Excited-State Proton-Transfer Reactions of Naphthylammonium Ion–18-Crown-6 Complexes[1]

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Abstract: Proton-transfer reactions in the excited singlet state of naphthylammonium ion–18-crown-6 complexes in MeOH–H$_2$O (9:1) mixtures have been studied by means of the single photon counting method with fluorimetry. It is found that the complex formation of naphthylammonium ions with 18-crown-6 decreases markedly the proton-transfer rate (k_1) in the excited state, resulting in an increase of its lifetime. The back protonation rate in the excited state is negligibly small compared with those of the other decay processes; there is no excited-state prototropic equilibrium in the naphthylammonium ion–crown complexes (RN$^+$H$_3$–crown). The one-way proton-transfer reaction is elucidated by the presence of the excited neutral amine–crown complex (RNH$_2$–crown)* produced by deprotonation of (RN$^+$H$_3$–crown)*, where protonation to the amino group is structurally blocked by 18-crown-6 and the naphthyl group (R) of the complex. However, proton-induced quenching (k_q') occurs effectively especially in the 1-naphthylammonium ion–crown complex. The ground-state association constants (K_g) of the complexes can be determined easily by the fluorescence titration method. Temperature effects upon the excited-state proton-transfer reactions of the complexes have been also carried out in order to study their thermodynamic properties. A Corey–Pauling–Kolton model of the anilinium ion–18-crown-6 complex proposed by Izatt et al.[2] is strongly supported by the present work.

Proton association and dissociation in the excited state of aromatic compounds are elementary processes both in chemistry and biochemistry. The acid–base properties of aromatic compounds in the excited state are closely related to the corresponding electronic structure, which is considerably different from that in the ground state. Since the pioneering work of Förster[3] (1950) and Weller[4] (1952) showing that the acidity constant pK_a* in the excited state is significantly different from that in the ground state, a large number of studies on pK_a* values have been reported.[5-11] Our group has studied excited-state proton-transfer reactions of aromatic compounds by means of dynamic analyses containing proton-induced quenching (k_q') with fluorimetry, where a simple acid–base equilibrium cannot be established within the lifetime of the excited state because of the presence of k_q'.[12-16] It has been shown that the intramolecular charge-transfer character in the excited state plays an important role in the proton-induced quenching and that the quenching is caused by electrophilic attack of one of carbon atoms of the aromatic ring leading to proton (or deuterium) exchange.[17,18] Excited-state proton-transfer reaction

of naphthylammonium ions is found to be such a case.[12]

On the other hand, since the original work of Pedersen[19] in 1967, there has been considerable recent interest in the chemical and physical properties of crown ethers.[20-26] However, relatively little attention has been paid to the excited state of the crown ether complexes until recently. Sousa and Larson[27] have reported the fluorescence quenching and enhancement of crown ether–naphthalene derivatives by alkali metal ions. Fluorescence enhancement of dibenzo-18-crown-6 by alkali metal cations in liquid and rigid matrices has been shown.[28] Divalent europium complexes with crown ethers give a remarkably intense, blue emission under UV irradiation.[29] Photochemical reactions of crown ethers have been studied.[30] Photoreactive crown ethers containing azobenzene derivatives have been studied by Sinkai et al.[31]

In the ground state complex formation of organic (or inorganic) ammonium ion with crown ethers is well known.[2,32,33] In the

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Naphthylammonium Ion-18-Crown-6 Complexes

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course of a study on proton-transfer reactions in the excited state, we became interested in the excited-state proton-transfer reactions of naphthylammonium ion-18-crown-6 complexes from the following viewpoints: (1) What about the proton dissociation rate in the excited state of the complexes? (2) Is there an excited-state prototropic equilibrium in the complex system? (3) Is the excited neutral amine–crown complex broken during its lifetime or not? (4) Is there proton-induced quenching k_q'? (5) What about the steric effect of naphthylamines upon the ground-state association constants K_g? In order to answer these questions proton-transfer reactions in the excited state of the protonated naphthyl-amines-18-crown-6 complexes[1] were studied by means of the single photon counting method with measurements of the fluorescence quantum yields.

Experimental Section

Naphthylamines (G.R.-grade products of Tokyo Kasei) were purified by two recrystallizations from ethanol followed by vacuum sublimation. *N*,*N*-Dimethyl-1-naphthylamine (G.R. grade, Tokyo Kasei) was purified by repeated distillations. 18-Crown-6, 15-crown-5, and dicyclohexyl-18-crown-6 (Merck) were purified by repeated recrystallizations from dichloroethane. Sulfuric acid (97%, Wako) was used without further purification. Methanol (Spectrosol, Wako) and distilled water were used as a MeOH–H_2O mixture (9:1 in volume). The acid concentrations used (0.005–0.1 M) were sufficient to make protonated naphthylamines in the ground state. All samples were thoroughly degassed by freeze–pump–thaw cycles on a high-vacuum line.

Absorption and fluorescence spectra were measured with Hitachi 139 and 200 spectrophotometers and a Hitachi MPF-2A fluorimeter, respectively. Spectral corrections for emissions were made. The fluorescence quantum yields were measured by comparison with a quinine bisulfate–0.1 *N* H_2SO_4 solution ($\Phi_F = 0.54$);[34,35] the excitation wavelengths for protonated 1- and 2-naphthylamines (αRN^+H_3 and βRN^+H_3) were 278 and 275 nm, respectively. The fluorescence response functions were recorded with a nanosecond time-resolved spectrophotometer (Horiba NAES-1100, 2-ns pulse width). This single photon counting apparatus is able to measure both the exciting pulse and emission response functions simultaneously, and to compute the decay parameters by the deconvolution method.

Results and Discussion

Absorption and Fluorescence Spectra of Naphthylammonium Ion-18-Crown-6 Complexes. Figure 1a shows the absorption and fluorescence spectra of the 2-naphthylammonium ion (βRN^+H_3) in the absence (1) and presence (2) of 18-crown-6 in MeOH–H_2O (9:1) mixtures at 300 K. The ground-state pK_a value of 2-naphthylamine is 4.1,[12] and therefore in the presence of sulfuric acid (5 × 10^{-3} M) βRNH_2 is completely protonated on the nitrogen atom in the ground state. The absorption spectrum is similar to that of naphthalene, indicating that the π-electronic structure of βRN^+H_3 is isoelectronic to that of naphthalene. Spectral change in absorptions between (1) and (2) was scarcely observed, showing that addition of 18-crown-6 to βRN^+H_3 had little effect upon the π-electronic structure of βRN^+H_3. There is no absorption due to 18-crown-6 by itself at wavelengths longer than ~250 nm.

However, it was found that there were large difference in the fluorescence spectra and intensities between them, as shown in Figure 1a. It is known that the proton dissociation rate in the excited singlet state of βRN^+H_3 is very fast (~10^9 s^{-1}), resulting in a large fluorescence intensity of the excited βRNH_2 produced by deprotonation from (βRN^+H_3)* at a low concentration of protons, [H$^+$] ≤ 1 × 10^{-2} M.[12] As a result, the fluorescence intensity of βRN^+H_3 is very small. The fluorescence spectrum of system 1 in Figure 1a is such a case. The fluorescence quantum yield for (βRN^+H_3)* at shorter wavelengths (λ_{max} 333 nm) was observed to be ~10^{-3}, whereas the yield for (βRNH_2)* at longer wavelengths (λ_{max} 401.$_6$ nm) was relatively large (0.47 at 300 K). By addition of a certain amount of 18-crown-6 (6.4$_5$ × 10^{-2} M) to βRN^+H_3, the fluorescence spectrum with vibrational structures
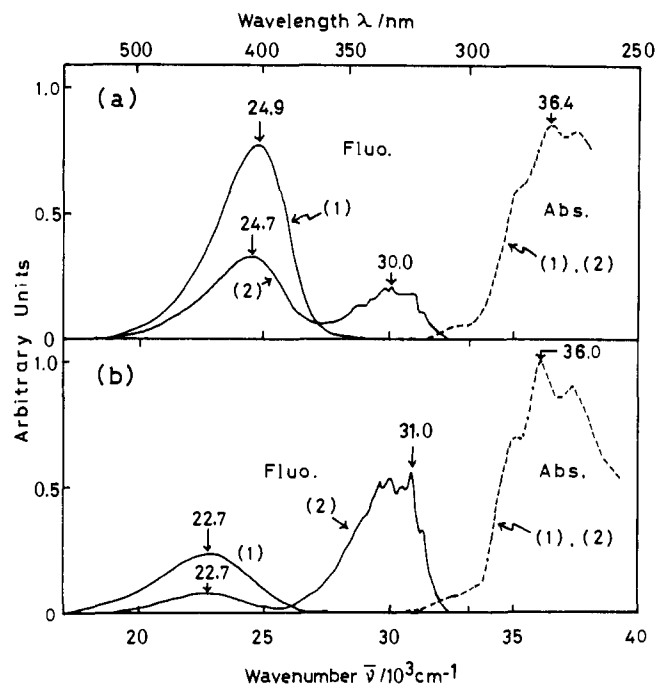

Figure 1. (a) Absorption and fluorescence spectra of (1) βRN^+H_3 ([βRNH_2] = 6.4$_5$ × 10^{-5} M and [H_2SO_4] = 5 × 10^{-3} M) and (2) βRN^+H_3 with 18-crown-6 ([βRNH_2] = 6.4$_5$ × 10^{-5} M, [H_2SO_4] = 5 × 10^{-3} M, and [crown] = 6.4$_5$ × 10^{-2} M) in MeOH–H_2O (9:1) Mixtures at 300 K. (b) Absorption and fluorescence spectra of (1) αRN^+H_3 ([αRNH_2] = 5.1$_2$ × 10^{-5} M and [H_2SO_4] = 5 × 10^{-3} M) and (?, αRN^+H_3 with 18-crown-6 ([αRNH_2] = 5.1$_2$ × 10^{-5} M, [H_2SO_4] = 5 10^{-3} M, and [crown] = 8.3$_5$ × 10^{-2} M in MeOH–H_2O (9:1) mixtures 300 K.

appeared at shorter wavelengths ($\bar{\nu}_{max}$ 30.0 × 10^3 cm^{-1}) with a quantum yield (Φ_{AH}) of 0.12 at 300 K. The shape of the fluorescence spectrum at longer wavelengths ($\bar{\nu}_{max}$ 24.7 × 10^3 cm^{-1}) was very similar to that for (βRNH_2)*. In case 2, the $\bar{\nu}_{max}$ value was shifted to the red by 200 cm^{-1} and the quantum yield (Φ_a) was observed to be 0.20 at 300 K. The excitation spectra monitored at the peaks of the dual emissions were very close to the absorption spectrum of system 2. Therefore, the dual emissions at shorter (λ_{max} 333 nm) and longer (λ'_{max} 405 nm) wavelengths correspond to those from (βRN^+H_3)* and (βRNH_2)*, respectively.

Similar features were observed in the case of 1-naphthyl-ammonium ion (αRN^+H_3). Figure 1b shows the absorption and fluorescence spectra of αRN^+H_3 in the absence (1) and presence (2) of 18-crown-6 in MeOH:H_2O (9:1) mixtures at 300 K. The ground-state pK_a value of αRNH_2 is known to be 3.9.[12] αRNH_2 was completely protonated under the experimental conditions. The fluorescence quantum yields (Φ_{AH} and Φ_A) for (αRN^+H_3)* and (αRNH_2)* were ~10^{-3} and 0.18 at 300 K, respectively. The corresponding quantum yields in the presence of 18-crown-6 (8.3$_5$ × 10^{-2} M) were observed to be 0.17 (λ_{max} 322 nm) and 0.07$_3$ (λ'_{max} 440 nm) at 300 K.

The concentration effects of 18-crown-6 on the fluorescence quantum yields (Φ_{AH} and Φ_A) for the dual emissions in MeOH–H_2O (9:1) mixtures have been measured. For example, Figure 2 shows the concentration effects of 18-crown-6 upon Φ_{AH} and Φ_A: (a) for the βRN^+H_3–crown system, [βRNH_2] = 6.4$_5$ × 10^{-5} M, [H_2SO_4] = 5 × 10^{-3} M, and [crown] ≤ 6.4$_5$ × 10^{-2} M; (b) for the αRN^+H_3–crown system, [αRNH_2] = 5.1$_2$ × 10^{-5} M, [H_2SO_4] = 5 × 10^{-3} M, and [crown] ≤ 8.3$_5$ × 10^{-2} M in MeOH–H_2O (9:1) mixtures at 300 K.

The Φ_{AH} values for RN$^+$H$_3$ markedly increased with increasing concentration of 18-crown-6 to give constant values of 0.12 for the former system (a) and 0.17 for the latter one (b) at 300 K. In contrast, the Φ_A values for the deprotonated species decreased significantly with increasing concentration of 18-crown-6 to yield the constant values 0.2$_0$ for (a) and 0.07$_3$ for (b). The fluorescence titration curves reflect the 1:1 complex formation between na-

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Table I. Concentration Effects of 18-Crown-6 on the Fluorescence Quantum Yields for Protonated and Neutral Amines (Φ_{AH} and Φ_A, respectively) in MeOH-H_2O (9:1) Mixtures at Various Temperatures[a]

compd	[RNH$_2$], 10^{-5} M	[H$_2$SO$_4$], 10^{-2} M	[18-crown-6], 10^{-2} M	Φ_{AH} at T (K)				Φ_A at T (K)			
				280	290	300	317	280	290	300	317
βRNH$_2$	6.4_5	0.5	0	b	b	b	b	0.47	0.48	0.47	0.45
			0.064_5	0.09	0.071	0.054	0.031	0.27	0.31	0.35	0.39
			0.32_3	0.11	0.10	0.093	0.062	0.16	0.20	0.24	0.28
			0.64_5	0.13	0.12	0.10	0.078	0.16	0.20	0.23	0.27
			1.6_1	0.14	0.13	0.12	0.095	0.15	0.19	0.21	0.25
			3.2_3	0.14	0.13	0.12	0.091	0.15	0.18	0.20	0.23
			6.4_5	0.14	0.13	0.12	0.091	0.15	0.18	0.20	0.23
αRNH$_2$	5.1_2	0.5	0	b	b	b	b	0.19	0.19	0.18	0.16
			0.054_3	0.04	0.031_7	0.022_8	0.013	0.18	0.18	0.17	0.17
			0.27_2	0.11	0.096_4	0.070_8	0.043	0.13	0.14	0.16	0.16
			0.54_3	0.14_9	0.13	0.10	0.062	0.095	0.11	0.13	0.14
			1.3_6	0.18_8	0.16_2	0.13_9	0.098	0.074	0.83	0.10	0.11
			5.3_7	0.21_4	0.19_3	0.17	0.13	0.051	0.063	0.076	0.087
			8.3_5	0.21_3	0.19_3	0.17	0.14	0.047	0.057	0.073	0.083

[a] Experimental errors within 5%. [b] The Φ_{AH} values were very low ($\sim 10^{-3}$), indicating that proton dissociation for protonated naphthylamine (α- and βRN$^+$H$_3$) took place very efficiently in the excited state in the absence of 18-crown-6.
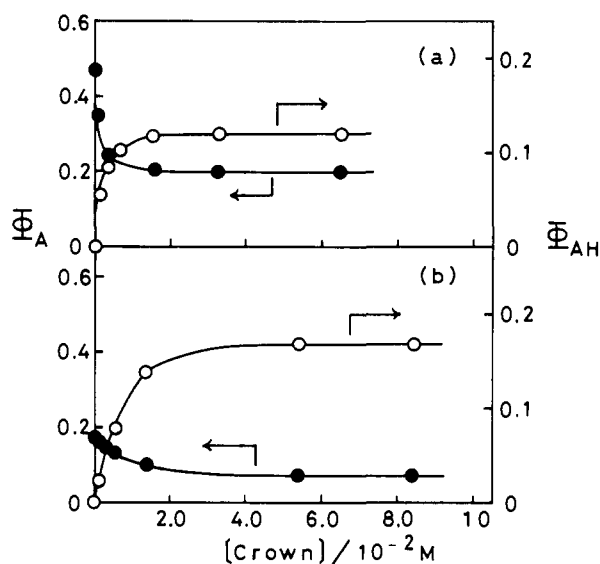

Figure 2. Concentration effects of 18-crown-6 upon the fluorescence quantum yields (Φ_{AH} and Φ_A for the protonated and deprotonated complexes, respectively) for (a) the βRN$^+$H$_3$crown system ([βRNH$_2$] = 6.4_5 × 10^{-5} M, [H$_2$SO$_4$] = 5 × 10^{-3} M, and [crown] $\leq 6.4_5$ × 10^{-2} M and (b) the αRN$^+$H$_3$–crown system ([αRNH$_2$] = 5.1_2 × 10^{-5} M, [H$_2$SO$_4$] = 5 × 10^{-3} M, and [crown] $\leq 8.3_5$ × 10^{-2} M) in MeOH-H_2O (9:1) mixtures at 300 K.

phthylammonium ion and 18-crown-6. It is known that the 1:1 complex of organic (or inorganic) ammonium ion with 18-crown-6 is produced.[2,32,33] The association constants K_g for the present systems can be easily determined by the fluorescence titration method, as shown in the next section. Measurements of concentration effects of 18-crown-6 on the fluorescence quantum yields Φ_{AH} for the protonated amine species and Φ_A for the neutral amine species in MeOH-H_2O (9:1) mixtures have been carried out at various temperatures.

The experimental results are listed in Table I. It is observed that the Φ_{AH} values decrease with increasing temperature while the Φ_A values increase with increasing temperature. These trends can be interpreted as follows: the stability of the excited RN$^+$H$_3$–crown complex may decrease at higher temperatures, resulting in formation of the neutral excited species by deprotonation. The experimental results for the fluorescence quantum yields Φ_{AH} and Φ_A suggest that the complex formation of naphthylammonium ions with 18-crown-6 decreases markedly the proton dissociation rate in the excited singlet state.

Determination of Association Constants K_g in the Ground State of Naphthylammonium Ion–18-Crown-6 Complexes. The fluorescence intensities (or quantum yields) as a function of concentration of 18-crown-6 (see Figure 2) are attributed to the

1:1 complex formation between RN$^+$H$_3$ and 18-crown-6 in the ground state. On the assumption that the fluorescence intensity at shorter wavelengths (~ 330 nm) is proportional to the concentration of the complex in the ground state, the ground-state association constants K_g of the complex can be easily determined by the fluorescence titration as follows. The concentration of the RN$^+$H$_3$–crown complex in the ground state can be expressed as

$$[\text{complex}] = \frac{\Phi_{AH} - \Phi_{AH}^0}{\Phi_{AH}^{max} - \Phi_{AH}^0}[\text{RN}^+\text{H}_3]_0 =$$

$$\frac{I_{AH} - I_{AH}^0}{I_{AH}^{max} - I_{AH}^0}[\text{RN}^+\text{H}_3]_0 \quad (1)$$

where Φ_{AH} and Φ_{AH}^0 represent the fluorescence quantum yields of the protonated amines with and without 18-crown-6, respectively, Φ_{AH}^{max} is the maximum value of the fluorescence quantum yields of the protonated amines in the presence of sufficient concentration of 18-crown-6 (e.g., 6.4_5 × 10^{-2} M for βRN$^+$H$_3$; 8.3_5 × 10^{-2} M for αRN$^+$H$_3$), and [RN$^+$H$_3$]$_0$ is the concentration of the protonated amine (i.e., the value of [RN$^+$H$_3$]$_0$ is equal to the concentration of the added naphthylamines to the system). In eq 1, the value of [RN$^+$H$_3$]$_0$ should be equal to the maximum concentration of the 1:1 complexes, [complex]$_{max}$. Similarly, I_{AH}, I_{AH}^0, and I_{AH}^{max} denote the corresponding fluorescence intensities at shorter wavelengths at 333 nm for βRN$^+$H$_3$ and 322 nm for αRN$^+$H$_3$. According to the law of mass action, the association constant K_g for the 1:1 complex between RN$^+$H$_3$ and 18-crown-6 in the ground state is given by

$$K_g = \frac{[\text{complex}]}{([\text{RN}^+\text{H}_3]_0 - [\text{complex}])([\text{crown}]_0 - [\text{complex}])} \quad (2)$$

where [crown]$_0$ represents the concentration of 18-crown-6 added to the system. Equation 3 is derived from eq 2:

$$([\text{crown}]_0 - [\text{complex}])^{-1} = K_g\frac{[\text{RN}^+\text{H}_3]_0 - [\text{complex}]}{[\text{complex}]} \quad (3)$$

Figure 3 shows the plots of ([crown]$_0$ − [complex])$^{-1}$ as a function of ([RN$^+$H$_3$]$_0$ − [complex])[complex]$^{-1}$: (a) for the βRN$^+$H$_3$–18-crown-6 system, [βRNH$_2$] = 6.4_5 × 10^{-5} M, [H$_2$SO$_4$] = 5 × 10^{-3} M, and [crown] = ~ 0–6.4_5 × 10^{-2} M; (b) for the αRN$^+$H$_3$–18-crown-6 system, [αRNH$_2$] = 5.1_2 × 10^{-5} M, [H$_2$SO$_4$] = 5 × 10^{-3} M, and [crown] = ~ 0–8.3_5 × 10^{-2} M in MeOH-H_2O (9:1) mixtures at various temperatures, which give the straight lines. The results are in fair agreement with eq 3. For instance, the K_g values in MeOH-H_2O (9:1) at 300 K are determined to be 1.6_2 × 10^3 M^{-1} for the βRN$^+$H$_3$–crown complex and 2.1_4 × 10^2 M^{-1} for the αRN$^+$H$_3$–crown complex. Plots of K_g vs. T^{-1} are shown in Figure 4. The values of thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) in MeOH-H_2O (9:1) mixtures were de-
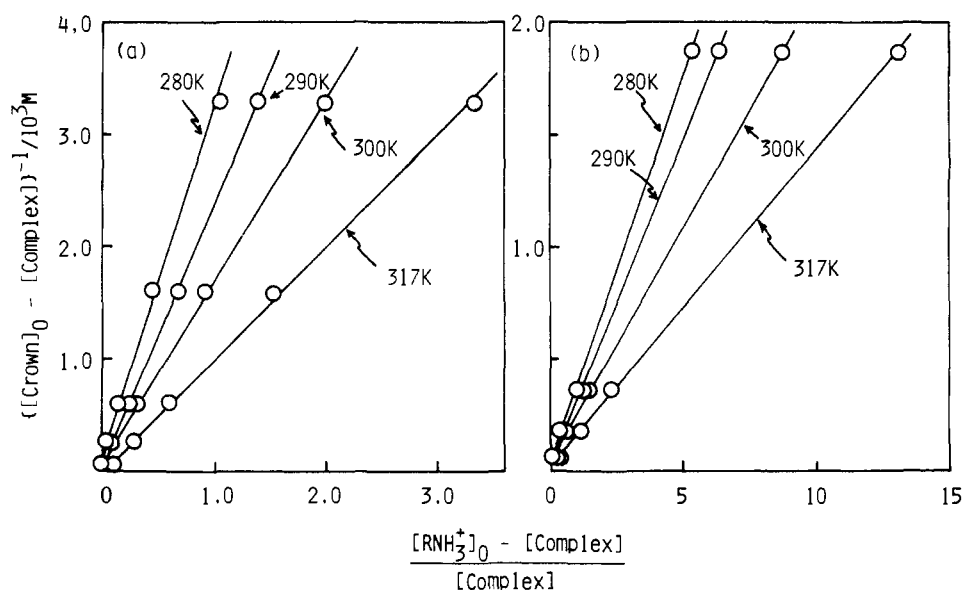
Figure 3. Plots of $([\text{crown}]_0 - [\text{complex}])^{-1}$ as a function of $([RN^+H_3]_0 - [\text{complex}])[\text{complex}]^{-1}$ for (a) the βRN^+H_3-18-crown-6 system ($[\beta RNH_2]$ = 6.4$_5$ × 10^{-5} M, $[H_2SO_4]$ = 5 × 10^{-3} M, and [crown] = 0-6.4$_5$ × 10^{-2} M) and (b) the αRN^+H_3-18-crown-6 system ($[\alpha RNH_2]$ = 5.1$_2$ × 10^{-5} M, $[H_2SO_4]$ = 5 × 10^{-3} M, and [crown] = 0-8.3$_5$ × 10^{-2} M) in MeOH-H$_2$O (9:1) mixtures at various temperatures.

Table II. Ground-State Equilibrium Constants K_g for Naphthylammonium Ion-18-Crown-6 Complexes in MeOH-H$_2$O (9:1) Mixtures Determined by Fluorometry[a]

compd	$K_g{}^b$/10³ M⁻¹ at T (K)				$\Delta G,^c$ kcal mol⁻¹	ΔH, kcal mol⁻¹	ΔS, eu
	280	290	300	317			
βRNH_2	3.1$_9$	2.4$_5$	1.6$_2$	0.81$_7$	−4.4$_3$	−6.9	−8.3
αRNH_2	0.35$_3$	0.29$_2$	0.21$_4$	0.14$_2$	−3.2$_0$	−2.3	−3.0

[a] Errors within 3%. [b] $K_g = k_2{}^0/k_1{}^0$. [c] At 300 K.
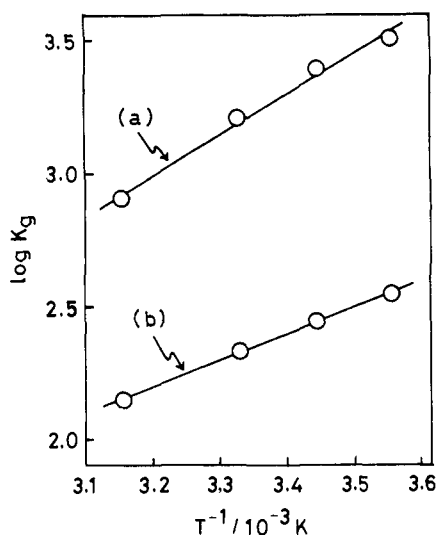
Figure 4. Plots of K_g vs. T^{-1} for (a) the βRN^+H_3-18-crown-6 complex and (b) the αRN^+H_3-18-crown-6 complex.

termined to be −4.4$_3$ kcal mol⁻¹, −6.9 kcal mol⁻¹, and ~8.3 eu for the βRN^+H_3-crown complex and −3.2$_0$ kcal mol⁻¹, −2.3 kcal mol⁻¹, and −3.0 eu for the αRN^+H_3-crown complex, respectively. The ΔG values are comparable to those (−9.0 < ΔG < −2.9 kcal mol⁻¹) of the complexes of *tert*-butylammonium salts with crown ethers reported by the Cram group.[36] The K_g values of the anilinium ion-18-crown-6 complex in methanol at 298 K[2] is greater than that of the βRN^+H_3-18-crown-6 complex in the present work. This may be due mainly to solvent polarity by adding 10% water to methanol. The K_g value for the RN⁺H₃-crown complexes can be determined easily by means of the fluorescence titration method compared to that of calorimetric titration.[33] The experimental data obtained are summarized in Table II. The K_g values for the βRN^+H_3-crown complex are greater than those for the αRN^+H_3-crown complex; the values of ΔG and ΔH for the former are much more negative than those for the latter. These differences may arise from the steric hindrance of the α-naphthyl group (peri effect) to 18-crown-6; one can clearly understand the difference in the Corey–Pauling–Kolton molecular models of the RN⁺H₃-crown complex as shown in Figure 5. The molecular
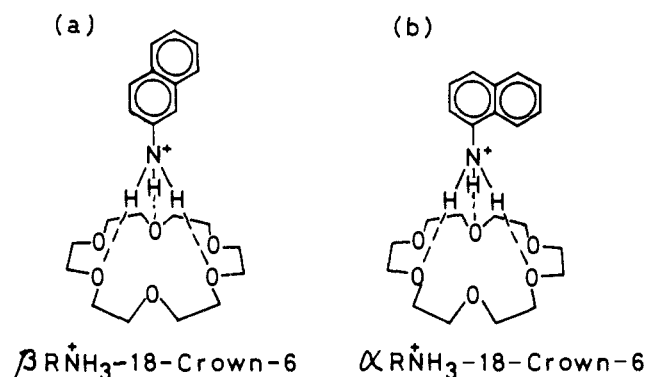
Figure 5. Corey-Pauling-Kolton molecular models for (a) the βRN^+H_3-18-crown-6 complex and (b) the αRN^+H_3-18-crown-6 complex.

models as shown in Figure 5 were originally proposed by Izatt et al.[2] The crystal structure of the ammonium bromide complex of 18-crown-6 has been studied by means of the X-ray method; the ammoinum cation is displaced by 1.00 Å from the mean oxygen plane of 18-crown-6.[37] It seems that the ammonium cation in the present system may be displaced by 1 Å or more from the mean oxygen plane of 18-crown-6. We assume that the nitrogen atom of the ammonium ion may have sp³ hybrid orbitals bonded with the naphthyl group and three hydrogen atoms. The three hydrogen atoms make three hydrogen bonds with three oxygen atoms in 18-crown-6 as shown in Figure 5. The CPK molecular models in Figure 5 are supported by the following results. The K_g value for βRN^+H_3-15-crown-5 in MeOH-H$_2$O (9:1) at room temperature was very low (less than 15 M⁻¹). As for the protonated *N,N*-dimethyl-1-naphthylamine (DMNA), the addition

(36) Timko, J. M.; Moore, S. S.; Walba, D. M.; Hiberty, P. C.; Cram, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4207.

(37) Nagano, O.; Kobayashi, A.; Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 790.

Table III. Fluorescence Quantum Yields (Φ_{AH} and Φ_A) of Naphthylammonium Ion-18-Crown-6 Complexes in MeOH-H$_2$O (9:1) Mixtures at Various Temperatures[a]

compound	[crown], 10^{-2} M	[H$_2$SO$_4$], 10^{-2} M	Φ_{AH} T (K)					Φ_A at T (K)				
			280	290	300	310	320	280	290	300	310	320
βRNH$_2$[b]	6.4$_5$	0.5	0.14	0.13	0.12	0.10$_1$	0.092	0.15$_3$	0.18$_1$	0.20	0.21$_2$	0.22$_3$
		2.5	0.15$_9$	0.13$_8$	0.12$_0$	0.10$_1$	0.091	0.14$_9$	0.17$_0$	0.18$_3$	0.19$_2$	0.20
		5.0	0.16$_5$	0.14$_3$	0.12$_3$	0.10$_3$	0.093	0.13$_9$	0.15$_9$	0.16$_8$	0.17$_8$	0.18$_2$
		7.5	0.16$_1$	0.14$_0$	0.12$_2$	0.10$_2$	0.093	0.12$_7$	0.14$_3$	0.15$_2$	0.15$_8$	0.16$_1$
		10	0.16$_1$	0.14$_3$	0.12$_3$	0.10$_5$	0.094	0.12$_0$	0.13$_5$	0.14$_1$	0.14$_4$	0.14$_7$
αRNH$_2$[c]	10.$_4$	0.25	0.21	0.19	0.17	0.14$_6$	0.12$_5$	0.051	0.057	0.076	0.084	0.09
		0.5	0.21$_2$	0.18$_9$	0.16$_6$	0.14$_7$	0.12$_5$	0.044$_2$	0.052$_7$	0.060$_5$	0.065$_5$	0.07
		2.5	0.21$_3$	0.19	0.16$_8$	0.14$_6$	0.12$_5$	0.022$_8$	0.025$_1$	0.028	0.027$_1$	0.042
		5.0	0.20	0.19	0.16$_8$	0.14	0.12	0.013$_3$	0.013$_8$	0.013$_8$	0.014$_6$	0.029
		7.5	0.21$_3$	0.19	0.17	0.14$_4$	0.12$_4$	0.010$_8$	0.010$_8$	0.011$_1$	0.011$_6$	0.012$_4$

[a] Errors within 5%. [b] [βRNH$_2$] = 6.4$_5$ × 10^{-5} M. [c] [αRNH$_2$] = 5.1$_2$ × 10^{-5} M.

of 18-crown-6 to the system scarcely affected the fluorescence properties of the species. The protonated DMNA contains only one N–H bond to produce a hydrogen bond with 18-crown-6, and therefore the protonated DMNA cannot form a stable CPK complex having three hydrogen bonds in the ground state. It is known that the steric interaction of the phenyl ring containing a methyl group at the ortho position with 18-crown-6 decreases the K_g value.[2c] Similarly, the steric effect for the αRN$^+$H$_3$–crown system was observed in the present work as stated above. A relatively low value of K_g [8.9$_1$ × 10^2 M^{-1} in MeOH-H$_2$O (9:1)] for the βRN$^+$H$_3$–dicyclohexyl 18-crown-6 was obtained, compared with that (1.6$_2$ × 10^3 M^{-1} at 300 K) for the βRN$^+$H$_3$–18-crown-6. This result suggests that there is a steric hindrance between the naphthyl and cyclohexyl moieties of the complex. These experimental results strongly support the CPK molecular model of the anilinium ion–18-crown-6 complex proposed by Izatt et al.[2]

Kinetic Analysis of the Excited-State Proton-Transfer Reactions of the RN$^+$H$_3$–18-Crown-6 Complexes. Kinetic analyses in the excited singlet state of the RN$^+$H$_3$–18-crown-6 complexes containing excited-state proton transfer have been carried out in MeOH-H$_2$O (9:1) mixtures by means of the single photon counting method with measurements of acid concentration effects on the fluorescence quantum yields (Φ_{AH} and Φ_A).

(1) Proton-Induced Quenching. Figure 6 shows the acid concentration effects on Φ_{AH} and Φ_A in MeOH-H$_2$O (9:1) mixtures at 300 K: (a) for the βRN$^+$H$_3$–18-crown-6 system, [βRNH$_2$] = 6.4$_5$ × 10^{-5} M, [crown] = 6.4$_5$ × 10^{-2} M, and [H$_2$SO$_4$] = ∼5 × 10^{-3}–1 × 10^{-1} M; (b) for the αRN$^+$H$_3$–18-crown-6 system, [αRNH$_2$] = 5.1$_2$ × 10^{-5} M, [crown] = 10.4 × 10^{-2} M, and [H$_2$SO$_4$] = ∼ 5 × 10^{-3}–7.5 × 10^{-2} M. The values of Φ_{AH} for the pronated amine complex with 18-crown-6 were nearly constants (0.12$_3$ for the βRN$^+$H$_3$ system and 0.17 for the αRN$^+$H$_3$ system) at 300 K. However, the Φ_A values for the neutral species decreased with increasing the concentration of H$_2$SO$_4$, especially for the αRN$^+$H$_3$ system. The results indicate that proton-induced quenching is involved in the excited singlet state of the neutral amine species. It is known that the proton–induced quenching occurs by electrophilic protonation at one of carbon atoms of the aromatic ring,[17] since electron migration from the amino group to the naphthalene ring (i.e., intramolecular charge transfer) occurs effectively in the excited singlet state of naphthylamines.[12,17,18] The intramolecular charge-transfer character in (αRNH$_2$)* is dominant compared with that in (βRNH$_2$)*, with the result that the proton-induced quenching for the (αRNH$_2$)* species is greater than that for the (βRNH$_2$)* speices.[12] Measurements of the fluorescence quantum yields (Φ_{AH} and Φ_A) have been performed under various conditions. The data are summarized in Table III.

(2) Dynamic Behavior of Excited RN$^+$H$_3$–18-Crown-6 Complexes Studied by The Single Photon Counting Method. The fluorescence decay functions have been measured by means of the single photon counting method (a Horiba NAES-1100). Typical results are shown in Figure 7: (a) the observed fluorescence response function $I_{AH}(t)$ for the βRN$^+$H$_3$–18-crown-6 complex monitored at 330 nm at various temperatures, and (b) the observed fluorescence response function $I_A(t)$ for the neutral βRNH$_2$–18-crown-6 complex monitored at 420 nm together with
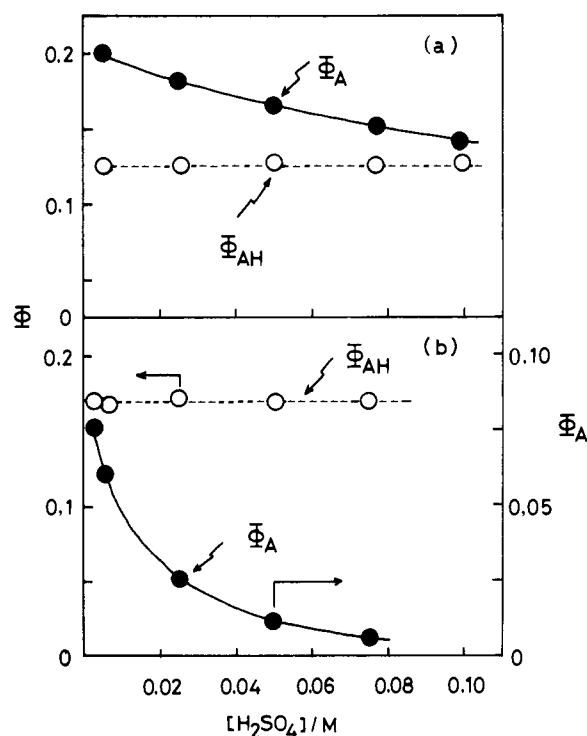

Figure 6. Acid concentration effects on the fluorescence quantum yields (Φ_{AH} and Φ_A) for (a) the βRN$^+$H$_3$–18-crown-6 system ([βRNH$_2$] = 6.4$_5$ × 10^{-5} M, [crown] = 6.4$_5$ × 10^{-2} M, and [H$_2$SO$_4$] = 5 × 10^{-3}–1 × 10^{-1} M) and (b) the αRN$^+$H$_3$–18-crown-6 system ([αRNH$_2$] = 5.1$_2$ × 10^{-5} M, [crown] = 10.$_4$ × 10^{-2} M, and [H$_2$SO$_4$] = 0.25–7.5 × 10^{-2} M) in MeOH-H$_2$O (9:1) mixtures at 300 K.

the lamp function, I_L, monitored at 278 nm. The $I_{AH}(t)$ and $I_A(t)$ functions in Figure 7 are significantly different from those for free βRN$^+$H$_3$ without 18-crown-6 whose lifetimes are ≲1 ns (βRN$^+$H$_3$*) and 21 ns (βRNH$_2$*). For example, the $I_{AH}(t)$ function in Figure 7a shows a single exponential decay with a lifetime of 41 ns at 300 K. From the $I_A(t)$ function in Figure 7b, the rise and decay rates at 300 K for the neutral amine species were obtained to be 2.5 × 10^7 and 6.5$_7$ × 10^7 s^{-1} respectively. The rise rate for the excited neutral amine species is equal to the decay rate (2.4$_2$ × 10^7 s^{-1}) of the (βRN$^+$H$_3$–crown)* complex in Figure 7a within experimental error. This is evidence for formation of the excited βRNH$_2$ species by deprotonation of the excited βRN$^+$H$_3$–crown complex. The decay rate λ_1 for the βRN$^+$H$_3$–crown complex increased with increasing temperature as shown in Figure 7a. Similar results were obtained for the αRN$^+$H$_3$–crown system. The decay parameters λ_1 and λ_2 were measured under various conditions. The experimental data are listed in Table IV.

The experimental data show that complex formation of RN$^+$H$_3$ with 18-crown-6 in the ground state plays an important role in the dynamic behavior of the excited protonated amine. That is, the lifetime in the excited singlet state of naphthylammonium ions

Table IV. Fluorescence Decay Parameters λ_1 and λ_2 for the RN$^+$H$_3$–18-Crown-6 Complexes under Various Conditions Measured by a Single Photon Counter[a]

complex	[H$_2$SO$_4$], M	$I_{AH}(t)^b$ $\lambda_1/10^7$ s^{-1} at T (K)					$I_A(t)^c$ — $\lambda_1/10^7$ s^{-1} at T (K)					$\lambda_2/10^7$ s^{-1} at T (K)				
		280	290	300	310	320	280	290	300	310	320	280	290	300	310	320
βRN$^+$H$_3$–crown[d]	0.005	1.9_2	2.2_1	2.4_2	2.7_2	3.0_4	1.8_9	2.3	2.5_2	2.8	3.2_2	5.1	5.7_1	6.5_7	6.7	6.9_4
	0.025	1.9_2	2.2_2	2.4_5	2.7_6	3.1	1.9_4	2.2_5	2.4_7	2.8_5	3.2	5.6	6.0_1	6.8_5	7.2	7.3_5
	0.05	1.8_9	2.2_1	2.4_2	2.7_8	3.1_5	1.9_4	2.2_4	2.4_6	2.8	3.1_8	5.8	6.5_1	7.4	7.9_4	8.8_6
	0.075	1.8_9	2.2_1	2.4_2	2.7_5	3.1_4	1.9_5	2.2_3	2.4_9	2.8_4	3.1_8	6.3_2	6.8_2	7.8_1	8.4	9.1
	0.1	1.8_6	2.1_6	2.4_5	2.7_6	3.1_8	1.9_4	2.2	2.4_2	2.8_4	3.2	6.4_1	7.1_2	8.3_3	9.1	$10._4$
αRN$^+$H$_3$–Crown[e]	0.005	2.0_2	2.3_6	2.6_9	3.0	3.4_4	1.9_3	2.2_9	2.5_5	2.8	3.3_5	g	6.1	7.5_8	9.6_7	$11._8$
	0.015	2.0_5	2.3_7	2.6_9	3.0_1	3.4_5	1.9_4	2.2_5	2.5_6	2.8	3.3		6.6[f]	9.5[f]	12.4[f]	$15._3$[f]
	0.025	2.0_1	2.3_5	2.7_0	3.0	3.5	1.9_3	2.2_4	2.5_6	2.7_9	3.3		9.9[f]	$14._3$[f]	$20._4$[f]	$25._5$[f]
	0.05	2.0_2	2.3_5	2.6_7	2.9_6	3.4_9	2.0_1	2.2_4	2.5_5	2.8	3.3		13.8[f]	$20._4$[f]	$30._1$[f]	$36._9$[f]

[a] Experimental errors within 5%. [b] Fluorescence response function $I_{AH}(t)$ of the RN$^+$H$_3$–crown complex excited at 278 nm and monitored at 320 nm. $\lambda_1 = \tau_{AH}^{-1}$ (see text). [c] Fluorescence response function $I_A(t)$ of the RNH$_2$–crown complex excited at 278 nm and monitored at 420 nm. $\lambda_1 = \tau_{AH}^{-1}$; $\lambda_2 = \tau_A^{-1}$ (see text). [d] [βRNH$_2$] = $6.4_5 \times 10^{-5}$ M; [18-crown-6] = $6.4_5 \times 10^{-2}$ M. [e] [αRNH$_2$] = $5.1_2 \times 10^{-5}$ M, [18-crown-6] = $1.0_4 \times 10^{-1}$ M. [f] The $I_A(t)$ functions for the αRNH$_2$–crown complex were too weak to measure at higher acid concentrations ([H$_2$SO$_4$] $\geq$ 0.015 M). The λ_2 values were estimated from the following equation: $\tau_A^{-1} = k_1\tau_{AH}k_f'/\Phi_A$ where $\tau_A^{-1} = \lambda_2$ and $\tau_{AH}^{-1} = \lambda_1$. For details see text. [g] It was impossible to measure the value of λ_2 since for αRN$^+$H$_3$–crown the fluorescence intensity I_A at 420 nm was very weak at 280 K.

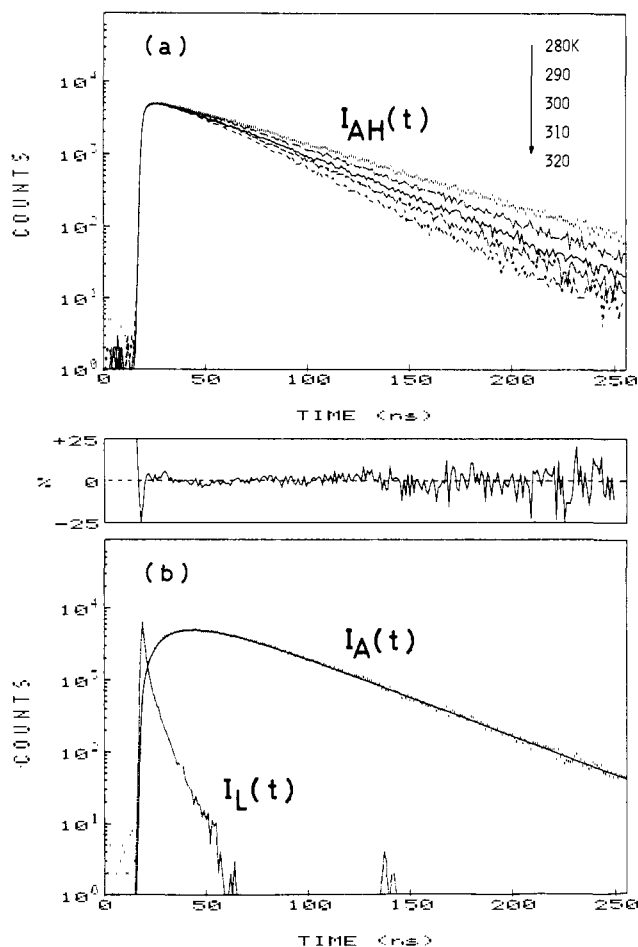**Figure 7.** (a) Observed fluorescence response functions $I_{AH}(t)$ excited at 278 nm and monitored at 320 nm for the βRN$^+$H$_3$–18-crown-6 complex: [βRNH$_2$] = $6.4_5 \times 10^{-5}$ M, [H$_2$SO$_4$] = 5×10^{-3} M, and [crown] = $6.4_5 \times 10^{-2}$ M in MeOH–H$_2$O (9:1) mixtures at various temperatures. (b) Observed fluorescence response function $I_A(t)$ excited at 278 nm and monitored at 420 nm at 300 K for the neutral βRNH$_2$–18-crown-6 complex (the sample is the same as that for (a)) and the lamp function $I_L(t)$ monitored 278 nm. For details see text.

increases markedly in the presence of 18-crown-6. This is mainly due to a decrease in the rate constant for excited-state proton transfer of the naphthylammonium ion–18-crown-6 complex as shown later. The $I_{AH}(t)$ function with a single exponential decay may indicate that the rate for the back protonation process between the excited neutral amine species and protons is negligibly small compared with those of the other decay processes. This assumption

is entirely supported from the experimental facts that (a) the Φ_{AH} values were constants even at higher proton concentrations (Figure 6 and Table 3), (b) the $I_AH(t)$ function comprised only one decay component, and (c) the single exponential decay rates λ_1 of the (RN$^+$H$_3$–crown)* complexes were constant regardless of the acid concentration at each temperature (Table IV). The back protonation rate of excited neutral amine species may be relatively slow because the deprotonation of the (RN$^+$H$_3$–crown)* complex leads to formation of the neutral (RNH$_2$–crown)* complex instead of decomposition into free RNH$_2$* plus 18-crown-6. This neutral complex may dissociate into RNH$_2$ plus 18-crown-16 in the ground state. Therefore, (RNH$_2$–crown)* may be called a "hydrogen-bonded exciplex". If one keeps CPK molecular models (Figure 5) in mind, it can be realized that the proton attack to the amino group of the excited neutral complex is structurally blocked by 18-crown-6 and the naphthyl group of the complex.

(3) Reaction Scheme for the Excited-State Proton-Transfer Reactions of RN$^+$H$_3$–18-Crown-6 Complexes. The experimental results can be accounted for by the reactions in Scheme I at sufficient concentration of 18-crown-6. In this scheme k_1 and k_2 denote the rate constants for the proton dissociation and association processes in the excited singlet state, k_f and k_d the rate constants for the radiative and nonradiative processes in (RN$^+$H$_3$–crown)*, and k_f' and k_d' those processes in (RNH$_2$–crown)*, respectively. k_q' is the rate constant for proton-induced quenching.

Under a δ function pulse excitation the undistorted fluorescence response functions $F_{AH}(t)$ of (RN$^+$H$_3$–crown)* and $F_A(t)$ of (RNH$_2$–crown)* are given by[38]

$$F_{AH}(t) = [k_f(\lambda_2 - X)/(\lambda_2 - \lambda_1)](e^{-\lambda_1 t} + Ae^{-\lambda_2 t}) \quad (4)$$

and

$$F_A(t) = [k_f'k_1/(\lambda_2 - \lambda_1)](e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (5)$$

where

$$A = (X - \lambda_1)/(\lambda_2 - X)$$

The decay parameters λ_1 and λ_2 are

$$\lambda_{1,2} = \tfrac{1}{2}\{X + Y \mp [(Y - X)^2 + 4k_1k_2[H^+]]^{1/2}\} \quad (6)$$

where

$$X = k_f + k_d + k_1 = (\tau_{AH}^0)^{-1} + k_1$$

and

$$Y = k_f' + k_d' + (k_2 + k_q)[H^+] = (\tau_A^0)^{-1} + (k_2 + k_q)[H^+]$$
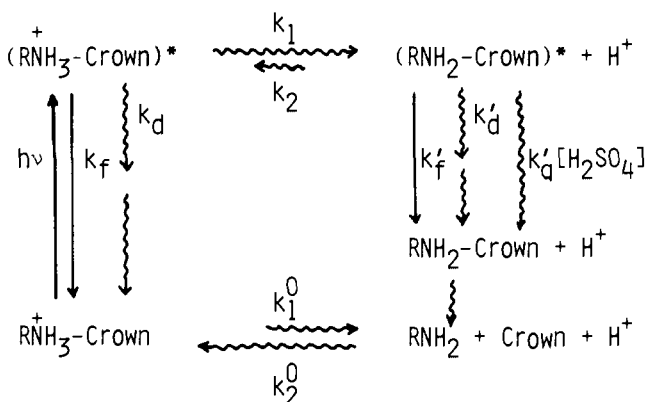
The output of the H$_2$ pulser is related to the undistorted

(38) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: London, 1970.

Table V. Fluorescence Lifetimes (τ_{AH} and τ_A), Proton-Transfer Rate Constants (k_1), Proton-Transfer Efficiency (ϕ_{PT}), and Rate Constants for Proton-Induced Quenching (k_q') in the Excited Singlet State of the RN^+H_3-18-Crown-6 Complexes in $MeOH-H_2O$ Mixtures[a]

complex	T, K	k_1,[b] 10^6 s^{-1}	A_1,[d] 10^{10} s^{-1}	ΔE_1,[e] kcal mol^{-1}	ϕ_{PT}	k_q', 10^9 M^{-1} s^{-1}	τ_{AH}, ns	τ_A, ns
βRN^+H_3-Crown[b]	280	5.4_3			0.28	0.13_5	52	$19._6$
	290	7.8_8			0.36	0.15	45	$17._5$
	300	$10._9$	1.9_5	4.5	0.45	0.20	41	$15._2$
	310	$13._3$			0.49	0.25	37	$14._9$
	320	$16._2$			0.53	0.35	33	$14._4$
αRN^+H_3-crown[c]	280						50	
	290	2.7			0.10	2.2	42	$16._3$
	300	4.6			0.17	2.9	37	$13._3$
	310	7.3	8.1×10^2	8.6	0.24	4.6	33	$10._3$
	320	$10._9$			0.32	5.5	29	$8._5$

[a] Errors within 5%. [b] $[\beta RN^+H_3] = 6.4_5 \times 10^{-5}$M, $[H_2SO_4] = 5 \times 10^{-3}$ M, [18-crown-6] $= 6.4_5 \times 10^{-2}$ M. [c] $[\alpha RN^+H_3] = 5.1_2 \times 10^{-5}$ M, $[H_2SO_4]$ $= 5 \times 10^{-3}$ M, [18-crown-6] $= 1.0_4 \times 10^{-1}$ M. [d] Frequency factor for k_1. [e] Activation energy for k_1.

Scheme I

$(\overset{+}{RNH_3}\text{-Crown})^* \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (RNH_2\text{-Crown})^* + H^+$

$h\nu \downarrow\uparrow k_f \downarrow \} k_d$ $k_f' \downarrow \} k_d' \} k_q'[H_2SO_4]$

$RNH_2\text{-Crown} + H^+$

$\overset{+}{RNH_3}\text{-Crown} \underset{k_2^0}{\overset{k_1^0}{\rightleftharpoons}} RNH_2 + Crown + H^+$

fluorescence response function of $F_{AH}(t)$ or $F_A(t)$ by the convolution integral

$$I_{AH}(t) = \int_0^t F_{AH}(t')I_L(t-t')\,dt \qquad (7)$$

or

$$I_A(t) = \int_0^t F_A(t')I_L(t-t')\,dt \qquad (8)$$

where $I_L(t)$ is the corresponding lamp function and $I_{AH}(t)$ or $I_A(t)$ the observed fluorescence response function of $(RN^+H_3$-crown)* or $(RNH_2$-crown)*, respectively. The observed function $I_{AH}(t)$ or $I_A(t)$ was analyzed using eq 4 and 7 or eq 5 and 8, respectively. The decay parameters λ_1 and λ_2 obtained are shown in Table IV. The $I_{AH}(t)$ function shows a single exponential decay [the value of A in eq 4 is negligibly small and the value of $k_2[H^+]$ is smaller than those of the other competitive processes as described above. Thus, for the present system eq 4 and 5 can be simplified to

$$F_{AH}(t) = C_1 e^{-\lambda_1 t} \qquad (9)$$

$$F_A(t) = C_2(e^{-\lambda_1 t} - e^{-\lambda_2 t}) \qquad (10)$$

where $\lambda_1 = X = k_f + k_d + k_1 = \tau_{AH}^{-1}$; $\lambda_2 = Y = k_f' + k_d' + k_q[H^+]$ $= \tau_a^{-1}$, and C_1 and C_2 denote constant values. In $MeOH-H_2O$ (9:1) mixtures, we have no information of the activity of sulfuric acid at various temperatures, and here it is better that the term of $k_q[H^+]$ is expressed as $k_q'[H_2SO_4]$.

The rate constant k_1 for the excited-state proton transfer of $(RN^+H_3$-crown)* can be obtained from

$$\Phi_A = k_1\tau_{AH}k_f'\tau_A \qquad (11)$$

where τ_{AH} $(=\lambda_1^{-1})$ and τ_A $(=\lambda_2^{-1})$ denote the lifetimes for $(RN^+H_3$-crown)* and $(RNH_2$-crown)*, respectively. The values of k_f' could be estimated from the radiative rate constants of free $(RNH_2)^*$, which were equal to 2.9×10^6 s^{-1} for $(\beta RNH_2)^*$ and 4.6×10^6 s^{-1} for $(\alpha RNH_2)^*$ in $MeOH-H_2O$ (9:1) mixtures. For example, the values of k_1 for $(\beta RN^+H_3$-crown)* and $(\alpha RN^+H_3$-crown)* were determined to be 10.9×10^6 and 4.6×10^6 s^{-1} at 300 k, respectively. The k_1 values decrease significantly to $\sim 1/_{100}$th by complex formation with 18-crown-6. The excit-
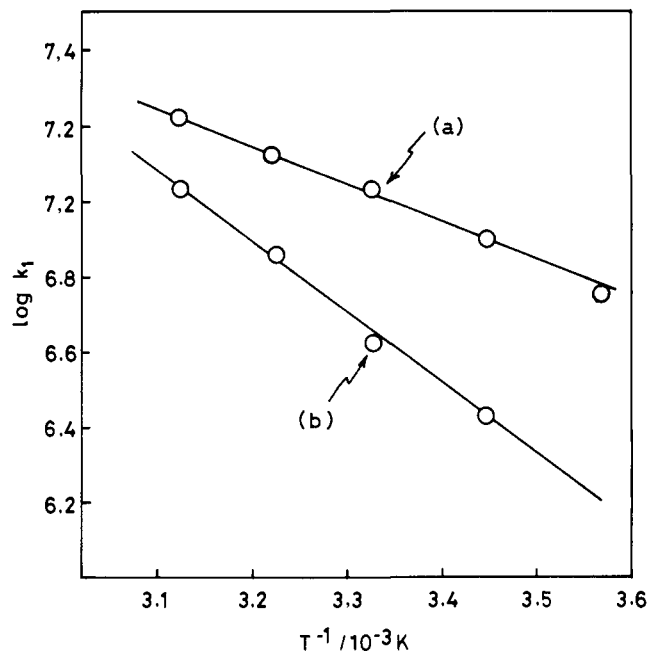
Figure 8. Plots of log k_1 vs. T^{-1} for (a) the βRN^+H_3-crown complex and (b) the αRN^+H_3-crown complex.

ed-state proton transfer efficiencies ϕ_{PT} $(=k_1\tau_{AH} = k_1\lambda_1^{-1})$ decreased from 1 to 0.45 for $(\beta RN^+H_3$-crown)* and from 1 to 0.17 for $(\alpha RN^+H_3$-crown)* at 300 K. It can be said that the complex formation of naphthylammonium ions with 18-crown-6 controls the rate constants for the excited-state proton transfer without any spectral change. The k_1 and ϕ_{PT} values at various temperatures are listed in Table V. Plots of log k_1 vs. T^{-1} gave straight lines as shown in Figure 8: (a) for the βRN^+H_3-crown system and (b) for the αRN^+H_3-crown system. From the plots in Figure 8, frequency factors A_1 and activation energies ΔE_1 in the k_1 process were determined to be $1.9_5 \times 10^{10}$ s^{-1} and 4.5 kcal mol^{-1} for the βRN^+H_3-crown system and 8.1×10^{12} s^{-1} and 8.6 kcal mol^{-1} for the αRN^+H_3-crown system. The kinetic parameters containing the relatively small A_1 values and relatively large ΔE_1 values suggest that excited-state proton transfer k_1 of RN^+H_3-crown complex does not proceed via proton tunneling[39] but across a potential barrier at higher temperatures (≥ 280 K).

The proton-induced quenching rate constant k_q' can be determined using eq 12. Figure 9 shows the plots of τ_A^{-1} as a

$$\tau_A^{-1} \, (=\lambda_2^{-1}) = k_f' + k_d' + k_q'[H_2SO_4] \qquad (12)$$

function of $[H_2SO_4]$. The linear lines agree well with eq 12. From the slopes the k_q' values were determined to be 2×10^8 M^{-1} s^{-1} for $(\beta RNH_2$-crown)* and 2.9×10^9 M^{-1} s^{-1} for $(\alpha RNH_2$-crown)*

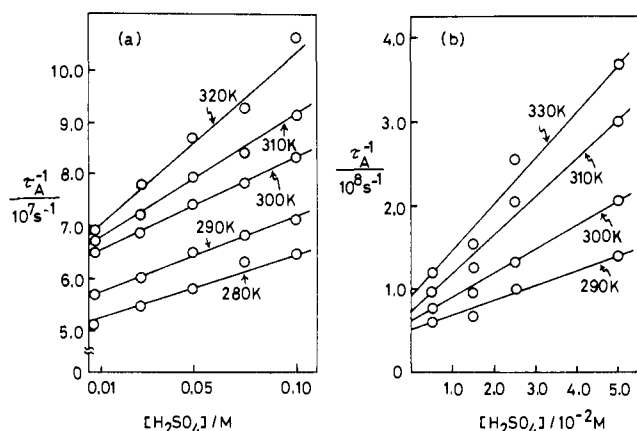(39) Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London, 1980.

Figure 9. Plots of τ_A^{-1} as a function of [H$_2$SO$_4$] for (a) the βRN$^+$H$_3$–crown complex and (b) the αRN$^+$H$_3$–crown complex.

at 300 K. The k_q' value in the α isomer is about 10 times greater than that for the β isomer, indicating that the intramolecular CT character in (αRNH$_2$–crown)* is superior to that in (βRNH$_2$–crown)*. These results for k_q' are consistent with those in free naphthylammonium ions.[12] The k_q' values at various temperature are also listed in Table V. It should be noted that proton-induced quenching k_q' occurs via electrophilic protonation at one of the carbon atoms of the aromatic ring.[17] For 1-methoxynaphthalene (a model compound for k_q' experiments), it is known that protons mainly attack the 5 position of the naphthalene ring.[17] The 5 position of the (αRNH$_2$–crown)* complex is situated in the opposite site of 18-crown-6 of the complex, and protons can, therefore, attack the electronegative 5 position of the naphthalene ring of (αRNH$_2$–crown)*, whereas the amino group is effectively protected by the naphthyl group and 18-crown-6. A considerable steric effect on the protonation process is observed[17] since protons behave as hydronium ions in the presence of water.[40] Recently,

(40) Protons exist in water as hydronium ions. However, protonation proceeds via proton transfer involving only the movement of a nucleus as has been stated by Bell: Bell, R. P. "The Proton in Chemistry"; Chapman and Hall: London, 1973.

it has been reported that protons produced by deprotonation in the excited state are trapped in water clusters.[41] The protons trapped by several water molecules seem to be unexpectedly bulky, and they are subject to the steric effect on protonation to the substrate. The proton-transfer reaction of (RN$^+$H$_3$–crown)* is a one-way process since the rate for the back protonation is negligibly small compared to the other processes. Thus, it can be said that there is no prototropic equilibrium in the excited state of the RN$^+$H$_3$–crown complex because of no reversible reaction k_2.

Summary

(1) Complex formation of naphthylammonium ions with 18-crown-6 decreases markedly the proton dissociation rate k_1 in the excited singlet state, resulting in an increase of its lifetime.

(2) It is found that the excited naphthylamine–18-crown-6 complex (RNH$_2$–crown)* is produced by deprotonation of (RN$^+$H$_3$–crown)*.

(3) The excited-state proton-transfer reaction of (RN$^+$H$_3$–crown)* is a one-way process, since the back protonation rate is negligibly small compared with those of the other decay processes. There is a large steric effect on protonation of the amino group of the excited neutral complex. Thus, there is no excited-state prototropic equilibrium in the RN$^+$H$_3$–crown complexes.

(4) The excited-state proton-transfer reactions of the RN$^+$H$_3$–crown complexes can be expressed as the reaction scheme containing proton-induced quenching k_q'.

(5) The association constants K_g in the ground state of the RN$^+$H$_3$–crown complexes can be easily determined by means of the fluorescence titration method. There is a steric effect of the aromatic ring on K_g; the K_g value for the βRN$^+$H$_3$–crown complex is greater than that for the αRN$^+$H$_3$–crown complex.

(6) The Corey–Pauling–Kolton molecular model proposed by Izatt et al.[2] is strongly supported by the present work. The CPK molecular models were discussed using the K_g values and excited-state kinetic parameters.

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(41) Huppert, D.; Kolodney, E.; Gutman, M.; Nachliel, E. *J. Am. Chem. Soc.* **1982**, *104*, 6946.

Cumulene Photochemistry: Photorearrangements of Tetraphenyl and Triphenyl C_3 Isomers

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Abstract: Photoreactions in aprotic solvents of tetraphenylallene (**1**), triphenylallene (**2**), 1,3,3- and 1,2,3-triphenylcyclopropenes, and related isomeric indenes are described. Irradiation of tetraphenylallene (**1**) slowly yields 1,2,3-triphenylindene (**6**) as a primary product. Irradiation of triphenylallene (**2**) yields 1,3,3-triphenylcyclopropene (**10**; $\Phi = 0.004$), 1,3-diphenylindene (**9**; $\Phi = 0.019$), and 1,3,3-triphenylpropyne (**11**; $\Phi = 0.002$). A significant deuterium kinetic isotope effect is observed for these reactions. The common, but not exclusive, intermediacy of vinylcarbenes in cyclopropene and linear allene photochemistry is strongly indicated by product studies and independent generation experiments. Allenes are shown to be minor products of vinylcarbenes generated from photolysis of tosylhydrazone sodium salts and from cyclopropene photolysis. Ab initio configuration interaction calculations along pathways connecting allene with propyne and cyclopropene are described. In-plane hydrogen migration in singlet excited allene can lead to several excited-state minima. Internal conversion can result in the formation of vinylcarbenes, cyclopropene, or propyne, depending on the geometry at which this occurs.

Despite prolonged interest in photoreactions of cyclopropenes,[1,2] and numerous ethylene and 1,3-butadiene[3] derivatives, allenes

(1,2-propadienes) have received surprisingly little attention.[4-6] Our interest in allene photochemistry was stimulated by the