier. An ordinary flash photolysis apparatus with photoelectric detection of the transient absorption spectrum was used. A small computer (1K) was used to analyze the time dependence of transient species. The nanosecond laser photolysis method was the same as reported elsewhere.[5]

GR-grade *N*-methylaniline (NMA), *N*-ethylaniline (NEA), *N*-butylaniline (NBA), dibutylamine (DBAm), butylamine (BAm), and diethylamine (DEAm) were carefully distilled and stored in a vacuum. GR-grade aniline (AN) was steam-distilled, dried over potassium hydroxide, distilled under reduced pressure and stored in a vacuum. GR-grade diisobutylamine (DIBAm) was distilled in a vacuum and stored. Diphenylamine (DPA) was recrystallized from ethanol and sublimed. Spectro-grade hexane was distilled over metallic sodium.

All solutions for the measurement were deaerated by freeze-pump-thaw cycles, amines being added by the method of vacuum distillation to the solution for the measurements. The concentration of pyrene was 2×10^{-5} M. A cylindrical quartz cell (10 cm long, 1 cm i. d.) was used for the flash photolysis.

Results and Discussion

Quenching Rate Constant. The fluorescence quenching rate constants, k_q, for pyrene–amine–hexane systems at room temperature were determined. The plot of $\log k_q$ *vs.* ionization potential I_p of amines is given in Fig. 1. The values of the quenching rate constant for aliphatic amine systems are considerably smaller as compared with those of aromatic ones. This seems to indicate that an additional activation energy over that for the aromatic amine system is necessary for the quenching processes in the pyrene–aliphatic amine systems. The difference in the quenching rate constant of aromatic and aliphatic amines was also observed in the case of the heteroexcimer formation of such systems as pyrene–DMA and pyrene–tributylamine (TBA) studied by Nakashima *et al.*[6] According to them, additional activation energy is necessary for the change of the structure of TBA from a pyramidal one to a planar one in the course of the electron transfer. Such a structural change may occur also in the case of the present systems.

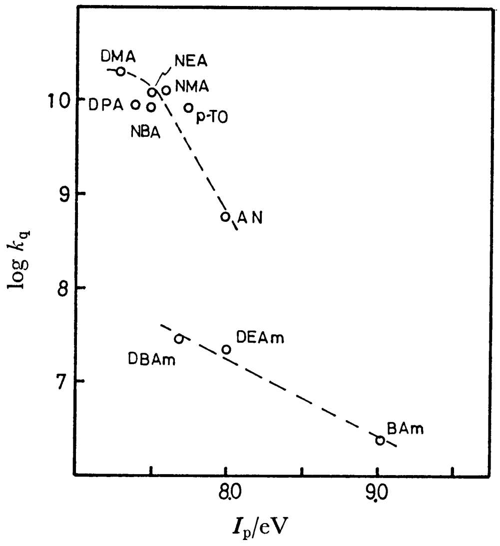


Fig. 1. Plot of $\log k_q$ *vs.* I_p for pyrene-amine-hexane systems at room temperature.

The relation between log k_q and I_p (Fig. 1) suggests that the mechanism of the quenching of the pyrene fluorescence may be charge transfer interaction in the encounter complex between excited pyrene and amine. The k_q for DMA is close to the rate constant of the diffusion-controlled reaction. Although k_q and I_p values of NMA or NEA are rather close to those of DMA, the heteroexcimer fluorescence can be observed only in the case of DMA. In view of this fact, we assume the following mechanism for the quenching by the primary or secondary amines:

$$\begin{tikzcd} A^* + HD \arrow[r, "k_q"] & (A^-\cdots HD^+) \arrow[r, "k_p"] \arrow[d, "k_f'"'] \arrow[d, "k_i'"] & (\dot{A}H\cdots\dot{D}) \arrow[r, "k_d"] \arrow[d, "k_i''"] & \dot{A}H + \dot{D} \\ & {} & {} & \end{tikzcd} \tag{1}$$

If one assumes that the rate constants of radiative (k_f') and radiationless (k_i') transitions of the charge transfer state ($A^-\cdots HD^+$) are equal to those of the pyrene–DMA heteroexcimer in hexane, respectively, one can estimate the order of magnitude of the rate constant k_p in Eq. 1 by means of the following quantities.

$$\Phi'_{\mathrm{DMA}} = \tau_f' k_f' = 0.66$$

$$\Phi'_{\mathrm{NEA}} = \frac{k_f'}{k_f' + k_i' + k_p} \lesssim 10^{-4} \quad \text{(limit of the detection system)}$$

$$1/\tau_f' = 2.6 \times 10^6\ \mathrm{s}^{-1}$$

where Φ'_{DMA} and Φ'_{NEA} are the fluorescence quantum yields of pyrene–DMA and pyrene–NEA heteroexcimers, respectively, and τ_f' is the lifetime of pyrene–DMA heteroexcimer. Thus, $k_p + k_i' \sim k_p \gtrsim 2 \times 10^{10}\ \mathrm{s}^{-1}$.

A reaction mechanism similar to the above was also assumed by Yang and Libman for the primary process in photochemical addition of secondary amines to anthracene.[7]

Transient Absorption Spectra. If the reaction mechanism described above is valid, the transiently produced radicals may be detected by means of laser photolysis or conventional flash photolysis. The results of measurements for pyrene–NMA–hexane and pyrene–DBAm–hexane systems are given in Figs. 2 and 3, respectively. Absorption bands were observed in the 380—430 nm region, which could be explained as a superposition of absorption bands of pyrene triplet state and some unknown transient species. At the delay time of 50 μs, the T-T absorption band becomes much weaker while another absorption band remains fairly strong. Similar spectra were observed for all the systems of pyrene–primary and secondary amines. As an example, the transient spectra of pyrene–aniline–cyclohexane system obtained by means of the conventional flash photolysis method are shown in Fig. 4.

In order to identify the long lived transient species, 1,2-dihydropyrene in methylcyclohexane–isopentane (3 : 1) mixture was irradiated with a low pressure mercury lamp, and absorption spectra of photoproduct were measured. The spectrum obtained (Fig. 5a) might be assigned to the photoproduct radical (1-hydro-1-pyrenyl radical), being similar to the spectra shown in Figs. 2—4. As regards these results, we

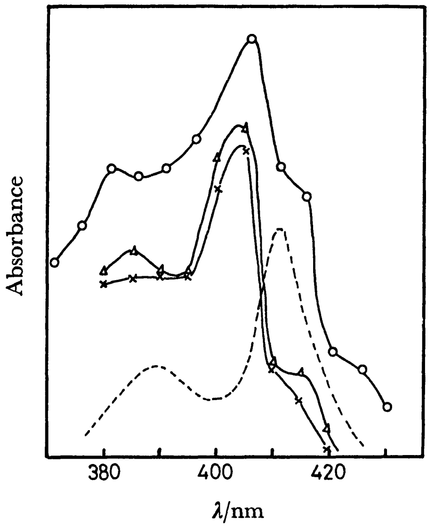


Fig. 2. Transient absorption spectra of pyrene-NMA-hexane system at room temperature.
—○—: 500 ns after laser oscillation, —△—: 50 μs after flash excitation, —×—: 200 μs after flash excitation, ----: T-T absorption spectrum of pyrene.

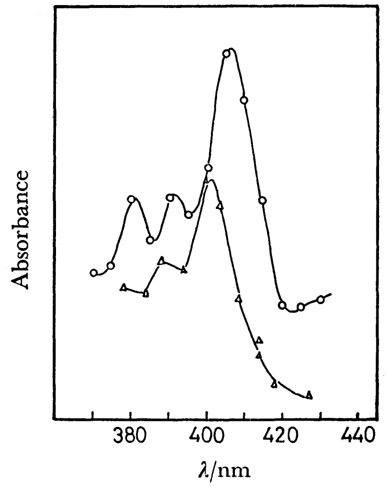


Fig. 3. Transient absorption spectra of pyrene–DBAm–hexane system at room temperature.
—○—: 1 μs after laser oscillation, —△—: 50 μs after flash excitation.

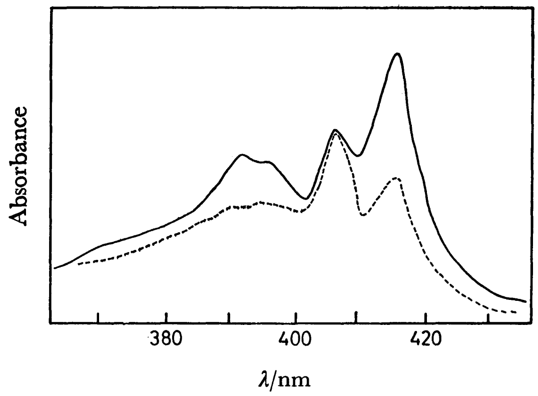


Fig. 4. Transient absorption spectra of pyrene–AN–cyclohexane system at room temperature obtained with conventional flash photolysis. Delay time from flash excitation, ——: 0 μs, ----: 50 μs.

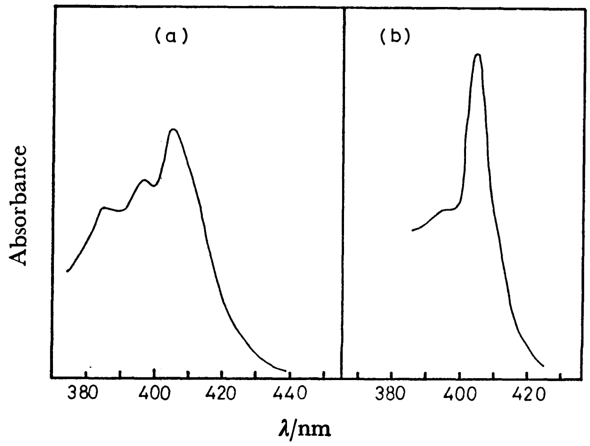


Fig. 5. (a) Absorption spectrum obtained by photolyzing 1,2-dihydropyrene at 77 K.
(b) Transient spectrum obtained by pulse radiolysis of ethanol solution of pyrene containing 1 vol% sulfuric acid.

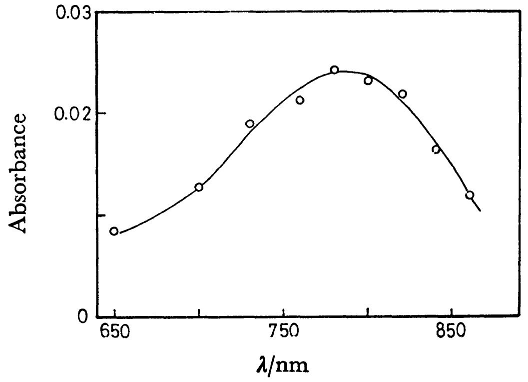
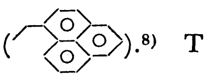


Fig. 6. Transient absorption spectrum of pyrene-DPA-hexane system at 200 μs after flash excitation. [Pyrene]$=2\times10^{-4}$ M, [DPA]$=1\times10^{-2}$ M.

made a semi-empirical open shell SCFMO calculation on the π-electronic state of the odd alternant hydrocarbon ().[8] The result indicates strong absorption bands at 3.7 and 4.9 eV, respectively, of which the lower energy one might be identified with the spectrum observed by means of the low temperature photolysis of 1,2-dihydropyrene and of the flash photolysis of the pyrene–amine systems.

On the other hand, pulse radiolysis studies on pyrene in ethanol containing 1 vol % sulfuric acid were made by Kira.[9] The reaction scheme of this system may be written as follows:

$$C_2H_5OH \rightsquigarrow e^-_{sol},\ \dot{H},\ C_2H_5OH_2^+,\ C_2H_5\dot{O},$$
and other neutral radicals

$$e^-_{sol} + H^+ \longrightarrow \dot{H}$$

$$\dot{H} + P_y \longrightarrow P_y\dot{H}$$

where P_y and $P_y\dot{H}$ are pyrene and 1-hydro-1-pyrenyl radical, respectively. The spectrum obtained by Kira is given in Fig. 5b. The spectrum shows peaks at 405 nm and 395 nm, being essentially the same as the spectrum obtained by subtracting the T-T absorption band of pyrene from the transient spectra observed in pyrene–amine systems.

Since the absorption spectra of anilino radicals were observed in the wavelength region of *ca.* 400 nm and their intensities are rather weak,[10,11] we cannot distinguish these bands from the observed spectra. However, in the case of pyrene–DPA–hexane system, the absorption spectrum of the diphenylamino radical with maximum at *ca.* 770 nm[12] was observed clearly by means of flash photolysis (Fig. 6). Thus, the formation of both kinds of radicals has been confirmed exprimentally.

The decay processes of transient species were examined by analyzing precisely the time dependence of the transient absorption intensity at several wavelengths. It was found that the pyrene triplet state shows a single exponential decay with a lifetime of *ca.* 30 μs in the case of pyrene–aniline system and that the decay of diphenylamino radical monitored at 780 nm is due to the bimolecular reaction. In contrast to the results of amino radical and pyrene triplet state, the decay process of 1-hydro-1-pyrenyl radical detected at 400 nm is rather complex. Namely, it shows an exponential decay at first over several hundred μs followed by a bimolecular decay. The two component decays in the wavelength region of the absorption band of 1-hydro-1-pyrenyl radical was observed for all pyrene-amine systems studied here. By analyzing the decay curves and time dependences of the spectra, it was established that the transient species which shows the bimolecular decay is formed from the 1-hydro-1-pyrenyl radical decaying unimolecularly. The mechanism of this two component decay process is not very clear at the present stage of investigation.

For interpretation of the fluorescence quenching mechanism in terms of the hydrogen atom transfer reaction, we assume that the reaction occurs in the singlet excited state. There is a possibility that the radicals are formed by the reaction in the triplet state. It is rather difficult to confirm this possibility since the absorption bands of the pyrene triplet state are overlapped with those of the radical. We have examined the problem by using the dilute solution of anthracene–DPA–hexane system with [anthracene]$=1\times10^{-4}$ M and [DPA]$=1\times10^{-3}$ M, since the T-T spectrum of anthracene is not overlapped with that of the hydrated radical as those of pyrene. The results of measurements by flash photolysis clearly show that no hydrogen atom transfer reaction occurs in the triplet state since no absorption of the diphenylamino radical is detected by the addition of DPA.

In order to evaluate the relative yield of 1-hydro-1-pyrenyl radical, the transient absorption due to the triplet state of the equimolar pyrene solution without amine was used as a standard. The relative yield was estimated by OD_R/OD_T, where OD_R and OD_T are absorbance extrapolated to $t=0$ of the 1-hydro-1-pyrenyl radical observed at 400 nm and that of pyrene triplet state of the standard solution observed at 415 nm, respectively. The values of OD_R/OD_T for various amines are summarized in Table 1, together with the

Table 1. Values of OD_R/OD_T for the pyrene-amine-hexane systems at room temperature

Amines	OD_R/OD_T	I_p (eV)
Aniline (AN)	0.28	7.95[a)]
N-Methylaniline (NMA)	0.78	7.6[a)]
N-Ethylaniline (NEA)	0.87	7.5[a)]
N-Butylaniline (NBA)	0.52	7.5[a)]
Diphenylamine (DPA)	0.82	7.4[a)]
Butylamine (BAm)	0.13	9.2[b)]
Diethylamine (DEAm)	0.12	8.0[c)]
Dibutylamine (DBAm)	0.52	7.7[c)]
Diisobutylamine (DIBAm)	0.62	—

a) G. Briegleb and J. Czekalla, *Z. Electrochem.*, **63**, 6 (1959). b) J. D. Morrison and A. J. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952). c) K. Watanabe and J. R. Mottl, *J. Chem. Phys.*, **26**, 1773 (1957).

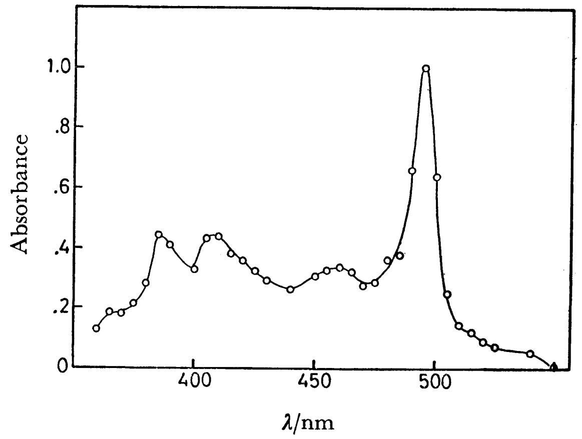


Fig. 7. Transient absorption spectra of pyrene-AN-acetonitrile system obtained by laser photolysis. [Pyrene]$=2\times10^{-4}$ M, [AN]$=1$ M.

values of I_p of amines. Since the k_q values for an amine differ, we should make correction for the difference by changing the concentrations of amines so that the extent of fluorescence quenching by various amines is equal. However, because of the large difference between the k_q values of the aromatic and aliphatic amines, it is difficult to adjust the quenching degree to the same extent. Thus, the fluorescence of pyrene in solutions examined here was quenched more than 99% in the case of aromatic amines and 90% in the case of aliphatic amines.

We see from Table 1 that OD_R/OD_T values for AN, BAm and DEAm are small as compared with the values for the other amines though the fluorescence of pyrene is quenched almost completely. The result suggests that in the case of these amines a process of returning to the ground state from radical pair $\dot{A}H....\dot{D}$ is predominant.

The quenching process of triplet benzophenone by amine has been directly demonstrated with the laser photolysis method by Arimitsu *et al.*[4,13] It has been found that no ketyl radical formation but ionic photodissociation to benzophenone anion and amine cation occurs in a strongly polar solvent such as acetonitrile, while photoreduction due to the hydrogen atom transfer from amine to ketone occurs efficiently in a nonpolar solvent, and these processes compete with each other, depending upon the solvent polarity.

In the present system, analogous solvent effects upon the transient absorption spectra as well as those upon the quenching rate constant have been observed. The k_q values for pyrene–AN, pyrene–DEAm and pyrene–DBAm systems in various solvents of different polarity are given in Table 2. We see that k_q increases with an increase in solvent polarity. The transient spectra of pyrene–AN–acetonitrile system show strong absorption bands of solvated radical ions (Fig. 7).

The k_q values for the pyrene–aniline system are much smaller than those of the other pyrene–aromatic amine systems. This seems to indicate that a considerable additional activation energy over that for the diffusional motion is necessary not only in the case of the pyrene–aliphatic amine systems but also for the quenching process in the pyrene–aniline system. The additional activation energy necessary for the charge transfer in the encounter complex becomes smaller with a decrease in the I_p values of amines. The result for the solvent effect upon the k_q value indicates that not only the I_p value of the quencher but also the solvent polarity affect the additional activation energy. Namely, it decreases with an increase in the solvent polarity, and the k_q value in polar solvents involves both hydrogen atom transfer and ionic dissociation. These two processes compete with each other, the ionic dissociation being predominant in a strongly polar solvent such as acetonitrile.

Since the $(A^-...HD^+)$ state is stabilized in polar solvents while the energy of $(\dot{A}H\cdots\dot{D})$ is independent of solvent polarity, the heteroexcimer fluorescence may be detected in slightly polar solvents, where the ionic dissociation is not predominant.

The authors are grateful to Professor S. Kato and his co-workers for use of the apparatus for flash photolysis, and for their valuable discussions concerning the experimental technique. The authors express their

Table 2. Solvent effects upon k_q values of pyrene-amine systems at room temperature

Solvent	AN	NMA	DEAm	DBAm
Hexane	5.7×10^8 M^{-1} s^{-1}	1.0×10^{10} M^{-1} s^{-1}	2.7×10^7 M^{-1} s^{-1}	3.0×10^7 M^{-1} s^{-1}
Diethyl ether			1.7×10^8	2.0×10^8
2-Propanol	2.6×10^9			
Acetone			3.8×10^8	8.4×10^8
Methanol		9.0×10^9		
Acetonitrile	5.3×10^9	1.5×10^{10}	2.7×10^8	8.7×10^8

cordial thanks to Dr. A. Kira of the Institute of Physical and Chemical Research for the measurement of the absorption spectrum of 1-hydro-1-pyrenyl radical by means of pulse radiolysis. The authors' thanks are also due to Mr. Y. Fujiwara and Mr. K. Mochizuki for their assistance.

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