Conclusions

The group 8 transition-metal ions Fe⁺, Co⁺, and Ni⁺ all show similar reactivity with linear alkanes. Differences in reactivity can be understood by considering the thermochemistry in Tables IV and V. All three metal ions dehydrogenate linear alkanes via initial insertion into C–C bonds (Scheme III), producing a bis-(olefin) complex. In addition, Fe⁺ also dehydrogenates linear alkanes via initial insertion into C–H bonds (Scheme II).

Collision-induced dissociation (CID) is a powerful technique for studying the structures of organometallic complexes and hence yielding mechanistic information on ion product formation. In addition, a variety of fundamental chemical information is available from studying the CID fragmentation pathways of known structures. Ligand rearrangements are encountered in CID of olefins larger than butene bound to metal ion centers. Therefore, caution must be exercised in interpreting the CID spectra of organometallic ions since the observation of cleavage products does not necessarily imply attachment of that species directly onto the metal. This also holds for interpretation of ion–molecule reactions where the ion–molecule reaction complex may contain sufficient internal energy for rearrangement to occur prior to displacement.

In the case of organometallic species, displacement by multi-coordinating ligands such as benzene may occupy sufficient coordination sites that can, in turn, decrease metal-centered rearrangements.

We are currently studying the reactions of Fe⁺, Co⁺, and Ni⁺ with a host of branched alkanes, olefins, and ketones. Determination of product structures will aid in the elucidation of reaction mechanisms. Secondary and tertiary reactions are also being investigated for olefins and ketones. In addition, we are also looking at the chemistry of the second- and third-row group 8 transition-metal ions.

Picosecond Laser Photolysis Studies of Deactivation Processes of Excited Hydrogen Bonding Complexes. 3. Detection of the Nonfluorescent Charge-Transfer State in the Excited 1-Aminopyrene–Pyridine Hydrogen Bonded Pair and Related Systems[†]

Noriaki Ikeda, Hiroshi Miyasaka, Tadashi Okada, and Noboru Mataga*

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan. Received December 20, 1982

Abstract: The mechanism of the fluorescence quenching observed when two conjugated π-electron systems are directly combined by hydrogen bonding has been studied in the case of the 1-aminopyrene–pyridine system by means of the picosecond laser photolysis method. Time-resolved transient absorption spectra were observed for the excited hydrogen bonded pair and fluorescence decay curves of 1-aminopyrene in the presence of pyridine were determined by means of a picosecond streak camera. It has been confirmed that a rapid equilibrium between the locally excited state (D*–H···A) and the charge-transfer state (D⁺–H···A⁻) of the hydrogen bonded pair is realized within the time resolution of our picosecond apparatus. It has been established that the fluorescence quenching in the 1-aminopyrene–pyridine system is due to the formation of a nonfluorescent charge-transfer state in the excited hydrogen bonded pair. In relation to these studies, it has been demonstrated that, although the fluorescence of N,N-dimethyl-1-aminopyrene in nonpolar solvents is not affected by added pyridine, indicating the crucial importance of the hydrogen bonding for the charge transfer to occur, it forms a short-lived nonfluorescent exciplex with 4-cyanopyridine which is a much weaker proton acceptor but a stronger electron acceptor than pyridine.

Inter- and intramolecular hydrogen bonding interactions can affect rather drastically the photophysical and photochemical properties of a large number of molecular systems. It is well-known that hydrogen bonding interaction frequently leads to the quenching of fluorescence, especially when two conjugate π-electronic systems are directly combined by hydrogen bonding interaction.[1–4]

CT (charge transfer) interaction between proton-donor and -acceptor π-electron systems via the hydrogen bond was suggested as a possible mechanism of the quenching.[1] Namely, a kind of nonfluorescent exciplex was assumed to be formed in the course of this quenching process. Hydrogen atom transfer from proton donor to acceptor in the hydrogen bonded pair was also suggested as a possible mechanism of quenching.[2]

In relation to this problem, we have undertaken a systematic picosecond (ps) laser photolysis study of a series of conjugated π-electronic hydrogen bonding systems, in view of the importance

of this problem in elucidating the photochemical and photobiological primary processes. We have detected for the first time the formation of a transient CT state in the excited state of several conjugated π-electronic hydrogen bonding systems.[5–8] In this paper results of 1-aminopyrene–pyridine and related systems will be reported.

(1) (a) Mataga, N.; Tsuno, S. *Naturwissenschaften* **1956**, *10*, 305. (b) Mataga, N.; Tsuno, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 711. (c) Mataga, N. *Ibid.* **1958**, *31*, 481. (d) Mataga, N.; Torihashi, Y.; Kaifu, Y. *Z. Phys. Chem. (Frankfurt/Main)* **1962**, *34*, 379. (e) Mataga, N.; Tanaka, F.; Kato, M. *Acta Phys. Pol.* **1968**, *34*, 733.
(2) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.
(3) (a) Kikuchi, K.; Watarai, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 749. (b) Yamamoto, S.; Kikuchi, K.; Kokubun, H. *Ibid.* **1976**, *49*, 2950.
(4) Martin, M. M.; Ware, W. R. *J. Phys. Chem.* **1978**, *82*, 2770.
(5) (a) Ikeda, N.; Okada, T.; Mataga, N. *Chem. Phys. Lett.* **1980**, *69*, 251. (b) Ikeda, N.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1025.
(6) Martin, M. M.; Ikeda, N.; Okada, T.; Mataga, N. *J. Phys. Chem.* **1982**, *86*, 4148.
(7) Ikeda, N.; Okada, T.; Mataga, N., to be published elsewhere.
(8) Ikeda, N.; Nishida, T.; Mataga, N. to be published elsewhere.

[†]Parts 1 and 2 of this series are published respectively in ref 5b and 6.

Experimental Section

Methods. Picosecond transient absorption spectra and fluorescence decay curves were measured by using a microcomputer-controlled ps laser photolysis system with a repetitive mode-locked Nd^{3+}:YAG laser as the excitation source. The third harmonic of a single ps pulse, producing typically a pulse of 25-ps duration (fwhm) and about 0.7-mJ output energy, was used for exciting aminopyrenes.

A ps continuum generated by focusing the fundamental pulse into D_2O was used as the monitoring light source for the transient absorption spectral measurements. The monitoring light transmitted by the excited sample is detected by a multichannel photodiodes array (MCPD1, 512 channel) through a spectrograph. A part of the continuum beam is directed to another spectrograph multichannel photodiodes array arrangement (MCPD2) and is used as the reference for the spectral distribution of the analyzing light. Transient absorption spectra covering a wavelength range of 380 nm can be obtained by two laser shots with and without an excitation pulse. Both MCPD's are connected to a microcomputer system which calculates the transient spectra and averages the results obtained by a series of laser shots under approximately the same conditions at each delay time.

Fluorescence decay curves were measured with a streak camera (Hamamatsu C979). The output of the streak camera was imaged onto a SIT camera (Hamamatsu C1000-18X). The signal was transferred to a microcomputer system for storage and analysis. The spatial sensitivity of these cameras was calibrated and a deviation from the constant streak speed was also corrected. Details of this ps laser photolysis apparatus are given elsewhere.[9]

Measurements of relatively long fluorescence lifetimes were made as follows. The sample solution was excited by the second harmonic of a ps ruby laser and the fluorescence decay curve was observed with a high-speed tandem microchannel plate photomultiplier (HTV R-1194 UX) and a fast storage oscilloscope (Tektronix 7834-7A19-7B80) combination, or a N_2 laser with 1-kW peak power as an exciting light source combined with a 1P28 photomultiplier and a sampling oscilloscope was employed for the determination of the lifetime.

A microcomputer-controlled N_2 laser photolysis system was used for the measurements of transient absorption spectra in the μs region.[10] The usual absorption and fluorescence spectra were recorded by using respectively a JASCO UVIDEC-1 type spectrophotometer and an Aminco-Bowman spectrophotofluorometer.

Materials. 1-Aminopyrene (Tokyo Kasei) was recrystallized twice from ligroin and sublimated under vacuum. Synthesized and purified N,N-dimethyl-1-aminopyrene was kindly supplied by Dr. M. Furue of this University and used as received. Pyridine (spectrograde, Kishida) was refluxed over calcium hydride and distilled. 4-Cyanopyridine (GR grage, Nakarai) was recrystallized twice from ligroin and sublimated under vacuum. Hexane (spectrograde, Dotaito) was refluxed on sodium metal wire and distilled. Acetonitrile (spectrograde, Merck) was refluxed over calcium hydride and distilled. *sec*-Butyl chloride (*sec*-BuCl) (Tokyo Kasei) was passed through a column of alumina and distilled twice. All sample solutions for measurements were deaerated by freeze-pump-thaw cycles.

Results and Discussion

Hydrogen Bonding in the Ground State. Hydrogen bonding interaction between 1-aminopyrene (AP) and pyridine (P) in the ground state is rather weak, but we can recognize the red shift and broadening of the absorption band due to hydrogen bonding interaction in hexane solution. The equilibrium constant K_g of 1:1 hydrogen bonding is estimated to be $\sim 3\ M^{-1}$ (20 °C). The absorption spectra of AP in hexane, however, were little affected by the addition of 4-cyanopyridine (CNP), which means that the ability of CNP to make hydrogen bond with AP is much smaller than that of P. Moreover, the hydrogen bonding interaction between AP and pyridines in polar solvents becomes much weaker than in nonpolar solvents due to solvation of AP and pyridines.

Hydrogen Bonding Effect upon Fluorescence. The hydrogen bonding ability of aromatic amine compounds is considerably larger in the lowest excited singlet state than in the ground state, which results in the red shift of the electronic spectra due to hydrogen bonding. The larger hydrogen bonding ability in the excited state will result in the change of fluorescence spectra caused
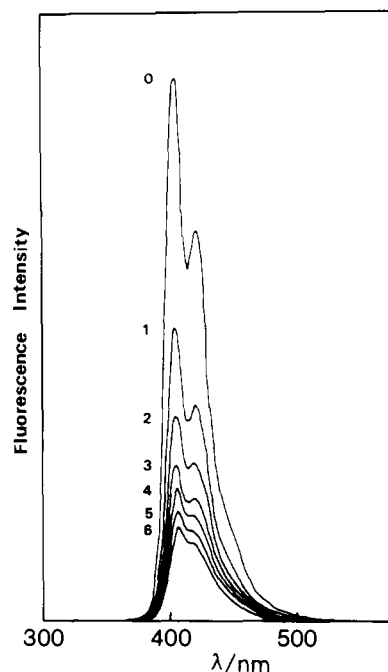
(9) (a) Masuhara, H.; Ikeda, N.; Miyasaka, H.; Mataga, N. *J. Spectrosc. Soc. Jpn.* **1982**, *31*, 19. (b) Miyasaka H.; Masuhara, H.; Mataga, N. *Laser Chem.*, in press.

(10) Yasohima, S.; Masuhara, H.; Mataga, N.; Suzaki, H.; Uchida, T.; Minami, S. *J. Spectrosc. Soc. Jpn.* **1981**, *30*, 93.


Figure 1. Fluorescence spectra of the AP–P system in hexane. [AP] = 5×10^{-5} M. [P]: (1) 0.0052 M, (2) 0.0103 M, (3) 0.0155 M, (4) 0.0207 M, (5) 0.0258 M, (6) 0.0310 M.

Table I. Fluorescence Quenching Rate Constants of the AP-P and AP-CNP Systems

solvent	τ_0, ns	k_q, M^{-1} s^{-1}	
		(P)	(CNP)
hexane	12.5	1.2×10^{10}	2.2×10^{10}
acetonitrile	9.2	1.0×10^{8}	1.4×10^{10}
water	5.5	6.2×10^{9}	

by the hydrogen bonding at much smaller acceptor concentrations than those necessary for the change of the absorption spectra. Actually, this is confirmed in the case of the AP–P system. Since the fluorescence quenching occurs in the region of P concentrations where the AP absorption spectrum is not affected by the hydrogen bonding interaction, the simple Stern–Volmer equation was used for the analysis of the quenching reaction. As an example, progressive changes of fluorescence spectra of AP caused by adding P in hexane solution are indicated in Figure 1, and values of the quenching rate constant (k_q) of the AP–P as well as the AP–CNP systems in hexane, acetonitrile, and water are shown in Table I together with the values of the observed fluorescence lifetime (τ_0) of AP.

The quenching by pyridine in hexane solution is diffusion controlled but k_q in acetonitrile solution is much smaller than that in hexane solution, which may be ascribed to the hindering of hydrogen bonding interaction between AP and P due to the solvation of both molecules by strongly polar acetonitrile. We have confirmed that the fluorescence of N,N-dimethyl-1-aminopyrene (DMAP) is not affected by P in both hexane and acetonitrile solutions, which shows clearly that the hydrogen bonding interaction is crucial for the quenching to occur.

In the case of the quenching by CNP, the reaction is diffusion controlled in both hexane and acetonitrile solutions, which indicates that the quenching is due to direct charge transfer complex formation or electron transfer in the excited state rather than hydrogen bonding interaction. This interpretation is supported by the fact that the fluorescence of DMAP is quenched by CNP in both hexane and acetonitrile solutions.

At high concentrations of added pyridine in hexane solution and even in a pure pyridine solution, fluorescence of AP is not completely quenched. We can recognize a weak and red shifted fluorescence band of the hydrogen bonded complex. For example,
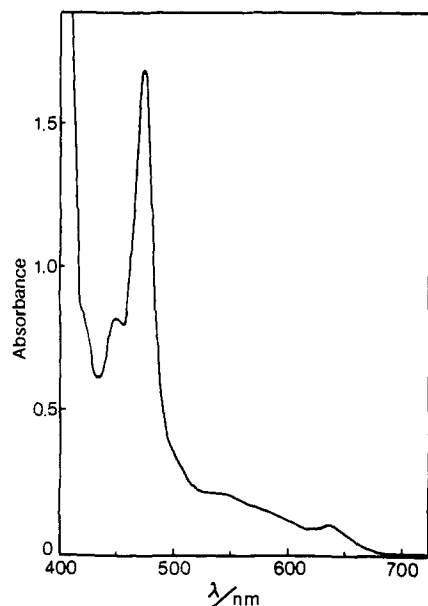
Figure 2. The absorption spectrum of the AP cation radical produced by ^{60}Co γ radiolysis in *sec*-BuCl matrix at 77 K.
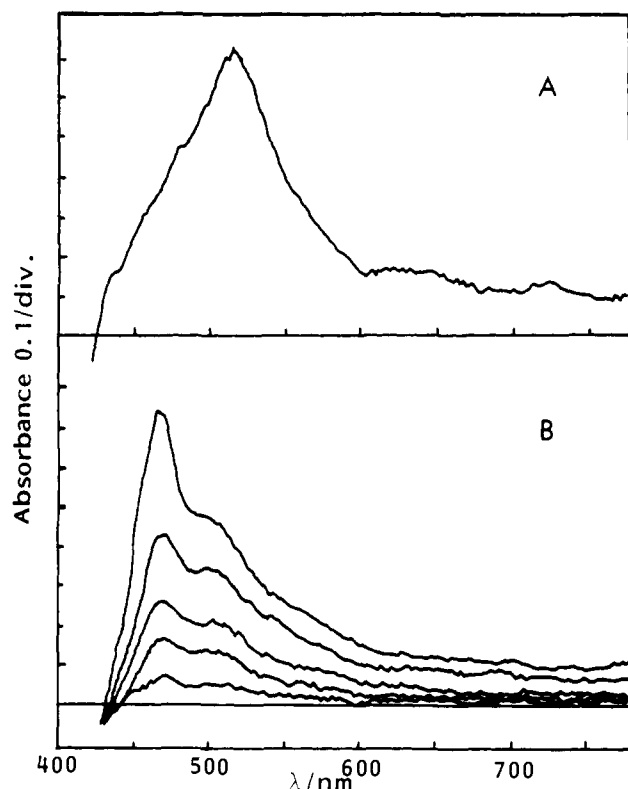

Figure 3. Transient absorption spectra of AP in hexane (A) and in acetonitrile (B) at 100-ps delay time from the exciting pulse. In B, spectra with higher absorbance were obtained by exciting the solution with a stronger pulse.

the red shift of the absorption band due to hydrogen bonding with pyridine in hexane amounts to ca. 680 cm^{-1} while that of the fluorescence band is about 2000 cm^{-1}.

Transient Absorption Spectra of AP Obtained by means of the Picosecond Laser Photolysis Method. If the CT interaction between the hydrogen bonded pair in the excited state is responsible for the fluorescence quenching, one may expect to observe the transient CT state, (AP$^{+}\cdots$P^{-}), in addition to the locally excited state, (AP$^{*}\cdots$P), by means of ps spectroscopy.

In order to compare our spectrum with the transient spectra of the hydrogen bonded pair, we have measured the absorption spectrum of the AP cation radical produced in *sec*-BuCl matrix
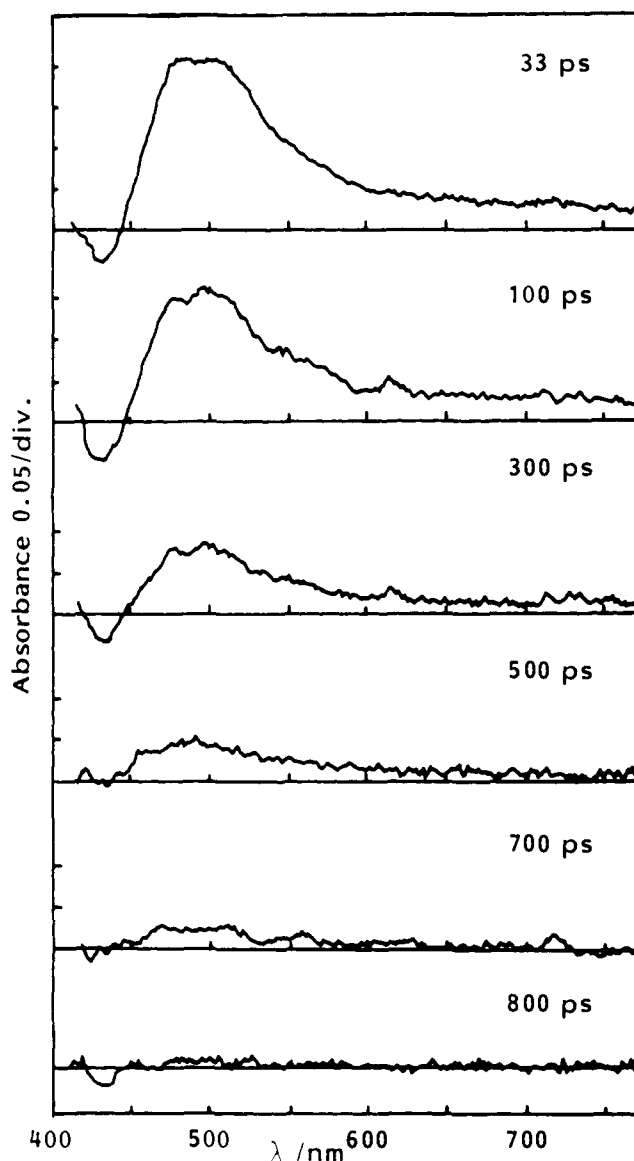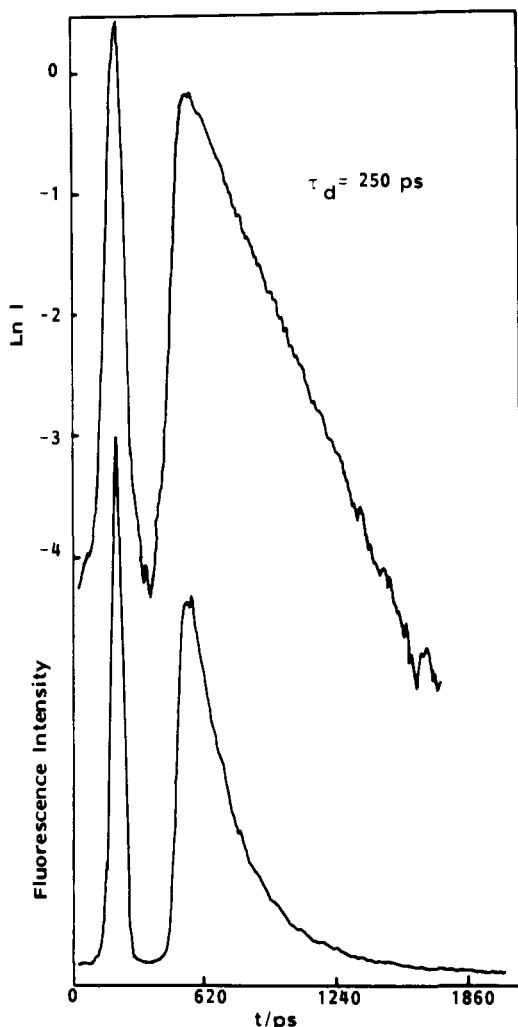

Figure 4. Transient absorption spectra of the AP–P system in hexane. The delay times from the exciting pulse are indicated in the figure. [AP] = 5 × 10^{-5} M, [P] = 1.3 M.

at 77 K by ^{60}Co γ radiolysis as shown in Figure 2, which shows a sharp peak at 475 nm. The S$_n$ ← S$_1$ absorption spectra of AP in hexane as well as that in acetonitrile solutions are shown in Figure 3. The transient absorbance in hexane solution is proportional to the exciting laser pulse intensity. However, the transient absorbance is proportional approximately to the square of the exciting pulse intensity, when it is relatively strong, in acetonitrile solution. Accordingly, the spectrum in the latter solution is mainly due to the AP cation radical produced by biphotonic ionization. In accordance with this reasoning, the position of the absorption peak in acetonitrile solution is close to the AP cation radical indicated in Figure 2. Since the polarity of solution may be affected considerably by addition of a high concentration of P in hexane solution, the examination of the exciting pulse intensity effect upon the observed transient absorbance will be of crucial importance for the detection of the CT state in the excited AP–P hydrogen bonded system.

Picosecond Transient Absorption Spectra and Fluorescence to the AP–P System. ps laser photolysis studies of the AP–P system were made under the condition that the AP fluorescence is sufficiently quenched by added P. An example of the transient absorption spectra of the AP–P system in hexane is shown in Figure 4, where it has been confirmed that the absorbance at 470 nm is proportional to the exciting pulse intensity and almost all AP molecules are hydrogen bonded with P already in the ground

Figure 5. Fluorescence decay curve of the AP–P hydrogen bonded complex. (The same sample as was used for the transient absorption measurement indicated in Figure 4 was used here.)

state. The proportionality between the 470-nm absorbance and exciting pulse intensity was confirmed also for other systems with a higher concentration of P ([P] = 2.15 M in hexane and pure pyridine solution).
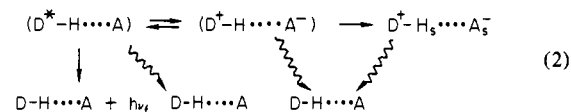
The transient absorption spectra in Figure 4 can be expressed by superposing the absorption bands of the CT state (D^+–H···A^-) and those of the locally excited state (D^*–H···A) of the hydrogen bonded pair, where D–H and A represent AP and P, respectively. The shape of the transient spectra does not show any characteristic change during the course of the decay which has been confirmed to be single exponential with lifetime τ_d = 260 ps. We have measured also the decay curve of the weak fluorescence of the hydrogen bonded complex as shown in Figure 5. The fluorescence decay was single exponential with lifetime τ_d = 250 ps which agrees satisfactorily with the value obtained from the transient absorption measurements.

The above results suggest strongly that a rapid equilibrium between (D^+–H···A^-) and (D^*–H···A) states is established immediately after excitation of the hydrogen bonded complex. The fluorescence will be emitted from the (D^*–H···A) state but the CT state will be nonfluorescent and rapidly deactivated.

$$(D^*\text{–H}\cdots A) \;\rightleftharpoons\; (D^+\text{–H}\cdots A^-) \tag{1}$$

$$D\text{–H}\cdots A + h\nu_f \qquad D\text{–H}\cdots A \quad D\text{–H}\cdots A$$
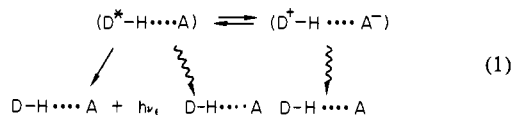
We have obtained quite similar results also in the case of 7*H*-dibenzocarbazole–pyridine system in nonpolar solvent, which can be interpreted on the basis of the same model.[6]

Similar results were obtained also for the solutions with higher concentrations of P. Namely, both decay times obtained from the transient absorption and fluorescence measurements were a few hundred picoseconds and agreed with each other. In the case of AP in pyridine, however, in addition to the few hundred picosecond decay times observed in both transient absorption and fluorescence measurements, a slow component with decay time of a few nanoseconds was observed only for the transient absorption. The spectra of the slow component was very similar to that of the AP cation radical. The slow component might be a solvated ion pair produced from the CT state.

$$(D^*\text{–H}\cdots A) \;\rightleftharpoons\; (D^+\text{–H}\cdots A^-) \;\longrightarrow\; D^+\text{–H}_s\cdots A_s^-$$

$$D\text{–H}\cdots A + h\nu_f \quad D\text{–H}\cdots A \qquad D\text{–H}\cdots A \tag{2}$$

It should be noted here that, according to our measurements, the AP–P–hexane as well as the AP–P two-component systems do not show any transient absorption due to reaction products or dissociated ion radicals in a few hundred nanosecond ($\sim$10 μs) regions. Therefore, the CT state of the AP–P–hexane system seems to be deactivated without any reaction and the slow component in the case of the AP–P system should be a geminate pair deactivating rapidly.

Transient Absorption Spectra of the AP–CNP System. Fluorescence of AP can be completely quenched by CNP in both nonpolar and polar solvents due to the direct CT interaction without hydrogen bonding as discussed already. Although we have not made detailed ps time-resolved absorption spectral measurements on the AP–CNP system, we have observed transient spectra which can be ascribed to the nonfluorescent CT complex in hexane and benzene solutions and also those of the solvated ion pairs in acetonitrile solution. We have made more detailed ps laser photolysis studies of nonfluorescent exciplex formation in the case of the DMAP–CNP system, results of which will be discussed in the following.

Picosecond Laser Photolysis Studies on the DMAP–CNP Nonfluorescent Exciplex Formation. Fluorescence of DMAP in hexane as well as acetonitrile solution is not quenched by P, which demonstrates clearly the importance of hydrogen bonding interaction in the fluorescence quenching of the AP–P system. However, DMAP fluorescence is quenched strongly by CNP in both hexane and acetonitrile solutions. The quenching by CNP is probably due to the direct CT interaction but no exciplex fluorescence can be detected in hexane solution. In order to confirm the CT state formation for the excited DMAP–CNP system and to compare the results with those for the AP–P system, we have examined the transient spectra of the DMAP–CNP system.

The time-resolved transient absorption spectra of the DMAP–CNP system in hexane solution are shown in Figure 6. The absorption spectra of the S_1 state of DMAP in hexane and DMAP cation radical produced by photoinduced electron transfer to CNP in acetonitrile solution respectively are indicated in Figure 7, parts A and B for comparison. The $S_n \leftarrow S_1$ spectrum in hexane is broad compared with that of AP and shows a peak around 550 nm and a shoulder at 500 nm. The lifetime of the S_1 state of DMAP in hexane has been determined to be 5.3 ns. The absorption spectrum of DMAP cation radical in Figure 7B, which was taken at sufficiently long delay time to avoid the contribution from the $S_n \leftarrow S_1$ absorption, is rather similar to that of the AP cation radical and shows maximum at ca. 470 nm. Since similar spectra can be observed also in the μs region by means of N_2 gas laser photolysis, the observed spectrum is due to the dissociated ions.

One can see clearly from Figure 6 that the absorption spectra at short delay times, which are rather similar to that of the S_1 state shown in Figure 7A, change gradually with an increase in the delay time and become quite similar to the spectrum of the DMAP cation indicated in Figure 7B. This spectral change is a direct demonstration that the nonfluorescent exciplex is formed between excited DMAP and ground-state CNP in hexane.
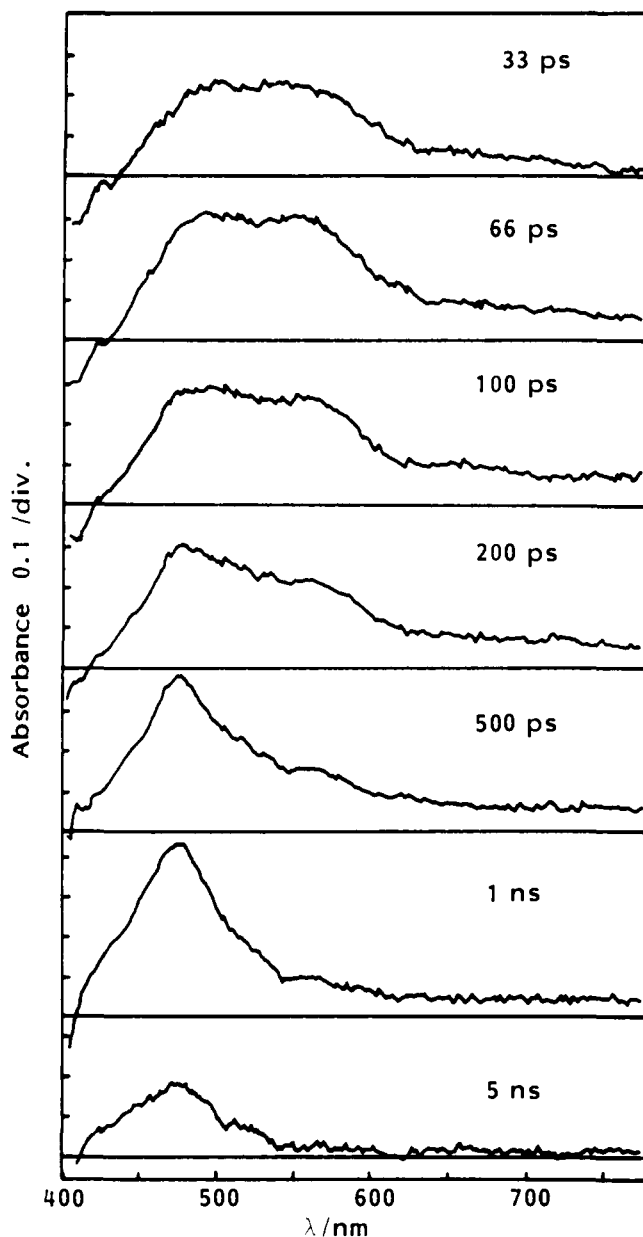
5210 *J. Am. Chem. Soc., Vol. 105, No. 16, 1983*

Ikeda et al.

Figure 6. Transient absorption spectra of the DMAP–CNP system in hexane solution. The delay times from the exciting pulse are indicated in the figure. [DMAP] = 1 × 10⁻⁴ M, [CNP] = 0.03 M.
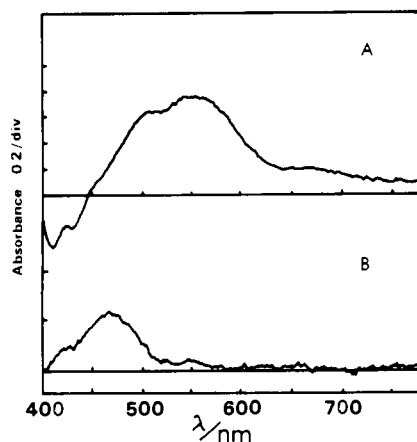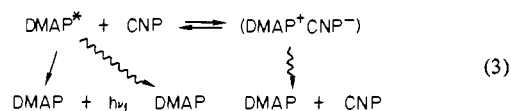

Figure 7. (A) The $S_n \leftarrow S_1$ absorption spectrum of DMAP in hexane measured at 100 ps from the exciting pulse. [DMAP] = 1 × 10⁻⁴ M. (B) The transient absorption spectrum of the DMAP–CNP system in acetonitrile measured at 5 ns from the exciting pulse. [DMAP] = 1 × 10⁻⁴ M, [CNP] = 0.1 M.

$$\text{DMAP}^* + \text{CNP} \rightleftharpoons (\text{DMAP}^+\text{CNP}^-)$$

$$\text{DMAP} + h\nu_f \quad \text{DMAP} \quad \text{DMAP} + \text{CNP} \tag{3}$$

Although the nonfluorescent character of this CT state of the DMAP–CNP system is the same as that of the AP–P hydrogen bonding system, the lifetime of the latter (200–300 ps) is much shorter than that of the former (~5 ns). This result indicates that the nonradiative deactivation process in the excited AP–P hydrogen bonding complex is faster compared with that in the DMAP–CNP exciplex. This is probably related to the existence of the

$$\text{>N–H}\cdots\text{N<}$$
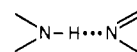
hydrogen bonding in the CT state. Details of the quenching mechanism will be discussed in the later part of the present paper. On the other hand, the relatively long lifetime of the DMAP–CNP exciplex suggests that the radiative transition probability (k_f) of this nonfluorescent exciplex is very small. Namely, since its fluorescence yield should be $\sim 10^{-4}$ and the observed lifetime is ca. 5 ns, $k_f \sim 2 \times 10^4$ s⁻¹. This k_f value is considerably smaller than that (5×10^6 s⁻¹) of the typical pyrene–N,N–dimethylaniline (DMA) exciplex in hexane solution.[11]

It might be possible that the structure of the DMAP–CNP exciplex is not plane-parallel because of a very weak hydrogen bonding interaction between the ring nitrogen of the CNP anion and the C–H hydrogen of the dimethylamino group of the DMAP cation in the CT state, which makes the orbital overlap between two π-electron systems very small, leading to the very small k_f value.

On the CT Interaction in the Excited Hydrogen Bonding Systems and the Mechanism of the Deactivation to the Ground State. The results of the ps laser photolysis studies described above have demonstrated clearly the formation of the state produced by CT from excited AP to P in the hydrogen bonded complex as a transient state in the quenching process. We had observed the formation of such a CT state also in the case of 2-naphthyl-amine–P, 13H-dibenzocarbazole–P and 7H-dibenzocarbazole–P systems. In the case of the present system, rapid equilibrium between (D*–H···A) and (D⁺–H···A⁻) is attained during the excited-state lifetime, which is quite similar to the case of the 7H-dibenzocarbazole–P system, as mentioned already. These studies have confirmed that the hydrogen bonding quenching of the fluorescence is due to the formation of the nonfluorescent CT state in the excited hydrogen bonded pair. Moreover, we have observed also the formation of the nonfluorescent exciplex state in the case of the DMAP–CNP as well as the AP–CNP system in hexane, where the direct CT interaction without forming the hydrogen bond is responsible for the fluorescence quenching in both systems.

The feasibility of the intermolecular electron transfer in the excited state may be examined by evaluating the standard free energy change $\Delta G°$ for the process, D*···A → D⁺···A⁻, according to eq 4, where $E(D/D^+)$ and $E(A^-/A)$ are respectively the oxi-

$$\Delta G° = E(D/D^+) - E(A^-/A) - (e^2/\epsilon R) - \Delta E + \Delta G_s$$

$$\Delta G_s = (e^2/2)\left(\frac{1}{R} + \frac{1}{R^-}\right)\left(\frac{1}{\epsilon} - \frac{1}{37.5}\right) \tag{4}$$

dation potential of the electron donor and the reduction potential of the electron acceptor in acetonitrile (vs. SCE). R is the center to center distance between D⁺ and A⁻ assumed to be 7 Å. ΔE is the $S_1 - S_0$ energy gap of D and ΔG_s is the correction term for the solvation energy of the cation and the anion with radius R^+ and R^-, respectively, in a solvent with dielectric constant ϵ. The value of $E(D/D^+)$ of AP is 0.43 eV according to our measurement (Pt vs. SCE in acetonitrile with 0.1 M LiClO₄) and that of DMAP is 0.76 eV.[12] With use of the $E(A^-/A)$ value of P taken from

(11) Mataga, N.; Okada, T.; Yamamoto, N. *Chem. Phys. Lett.* **1967**, *1*, 119.

literature,[2] the $\Delta G°$ values in hexane solution were obtained to be +21.6 kcal/mol for AP–P, –6.1 kcal/mol for AP–CNP, +28.2 kcal/mol for DMAP–P, and +2 kcal/mol for DMAP–CNP. At the actual distance of hydrogen bonding interaction or exciplex formation, the donor and acceptor will be closer resulting in the smaller $\Delta G°$ values.

Moreover, the hydrogen bonding interaction will decrease the ionization potential of the proton donor and increase the electron affinity of the proton acceptor facilitating the CT from the proton donor to the proton acceptor. The hydrogen bonding interaction between AP and P is stronger in the excited state than in the ground state, leading to the red shift of the electronic spectra. The stronger hydrogen bonding interaction in the excited state will make the proton in the hydrogen bond shift slightly toward acceptor, which will further lower the ionization potential of the π-electron system of AP and enhance the electron affinity of the π-electron system of P, resulting in the stronger CT interaction. As a result of the stronger CT interaction, the proton of the donor will be further shifted toward the acceptor. Such a shift of the proton in the CT state, however, seems to cause a large destabilization of the ground state where the CT from the proton donor to the acceptor is negligible. If this is the case, the energy gap between the CT state and the ground state becomes very small, making the nonradiative deactivation feasible.

The above interpretation of the deactivation mechanism due to the hydrogen bonding interaction is supported also by the results of recent detailed ab initio MO CI studies upon such model systems as aniline–pyridine and phenol–pyridine, which predict a strong CT from D–H in the S_1 state to hydrogen bonded A when the D–H proton is slightly moved toward A and a large destabilization of the ground state with the proton shift.[13]

It should be noted here with respect to the proton shift in the CT state that a neutral radical formation due to the mechanism of CT followed by proton transfer may be realized in an extreme case: $(D^*–H\cdots A) \rightarrow (\dot{D}^+–H\cdots\dot{A}^-) \rightarrow (\dot{D} + H–\dot{A})$. In the case

of the present system as well as dibenzocarbazole–P systems,[6] however, the formation of the neutral radicals is negligible, which indicates that the crossing to the ground state from the CT state is considerably faster than the neutral radical formation.

Comparison of Transient Behaviors of the AP–P Hydrogen Bonding System with Those of the DMAP–CNP Exciplex System. The lifetime of the CT state of the DMAP–CNP system in hexane (~5 ns) is much longer than that of the AP–P hydrogen bonding system in the same solvent (~260 ps). This difference is probably due to the fact that a very rapid nonradiative crossing to the ground state from the CT state is the most dominant process in the latter, which is a characteristic phenomenon observed when two conjugated π-electron systems are directly combined by hydrogen bonding, while the nonradiative process from the exciplex state of the former system is considerably slower owing to the absence of such a hydrogen bonding interaction directly combining the two conjugate π-electronic systems.

However, since the radiative transition probability k_f of the DMAP–CNP exciplex in hexane is much smaller than that of the typical pyrene–DMA exciplex, a nonparallel structure of the CT state where a weak hydrogen bonding interaction exists between the ring nitrogen of the CNP anion and the C–H hydrogen of the dimethylamino group of the DMAP cation has been assumed, as is discussed in a previous section. Notwithstanding the existence of the hydrogen bonding interaction assumed above, since it does not directly combine the two conjugate π-electron systems, it does not cause the rapid deactivation process in a few hundred picosecond region.

(12) Furue, M., private communication.
(13) Tanaka, E.; Nishimoto, K., private communication.

Electron Spin Resonance Studies of 1,4-Disilacyclohexa-2,5-diene Free Radical Reactions

Jonathan D. Rich and Robert West*

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. Received December 17, 1982

Abstract: The photolysis reaction between hexamethyl-1,4-disilacyclohexa-2,5-diene and *tert*-butyl peroxide in cyclopropane solvent has been studied by electron spin resonance. At low temperature (–105 °C) a *tert*-butoxy radical adds to one of the carbon–carbon double bonds to form an α-silyl carbon-centered radical. At higher temperatures (–30 °C) initial abstraction of a silane hydrogen apparently occurs. The resulting silyl radical is not observed but instead undergoes an unprecedented rearrangement to yield a silacycloprop-2-yl radical. A similar rearrangement reaction is seen when hexamethyl-1,4-dichloro-1,4-disilacyclohexa-2,5-diene is coirradiated with a tetrasubstituted tetraaminoethylene. Confirmation of the ESR assignments was done with the aid of deuterium-labeling experiments and computer simulation of the observed ESR spectra.

Organosilicon radicals which are substituted by aryl or olefinic groups are presently of considerable interest.[1] Electron spin resonance studies of these radicals can provide valuable information about spin delocalization onto the carbon framework,[2]

resulting from π interaction between silicon and the 2p orbitals of the adjacent carbon atoms. Such π delocalization may be related to the interactions in the recently discovered multiply bonded silicon species.[3,4] Only two arylsilyl radicals have been studied to date by ESR; both show spin delocalization onto the carbon π framework, but delocalization is much less than in

(1) (a) Sakurai, H.; Umino, H.; Sugiyama, H. *J. Am. Chem. Soc.* **1980**, *102*, 6837. (b) Gynane, M.; Lappert, M.; Riley, P.; Riviere, P.; Riviere-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.
(2) (a) McConnell, H. *J. Chem. Phys.* **1956**, *24*, 632. (b) Heller, C.; McConnell, H. *Ibid.* **1960**, *32*, 1535.

(3) Si=C: Brook, A. G.; Abdesaker, F.; Gutekunst, B.; Gutekunst, G.; Kallury, K. *Chem. Commun.* **1981**, 191.
(4) Si=Si: West, R.; Fink, M.; Michl, J. *Science* **1981**, *214*, 1343.