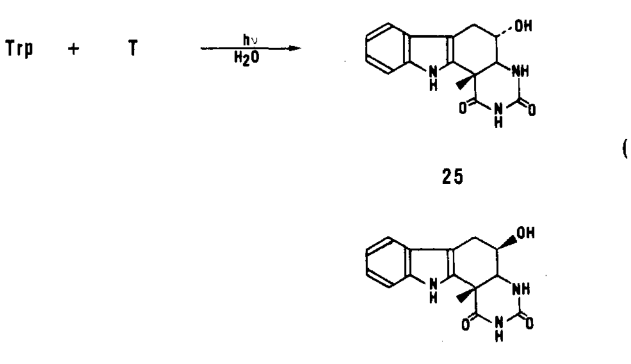
with an exact 1:1 stoichiometry as previously suggested by Reeve and Hopkins.[32] The Trp moiety suffers deamination and decarboxylation.



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(9)

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The formation of these photoadducts from Trp and T apparently involves a multistep photochemical and non-photochemical route. A similar type of adduct formation has been reported in irradiation of Trp–uracil[32] and Trp–poly U systems.[34] However, it is not known whether such adduct formation is responsible for the photo-cross-linking with Trp moieties of nucleoproteins.

Concluding Remarks

In this Account, we have described a novel photoreaction between thymidine and alkylamines leading to ring-opened adducts. A similar photoreaction between thymine and lysine has proved to be particularly important in photo-cross-linking of lysine ϵ-amino groups of proteins to thymine residues of DNA in DNA–protein systems of biological significance, namely, the chromatin of eukaryotic cells. The present result is an example in which careful study on a chemical model system could directly contribute to the elucidation of the actual chemical processes occurring in irradiation of complicated molecular assemblies in biological systems. Achievement of a full understanding of the chemistry occurring in irradiation of DNA–amino acids, DNA–peptides, and more complex DNA–protein systems remains as a challenge to researchers in the fields of photochemistry, photobiology, and molecular biology.

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Excited-State Proton-Transfer Reactions and Proton-Induced Quenching of Aromatic Compounds[†]

HARUO SHIZUKA

Department of Chemistry, Gunma University, Kiryu, Gunma 376, Japan

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Proton association and dissociation in the excited states of aromatic compounds are elementary processes in both chemistry and biochemistry. The acid–base properties in the excited state of aromatic compounds are closely related to electronic structure, which is considerably different from that in the ground state. A large number of studies on the acidity constants pK_a^* in the excited state of aromatic compounds have been reported showing that the pK_a^* values are markedly different from the acidity constants in the ground state.[1-9] It is well-known that the pK_a^* values can be estimated by means of the Förster cycle,[1-3,10,11] the fluorescence titration curve,[2,3] and the triplet-triplet absorbance titration curve.[12] These methods involve the assumptions that proton transfer in the excited state is very fast and that acid–base equilibrium may

Haruo Shizuka (a native of Gunma, Japan) is a professor of chemistry at Gunma University. He received his B.E. from Gunma University and his D.Sc. from Tokyo Institute of Technology where he worked with Ikuzo Tanaka. He stayed at the University of Western Ontario (1971/1972) as a research associate of Paul de Mayo and also at IBM San Jose Research Laboratory (1983) as a visiting scientist. His research interests are photochemical and photophysical processes of aromatic compounds.

[†] This paper is dedicated to Professor Ikuzo Tanaka (Tokyo Institute of Technology) on the occasion of his 60th birthday.

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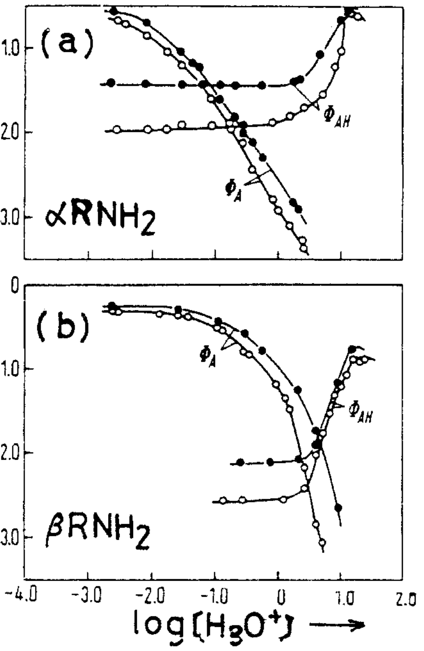

Figure 1. Logarithmic plots of the fluorescence quantum yields of neutral naphthylamines Φ_A and cations Φ_{AH} as a function of $[H_3O^+]$ (○, H_2SO_4/H_2O; ●, D_2SO_4/D_2O).[13]

be established during the lifetime in the excited state.

However, it has been shown recently that proton-induced fluorescence quenching (k_q') competitive with the proton-transfer reaction is present in the excited state of naphthylamines (that is, simple acid–base equilibrium cannot be accomplished in the excited state of aromatic amines) and that a dynamic analysis containing the quenching process is, therefore, needed in order to obtain the correct pK_a^* values.[13] The dynamic analyses by means of nanosecond time-resolved spectroscopy with fluorimetry have been applied to 1-aminopyrene,[14] 1-aminoanthracene,[15] phenanthrylamines,[16] and naphthols.[17] Our method to determine the pK_a^* values of naphthylamines has been supported.[18] Similar experiments for excited naphthols have been carried out.[19] Establishment of prototropic equilibrium has been reported in the case of 2-hydroxynaphthalene-6,8-disulfonate.[20]

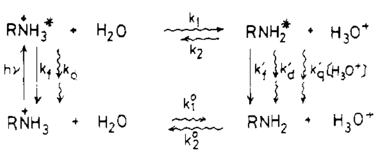

Figure 2. Reaction scheme of excited singlet state of naphthylamines in the presence of protons.[13]

For the proton-induced quenching mechanism, a complex in which a proton is shared between excited 2-naphthylamine and one water molecule[21] or a hydrated naphthylammonium cation in the ground state[22] was assumed as an intermediate for the quenching. Very recently, it has been shown that the proton-induced quenching k_q' at moderate acid concentrations $[H_2SO_4] \geq 0.1$ M is caused by electrophilic protonation at one of the carbon atoms of the aromatic ring in the excited singlet state (S_1), leading to proton exchange (or isotope exchange).[23,24]

In this Account, excited-state proton-transfer reactions of aromatic compounds are discussed from the following viewpoints: (1) determination of pK_a^* values of aromatic compounds containing proton-induced quenching k_q'; (2) what is the proton-induced quenching mechanism?; (3) is there a relation between k_q' values and the electronic struture in the excited state?; (4) effects of complex formation of ammonium ions with 18-crown-6 upon excited-state proton-transfer reactions and k_q'; (5) prototropic and hydrogen atom transfer reactions in the triplet state of aromatic compounds.

Determination of pK_a^* by Dynamic Analysis

The pK_a^* values of naphthylamines (RNH_2) can be determined as follows.[13] Figure 1 shows logarithmic plots of the fluorescence quantum yields of neutral amines Φ_A and cations Φ_{AH} as a function of $[H_3O^+]$. The midpoints of the fluorescence titration curves of Φ_A and Φ_{AH} are completely different from each other. The discrepancy between them indicates that for naphthylamines these curves do not correspond to simple two-component equilibria in the S_1 state. Therefore, the pK_a^* values cannot be determined directly from the midpoints of the curves. In this study, buffer solutions were not used since the fluorescence quenching by inorganic anions might occur.[25] The reaction scheme for excited-state proton-transfer reactions of naphthylamines in the presence of protons are shown in Figure 2, where k_1, k_2, and k_q' denote the rate constants for proton dissociation, association, and proton-induced quenching, respectively, k_f and k_f' are the radiative rate constants of the cation $RN^+H_3^*$ and RNH_2^*, respectively. From the steady-state approximation, the following equation can be obtained

$$\frac{\Phi_A^0}{\Phi_A} = 1 + \frac{1}{k_1\tau_{AH}^0} + \frac{\{k_2 + k_q'\,(1 + k_1\tau_{AH}^0)\}\tau_A^0}{k_1\tau_{AH}^0}[H_3O^+] \qquad (1)$$

(11) This method is based on the determination of the energy gap between the ground and excited states of the acid and basic forms of a molecule. ΔH and ΔH^* are, respectively, the enthalpy changes of reaction in the ground and excited states. ΔE_{AH} and ΔE_{A^-} are the energy differences between the two states whose values can be determined by absorption and emission measurements. We have $\Delta H - \Delta H^* = \Delta E_{AH} - \Delta E_{A^-}$. If the entropies of reaction are equivalent in the two states

$$pK_a - pK_a^* = (\Delta E_{AH} - \Delta E_{A^-})/2.303RT$$

where pK_a and pK_a^* denote the acidity constants in the ground and excited states, respectively. The pK_a^* value is, therefore, determined from the equation, since pK_a is a known value.

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Table I.
Proton Dissociation (k_1), Protonation (k_2), and Quenching (k_q') Rate Constants and the Acidity Constants (pK_a* and pK_a in the Excited Singlet and Ground States, Respectively) of Naphthylamines at 27 °C[13]

compds	quenchers	$k_1/10^9$ s^{-1}	$k_2/10^8$ M^{-1} s^{-1}	$k_q'/10^9$ M^{-1} s^{-1}	pK_a*			pK_a
					a	b	c	
αRNH_2	H^+	1.3	1.2	8.9	−1.0	2.7	−5.9	3.9
	D^+	1.1	0.75	6.0	−1.2	2.6	−5.9	
βRNH_2	H^+	1.0	1.5	0.33	−0.8	0.8	-4.0_5	4.1
	D^+	0.85	0.094	0.19_6	−0.96	0.3	−4.0	

[a] Determined by the dynamic analyses with fluorimetry. [b] Estimated by the midpoint of fluorimetric titration of $(RNH_2)^*$. [c] Estimated by the Förster cycle.

where Φ_A and $\Phi_A{}^0$ denote the fluorescence quantum yields for RNH_2 with and without acid, respectively, $\tau_{AH}{}^0$ denotes the maximum fluorescence lifetime of RN^+H_3* at higher acid concentrations (47.2 ns at $[H_3O^+]$ = 13.6 M for αRN^+H_3* and 28 ns at $[H_3O^+]$ = 16.4 M for βRN^+H_3), and $\tau_A{}^0$ denotes the lifetime of RNH_2* in the absence of acid (27 ns for αRNH_2* and 19 ns for βRNH_2*). Judging from the large value of $\tau_{AH}{}^0$ and $k_1 > k_2[H_3O^+]$ at $[H_3O^+] < 0.2$ M, the following equations should hold: $k_1\tau_{AH}{}^0 >> 1$ and $k_2(k_1\tau_{AH}{}^0)^{-1} << k_q'$. From the above relations, eq 1 can be simplified to

$$\Phi_A{}^0/\Phi_A = 1 + k_q'\,\tau_A{}^0[H_3O^+] \qquad (1')$$

A Stern–Volmer plot of $\Phi_A{}^0/\Phi_A$ vs. $[H_3O^+]$ gives a linear relationship:

$$(\Phi_A{}^0/\Phi_A)_{\alpha RNH_2} = 1.0 + 2.4 \times 10^2\,[H_3O^+] \qquad (2)$$

$$(\Phi_A{}^0/\Phi_A)_{\beta RNH_2} = 1.0 + 6.3[H_3O^+] \qquad (3)$$

From the slope of the linear plot, the k_q' values are determined to be 8.9×10^9 M$^-$ s^{-1} (αRNH_2) and 3.3×10^8 M^{-1} s^{-1} (βRNH_2).

Under a δ function pulse excitation, the fluorescence response functions $F_A(t)$ of RNH_2* and $F_{AH}(t)$ of RN^+H_3* are given by[26]

$$F_A(t) = [k_f'k_1/(\lambda_2 - \lambda_1)](e^{-\lambda_1 t} - e^{-\lambda_2 t}) \qquad (4)$$

$$F_{AH}(t) = [k_f(\lambda_2 - X)/(\lambda_2 - \lambda_1)](e^{-\lambda_1 t} + Ae^{-\lambda_2 t}) \qquad (5)$$

where

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

The decay parameters λ_1 and λ_2 are

$$\lambda_{1,2} = \frac{1}{2}[X + Y \mp \{(Y - X)^2 + 4k_1k_2[H_3O^+]\}^{1/2}] \qquad (6)$$

where

$$X = (\tau_{AH}{}^0)^{-1} + k_1 \qquad Y = (\tau_A{}^0)^{-1} + (k_q' + k^2)[H_3O^+]$$

The output of the hydrogen pulser is related to the undistorted fluorescence response function of $F_A(t)$ or $F_{AH}(t)$ by the convolution integral

$$I_A(t) = \int_0^t F_A(t')I_L(t - t')\,dt' \qquad (7)$$

or

$$I_{AH}(t) = \int_0^t F_{AH}(t')I_L(t - t')\,dt' \qquad (8)$$

where I_L is the corresponding lamp function and $I_A(t)$ or $I_{AH}(t)$ the observed fluorescence response function of RNH_2* or RN^+H_3*, respectively. In the cases of αRNH_2 and βRNH_2, kinetic treatment for the $I_{AH}(t)$ function is impossible since its intensity is very weak. Using eq 7 and the experimental values $\tau_{AH}{}^0$, $\tau_A{}^0$, and k_q' for the α- and β-isomers, the convolution method is applied by using a computer. The values of k_1 and k_2 are determined to be 1.3×10^9 s^{-1} and 1.2×10^8 M^{-1} s^{-1} for αRNH_2 and 1.0×10^9 s^{-1} and 1.5×10^8 M^{-1} s^{-1} for βRNH_2, respectively. The protonation rate constants k_2 are smaller than those of k_q' in naphthylamines. It is noteworthy that the protonation process to RNH_2* is not fast enough to allow a complete acid–base equilibrium in the S_1 state. This is why the fluorescence titration curves do not correspond to simple two-component equilibrium in the S_1 state.

Using the values of k_1 and k_2, one can determine the correct pK_a* values: pK_a* = −1.0 (αRNH_2) and pK_a* = −0.8 (βRNH_2). The pK_a* values determined by kinetic analyses with fluorimetry are quite different from those estimated by the fluorimetric titration curve or by the Förster cycle as shown in Table I. The pK_a* values in the S_1 state of RNH_2 are markedly smaller than those in the ground state. This well-known tendency can be understood considering electron migration from the amino group to the naphthalene ring in the S_1 state in polar media. The magnitude of electron migration in the S_1 state seems to correlate with the pK_a* values.[16a,27] In other words, the charge density or formal charge at the nitrogen atom in the S_1 state of aromatic amines is closely related to basicity of the species.

Isotope effects on k_1, k_2, and k_q' have also been examined.[13–16a] The pK_a* values for D_2O/D_2SO_4 system are somewhat greater than those for the H_2O/H_2SO_4 system.[13] For excited naphthols the kinetic isotope effects have been studied.[17,28,29] A quantitative analysis of kinetic isotope effects on the excited-state proton-transfer reactions has been carried out by using the multiphonon theory.[30] Theoretical treatments according to the golden-rule treatment[31] or the treatment of radiationless transition[32] will be applicable to the excited-state proton-transfer reactions. Although theoretical analyses of the kinetic isotope effects in the excited state are very complex, the studies on the problems of proton tunneling and proton transfer across a potential barrier[33] will be further expanded in future.

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Table II.
Stern–Volmer Constants (K_{SV}), Fluorescence Lifetimes (τ^0), and Quantum Yields (Φ_f^0) without Acids, Quenching Rate Constants (k_q'), and Ionization Potentials (I_P*) in the Excited State of Aromatic Compounds $^1A^*$) at 300 K[a] [24]

sample	solvent	quencher	K_{SV}/M^{-1}	τ^0/ns	Φ_f^0	$k_q'/10^9$ $M^{-1}\ s^{-1}$	$E_A^{*\,b}$/eV	$I_P^{*\,c}$/eV
1-methoxynaphthalene	20% CH_3CN in H_2O	H^+	9.6	8.9	0.43	1.08	3.87	3.91
	20% CH_3CN in D_2O	D^+	4.8	9.4	0.41	0.51		
	80% CH_3CN in H_2O	H^+	2.2	12.6	0.36	0.16		
	80% CH_3CN in D_2O	D^+	1.1	12.8	0.42	9.0×10^{-2}		
2-methoxynaphthalene	20% CH_3CN in H_2O	H^+	<0.03	10	0.33	$<3 \times 10^{-3}$	3.68	4.24
1-cyanonaphthalene	20% CH_3CN in H_2O	H^+	0.28	4.4	0.37	6.4×10^{-2}	3.87	5.43[d]
2-cyanonaphthalene	20% CH_3CN in H_2O	H^+	0.29	12	0.53	2.4×10^{-2}		
1-naphthylamine[e]	5% CH_3CN in H_2O	H^+	2.4×10^2	27	0.49	8.9	3.24	4.06
	5% CH_3CN in D_2O	D^+	$1.7_4 \times 10^2$	29	0.56	6.0		
2-naphthylamine[e]	5% CH_3CN in H_2O	H^+	6.3	19	0.45	0.33	3.32	3.93
	5% CH_3CN in D_2O	D^+	3.19	20	0.47	0.19_6		
1-naphthol[f]	H_2O	H^+	g	7.8[h]	1.3×10^{-3}[h]	0.75[g]	3.57	4.13[d]
	D_2O	D^+	g	9.0[h]	2.1×10^{-3}[h]	0.46[g]		
2-naphthol[f]	H_2O	H^+	g	7.9[h]	0.21_4[h]	<0.03[g]	3.64	4.18[d]
	D_2O	D^+	g	8.6[h]	0.23[h]	<0.02[g]		
naphthalene	20% EtOH in H_2O	H^+	$<4.3 \times 10^{-2}$	43		$<1 \times 10^{-3}$	3.98	4.20
1-aminoanthracene[i]	20% CH_3CN in H_2O	H^+	g	4.1	5.1×10^{-3}	0.12[g]	2.64	4.3[d]
	20% CH_3CN in D_2O	D^+	g	20	7.8×10^{-2}	0.02[g]		
anthracene[j]	MeOH	H_2SO_4	$<3.8 \times 10^{-2}$	3.8		$<1 \times 10^{-2}$	3.31	4.24
9,9′-bianthryl[j]	MeOH	H_2SO_4	57	37	0.21	1.54		
1-aminopyrene[k]	50% CH_3CN in H_2O	H^+	7×10^{-2}	5.4	0.54	1.3×10^{-2}	3.02	3.91[d]
	50% CH_3CN in D_2O	D^+	5.4×10^{-2}	8.0	0.61	0.68×10^{-2}		
pyrene	30% MeOH in H_2O	H^+	$<3.5 \times 10^{-2}$	3.5×10^2		$<1 \times 10^{-4}$	3.33	4.22

[a] Experimental errors within ±5%. [b] E_A* denotes the 0–0 transition energy for $^1A^*–^1A$. [c] $I_P^* = I_P - E_A^*$. The I_P* value is regarded as a measure of the tendency of electron-donating power of $^1A^*$, although it may involve a deviation from the real value. [d] The value of I_P was estimated by the usual CT method using tetracyanoethylene. [e] Data taken from ref 13. [f] Data taken from ref 17. [g] Determined by the dynamic analysis. [h] $[H^+]$ (or $[D^+]$) = 0.1 N in H_2O or D_2O at 300 K. [i] Data taken from ref 15. [j] Data taken from ref 40. [k] Data taken from ref 14.

Proton-Induced Quenching Mechanism[23,24]

Isotope-exchange reactions in the excited state of aromatic compounds have been studied extensively.[34-39] For naphthalene, the H–D isotope exchange and fluorescence quenching at higher acid concentrations (% H_2SO_4 = 30–77) was reported.[35] The demonstration of fluorescence quenching by acids suggests that the lowest excited singlet state is involved in prototropic reactions.[35-37] However, the reactive state for isotope exchange in excited anthracene was assumed to be the triplet state.[37] For *p*-hydroquinone, it was deduced that both singlet and triplet states are involved in the photochemical isotope-exchange reactions.[38] Similarly, from comparison of the observed substitution pattern of toluene with excited-state electron distributions involvement of the second excited singlet and the lowest triplet states as the reactive states was proposed.[39] These isotope-exchange reactions in the excited state give rise to a significant enhancement of the reaction rates and also changes in the relative positional reactivities compared to those in the ground state. However, the isotope-exchange mechanism in the excited state has not been established until very recently.[23,24]

Excited aromatic molecules having an intrmolecular charge-transfer (CT) structure in the fluorescent state (e.g., 1-methoxynaphthalene (αRH),[23,24] 1-naphthol,[17] naphthylamines,[13] phenanthrylamines,[16] 1-aminoanthracene,[15] 1-aminopyrene,[14] 9,9′-bianthryl,[40] and 2-(*p*-aminophenyl)pyrene[41]) are quenched effectively by protons, as shown in Table II. That is, electron migration from the electron-donating substituent (e.g., OH, OCH_3, NH_2, or $N(CH_3)_2$) to the aromatic ring (the naphthalene, phenanthrene, anthracene, or pyrene ring) in the excited state occurs considerably in polar media, and electronegative one of carbon atoms of the aromatic ring is attacked by protons. As for an electron-withdrawing group such as the cyano group, the reverse electron migration from the aromatic ring into the substituent may contribute to the quenching: the quenching may be caused by an interaction between the substituent and protons.[23] It is noteworthy that there is relatively little correlation between k_q' and I_p* [the ionization potential for the excited state of aromatic compounds $^1A^*$ estimated from I_p (ionization potential for the ground-state ^1A) minus E_A* (0–0 transition energy for $^1A^* - {}^1A$)]. The quenching mechanism of $^1A^*$ by protons is, therefore, different from that by inorganic anions $^1X^-$.[25] The former involves a chemical interaction (protonation) at one of the carbon atoms of the aromatic ring as is shown later, and the latter involves an electron-transfer (or charge-transfer) process. An electronic interaction between $^1A^*$ and H^+ (or D^+) in the quenching is locally restricted to one of the carbon atoms of the aromatic nucleus. This phenomenon may be attributed to the following reasons: the radius of the proton (10^{-5} A)[42] is too small to overlap widely with the

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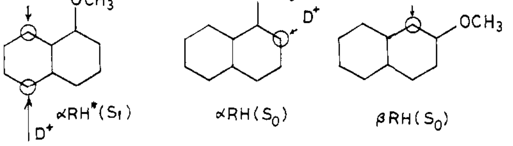
π-electron system of $^1A^*$ compared with those of $^1X^-$ (1.5–3 A), and electrostatic and covalent interactions between H^+ (or D^+) and the proper carbon atom of $^1A^*$ become large enough to give bond formation (e.g., protonation), leading to a fast decay process $(\tau_0')^{-1}$ (see Figure 3).[24]

In contrast, the quenching for aromatic compounds having no (or very weak) intramolecular CT character in the fluorescent state (S_1) such as naphthalene, 2-methoxynaphthalene (βRH), anthracene, and pyrene is scarcely observed at moderate acid concentrations ($[H_2O^+] \leq 0.1$ M).[23,24]

Methoxynaphthalenes (RH) were chosen as model compounds since the compounds were photochemically stable compared with those of naphthylamines.[13b] The proton-induced quenching in H_2O (or D_2O)–CH_3CN mixtures has been investigated by means of nanosecond time-resolved spectroscopy with fluorimetry, and the photochemical and thermal H–D isotope exchange reactions have been studied by means of ^1H NMR and mass spectroscopy and measurements of the reaction quantum yields with the aid of the usual MO methods (semiempirical SCF MO CI and extended Hückel MO methods). The following facts have been established:[24] (1) The proton-induced quenching k_q' of αRH proceeds via electrophilic protonation at one of carbon atoms of the aromatic ring in the S_1 state (^1L_a) in polar media, leading to hydrogen exchange (or isotope exchange) mainly at positions 5 [slightly at position 8; this is due to a steric effect[42] (perri effect)] of the naphthalene ring. It is found that the rate constant k_R^* for the electrophilic protonation is equal to that k_q' (see Figure 3). The isotope exchange reaction via the triplet state is very small (about 5% compared with that via the S_1 state). (2) For βRH, both proton-induced quenching and isotope exchange in the excited state (^1L_b) (this has no intramolecular CT character) scarcely occur at moderate acid concentrations ($[H_3O^+] \leq 0.1$ M) at room temperature. (3) At higher temperatures (≥45 °C), the thermal isotope exchange reactions of α- and βRH take place at positions 2 and 1, respectively; the exchange rate for the latter is faster than that for the former, contrary to that of photochemical reactions. (4) The H–D isotope exchange reactions in both excited (S_1) and ground (S_0) states can be elucidated by taking account of the reactive indices (the charge density,[43] the frontier electron density,[44a] superdelocalizability,[44b] and localizaiton energies[45] derived from the usual MO calculations), indicating that both photochemical and thermal isotope-exchange reactions proceed via electrophilic attack at one of carbon atoms of the aromatic ring (eq 9).



(9)

The experimental and theoretical results can be accounted for by a potential energy state diagram as shown in Figure 3. There are three types σ complexes **5***, **5**, and **2**, where **5*** denotes the excited state of the σ complex deuterated at position 5 of the naphthalene ring in the S_1 (^1L_a) state of αRH, **5** is the ground σ complex produced from the nonradiative decay $(\tau_0')^{-1}$ of **5***, **2** is the ground σ complex deuterated at position 2 of the naphthalene ring in the S_0 state of αRH, and k_R^* and k_R are the corresponding rate constants in the S_1 and S_0 states, respectively. Their energy levels were determined experimentally (full line) and theoretically (dotted line). The kinetic parameters of the enthalpy of activation ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$) for the deuteration processes (k_R^* and k_R) in D_2O–CH_3CN (1:4) are obtained to be 3.2 kcal mol^{-1} and −9.6 eu for k_R^* and 27.3 kcal mol^{-1} and −6.6$_7$ eu for k_R, respectively. The deuteration rate (e.g., $k_R^* \approx 10^8$ M^{-1} s^{-1} at 40 °C) in the S_1 state is very much greater than that (e.g., k_R 10^{-7} M^{-1} s^{-1} at 40 °C) in the S_0 state. The difference in the rates is mainly due to the potential barriers between them as can be seen in Figure 3. The quenching mechanism was also supported by laser flash photolysis experiments of 1-methoxynaphthalene.[46] Excited-state protonation to one of the carbon atoms in aromatic compounds is an important process, resulting in the hydration reaction of aromatic alkenes.[47,48]

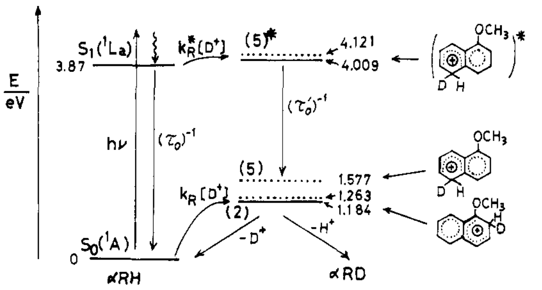


Figure 3. A potential energy state diagram for photochemical and thermal isotope-exchange reactions of 1-methoxynaphthalene (αRH), where k_R^* is equal to k_q'.[24] The energy levels are determined experimentally (full line) and theoretically (dotted line). For details, see text.

Relationship between Proton-Induced Quenching k_q' and Electronic Structure[49]

The k_q' values are expected to relate to the reactive indices (the charge density P* or the superdelocalizability S*) in the S_1 state since k_q' is caused by electrophilic protonation at one of the carbon atoms of the aromatic ring in the excited state. The plots of k_q' values obtined in our studies[13-17] vs. P_Σ^* (or S_Σ^*) gives a linear relation:[49]

$$\log k_q' = 8.84P_\Sigma^* - 10.59 \quad \text{(the correlation coeff } r = 0.792) \tag{10}$$

$$\log k_q' = 5.54\, S_\Sigma^* + 6.68 \quad (r = 0.737) \tag{11}$$

where P_Σ^* and S_Σ^* denote the summation values of charge densities and superdelocalizabilities at the two carbon atoms having large values P* and S* in the S_1 state, respectively. Thus, one can estimate the k_q'

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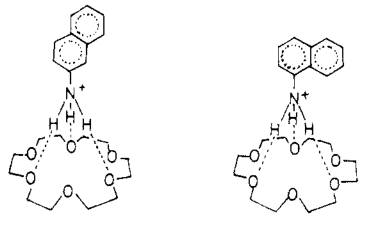

Figure 4. Corey–Pauling–Kolton molecular models of naphthylammonium ion–18-crown-6 complexes:[51] (a) βRN^+H_3–Crown; (b) αRN^+H_3–Crown.

values for the proton-induced quenching of other aromatic compounds using eq 10 or 11.

Complex Formation of Naphthylammonium Ions with 18-Crown-6[50,51]

As for crown ethers, there has been considerable interest in their chemical and physical properties.[52-58] The 1:1 complex formation of ammonium ions with 18-crown-6 in the ground state is known.[59] However, no attention to the excited-state proton-transfer reactions has been given until very recently.[50,51] The investigation on the naphthylammonium ion–18-corwn-6 complexes might provide much information on the proton-transfer reactions containing k_q'. Proton-transfer reactions in the excited singlet state of naphthylammonium ion–18-crown-6 complexes in $MeOH–H_2O$ (9:1) mixtures have been studied by means of the single photon counting method with fluorimetry. There is no change in the absorption spectrum by complex formation. It is found that the complex formation of naphthylammonium ions with 18-crown-6 decreases markedly the proton dissociation rate (k_1) in the excited state resulting in an increase of its lifetime.[50,51] The k_1 value ($\sim 10^7\ s^{-1}$) of the complex is about one-hundredth of that ($\sim 10^9\ s^{-1}$)[13] of free RN^+H_3. The back protonation rate (k_2) in the S_1 state is negligibly small compared to those of the other decay processes,[51] there is no establishment of 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 ${}^1(RNH_2{}^*$–Crown) produced by deprotonation of ${}^1(RN^+H_3{}^*$–Crown), where the protonation k_2 to the amino group is structurally blocked by 18-crown-6 and the naphthyl group (R) of the complex.[51] A considerable steric effect on the protonation process is observed,[23,24,50,51] suggesting that protons behave as bulky hydronium ions in the presence of water.[42] However, the k_q' process (protonation to the naphthalene ring) occurs effectively especially in 1-naphthylammonium ion–18-crown-6 complex as shown in eq 12, where $(\tau_0)^{-1}$

$$\begin{tikzcd} {}^1(R\overset{+}{N}H_3{}^*\text{-Crown}) \arrow[r, shift left, "k_1"] \arrow[d, "(\tau_0)^{-1}"] & {}^1(RNH_2{}^*\text{-Crown}) + H^+ \arrow[l, shift left, "k_2"] \arrow[d, "(\tau_0')^{-1}"] \arrow[d, shift left=8, "k_q'[H^+]"] \\ {} & {} \end{tikzcd} \qquad (12)$$

and $(\tau_0')^{-1}$ denote the decay rates for ${}^1(RN^+H_3{}^*$–Crown) and ${}^1(RNH_2{}^*$–Crown), respectively, and $k_2 << (\tau_0')^{-1} + k_q'[H^+]$. These experimental facts can be understood by using Corey–Pauling–Kolton molecular models (Figure 4).[51] The CPK molecular model of the anilinium ion was used originally.[59] The association constants K_g in the ground state of the RN^+H_3–Crown complexes can be easily determined by means of the fluorimetric titration method.[51] There is a steric effect of the aromatic ring on K_g: the K_g value ($1.6_2 \times 10^3\ M^{-1}$ at 27 °C) for the βRN^+H_3–Crown complex is greater than that for the αRN^+H_3–Crown complex ($2.1_4 \times 10^2\ M^{-1}$ at 27 °C).

Similar features in the excited state of phenanthrylammonium ion–18-crown-6 complexes are obtained.[60]

Proton and Hydrogen Atom Transfer Reactions

A laser study of the prototropic equilibrium of triplet benzophenone (BP) has been reported.[61] Similar equilibria in the triplet state of aromatic ketones have been demonstrated, since the lifetime is long enough to allow the acid–base equilibrium.[62] The values of the acidity constants $pK_a(T)$ in the triplet state markedly increase compared to those (–5.7 to –6.3)[63,64] in the ground state. The plot of $pK_a(T)$ values vs. the Taft σ^* values[65] of the substituents X gives a linear relation, indicating tha charge migration from X to the carbonyl group increases the $pK_a(T)$ value:[62]

$$pK_a(T) = -1.33\sigma^* + 0.60 \qquad (13)$$

$PhCOX$, $X(\sigma^*)$: CH_2CH_3 (–0.100);
CH_3 (0.00);CH_2Ph (+0.215); Ph (+0.600)

However, the $pK_a(T)$ value (0.2) of benzophenone (X = Ph) deviated from the line in a positive direction. This may be due to the +M effect from the phenyl group.

The proton-transfer reactions in the triplet state of 2-naphthylammonium ions βRN^+H_3 sensitized by triplet BP (or acetophenone AP) by means of nanosecond N_2 laser flash photolysis at 371 nm have been examined. It is found that the hydrogen atom transfer reaction from ${}^3\beta RN^+H_3{}^*$ (produced by triplet BP (or AP)) to the ground BP (or AP) occurs effectively to give the cation radical $\beta RNH_2{}^{+\cdot}$ and the benzophenone ketyl radical $>\dot{C}OH$.[66] This hydrogen atom transfer proceeds

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via the 1:1 triplet complex $^3(\beta RN^+H_3{}^*\cdots OC{<})$ (eq 14),[67]

$$\begin{tikzcd} {}^{3}\,\overset{+}{\mathrm{RN}}\mathrm{H}_3{}^{*} + {}^{1}{>}\mathrm{CO} \arrow[r, shift left, "K^*"] \arrow[d, "(\tau_0)^{-1}"] & {}^{3}(\overset{+}{\mathrm{RN}}\mathrm{H}_3{}^{*}\cdots\mathrm{OC}{<}) \arrow[l, shift left] \arrow[r, "k_{\mathrm{HT}}"] \arrow[d, "(\tau_0')^{-1}"] & \mathrm{RNH}_2^{\dot{+}} + {>}\dot{\mathrm{C}}\mathrm{OH} \quad (14) \\ {} & {} & \end{tikzcd}$$

where, e.g., at 17 °C, K^* is the equilibrium constant (1.2×10^2 M^{-1}), k_{HT} the rate constant for the hydrogen atom transfer ($3.2_6 \times 10^6$ s^{-1}), and $(\tau_0)^{-1} = 3.8 \times 10^4$ s^{-1}, and $(\tau_0') = 2.4 \times 10^5$ s^{-1} the corresponding decay rate constants. Similar hydrogen atom transfer takes place in the triplet state of 1-naphthol ($^3\alpha$ROH*) [sensitized by triplet BP (or AP)].[68] Hydrogen-atom transfer reactions of the triplet state of carbonyl compounds from a variety of substrates such as alcohols, hydrocarbons, and amines are well-known.[32,69–74] The reaction proceeds by either hydrogen atom transfer or electron transfer followed by proton transfer. For instance, ^{3}BP* abstracts a hydrogen atom from solvent molecules to yield $>\dot{C}OH$. The hydrogen atom transfer from $^3\beta RN^+H_3{}^*$ to the ground BP (or AP) is a new type photochemical reaction, whereas for $^1\beta RN^+H_3{}^*$ (or $^1\alpha$ROH*) the excited-state proton transfer occurs effectively.

Concluding Remarks

Proton-induced quenching (k_q') is involved in the excited state of aromatic compounds having an intramolecular CT structure in the excited state, and a simple acid–base equilibrium cannot be established during the lifetime in the excited state of such compounds. In order to obtain the correct p$K_a{}^*$ values, dynamic analyses with fluorimetry are, therefore, needed. The k_q' process is caused by electrophilic protonation $k_R{}^*$ at one of carbon atoms of the aromatic ring leading to hydrogen (or isotope) exchange; i.e., k_q' is equal to $k_R{}^*$. The proton-induced quenching k_q' mainly occurs in the lowest singlet state (S_1), since a polar structure (i.e., intramolecular CT structure) is dominant in the S_1 state but not in the triplet state. A prototropic equilibrium in the triplet state is established within the relatively long lifetime of the triplet state.

The complex formation of naphthylammonium ions RN^+H_3 with 18-crown-6 markedly decreases the proton dissociation rate k_1 in the excited state. There is no establishment of prototropic equilibrium in the S_1 state of the RN^+H_3–18-crown-6 complexes, since the protonation process k_2 becomes negligibly small compared to the other decay processes. The protonation k_2 to the amino group is structurally blocked by the 18-crown-6 and the naphthyl group of the excited neutral complex $^1(RNH_2{}^*$–Crown).

The hydrogen atom transfer reaction from $^3\beta RN^+H_3{}^*$ to the ground aromatic ketones occurs effectively to give the cation radical $\beta RNH_2{}^{+\cdot}$ and the ketyl radical $>\dot{C}OH$, whereas for $^1\beta RN^+H_3{}^*$ the excited-state proton transfer takes place markedly.

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