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The Relation between the Proton-induced Quenching Rate Constants and the Charge Densities of Aromatic Compounds[1)]

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Synopsis. A plot of log k'_q (the proton-induced quenching rate constants) *vs.* the charge densities P^*_Σ (or superdelocalizabilities S^*_Σ) in the excited state gave a straight line. The linear relation strongly supports the proton-induced quenching mechanism involving electrophilic protonation at the proper carbon atoms in the aromatic ring.[3)]

In previous papers,[4)] it has been shown that proton-induced fluorescence quenching competitive with proton transfer reactions is present (that is, the simple acid-base equilibrium cannot be accomplished in the excited state of aromatic amines) and the dynamic analyses containing the proton-induced quenching are, therefore, needed in order to obtain the correct pK_a* values. The dynamic analyses by means of nanosecond (or picosecond) time-resolved spectroscopy with fluorimetry are applied to 1-pyrenylamine,[5)] phenanthrylamines,[6)] 1-anthrylamine,[7)] and naphthols.[8)] The Stuttgart group[9)] has supported our method to determine the pK_a* values of naphthylamines. Similar experiments for excited naphthols have been reported by Harris and Selinger.[10)] The quenching mechanism induced by protons in polar media has been studied recently by this laboratory, and it is found that the fluorescence of aromatic compounds having an intramolecular CT structure is quenched effectively by protons and the proton-induced quenching is caused by electrophilic protonation at one of the carbon atoms of the aromatic ring leading to proton exchange (or isotope exchange).[3)] Hoytink[12)] and Waluk *et al.*[13)] have assumed a linear relationship between the logarithm of the protonation rate constant and π-electron density. It has been shown that the assumption fairly holds.[6)]

In the present paper, a plot of log k'_p (the proton-induced quenching rate constants) *vs.* the π-charge densities[14)] (or superdelocalizabilities)[15)] at the proper carbon atoms in the excited state of aromatic compounds was examined with the aid of a SCF–MO–CI method. The MO calculations of aromatic compounds were carried out by a semiempirical SCF–MO–CI method, which was described elsewhere.[11)] The calculations were performed by an electronic computer, HITAC 8800/8700, located at the Computer Center of the University of Tokyo. The rate constants k'_q for the proton-induced quenching are listed in Table 1.

Initially, the reaction parameter of the maximum charge density $P^*_{\max}$ (or superdelocalizability $S^*_{\max}$) at the proper carbon atom of the aromatic compounds for the electrophilic protonation in the excited singlet state was used. A linear relation between log k'_q and $P^*_{\max}$ was derived: log $k'_q=22.73\ P^*_{\max}\ -16.24$ (the correlation

Table 1. Proton-induced quenching rate constants (k'_q),[a)] the charge densities (P^*_Σ),[b)] and the superdelocalizabilities (S^*_Σ)[b)] of aromatic compounds

Compound	Quencher	Solvent	k'_q/M^{-1} s^{-1}	Ref.	$P^{*c)}_\Sigma$	$S^{*c)}_\Sigma$
1-Naphthylamine	H^+	5% CH_3CN in H_2O	8.9×10^9	4	2.274(5, 8)	0.4986(5, 8)
	D^+	5% CH_3CN in D_2O	6.0×10^9	4	2.274(5, 8)	0.4986(5, 8)
2-Naphthylamine	H^+	5% CH_3CN in H_2O	3.3×10^8	4	2.162(3, 5)	0.2867(5, 6)
	D^+	5% CH_3CN in D_2O	$1.9_6\times10^8$	4	2.162(3, 5)	0.2867(5, 6)
1-Anthrylamine	H^+	20% CH_3CN in H_2O	1.2×10^8	7	2.125(5, 9)	0.2956(3, 9)
	D^+	20% CH_3CN in D_2O	2.0×10^7	6	2.125(5, 9)	0.2956(5, 9)
1-Phenanthrylamine	H^+	10% CH_3CN in H_2O	1.6×10^8	6	2.070(7, 9)	0.2060(7, 9)
	D^+	10% CH_3CN in D_2O	5.4×10^7	6	2.070(7, 9)	0.2060(7, 9)
2-Phenanthrylamine	H^+	10% CH_3CN in H_2O	4.4×10^8	6	2.157(5, 7)	0.2148(5, 7)
	D^+	10% CH_3CN in D_2O	3.4×10^8	6	2.157(5, 7)	0.2148(5, 7)
3-Phenanthrylamine	H^+	10% CH_3CN in H_2O	9.3×10^7	6	2.081(4, 5)	0.2406(4, 5)
	D^+	10% CH_3CN in D_2O	4.4×10^7	6	2.081(4, 5)	0.2406(4, 5)
4-Phenanthrylamine	H^+	10% CH_3CN in H_2O	2.5×10^8	6	2.080(6, 8)	0.3094(6, 8)
	D^+	10% CH_3CN in D_2O	2.1×10^8	6	2.080(6, 8)	0.3094(6, 8)
9-Phenanthrylamine	H^+	10% CH_3CN in H_2O	1.9×10^8	6	2.102(5, 7)	0.2161(5, 7)
	D^+	10% CH_3CN in D_2O	1.6×10^8	6	2.102(5, 7)	0.2161(5, 7)
1-Pyrenylamine	H^+	20% CH_3CN in H_2O	3.7×10^7	5	2.123(4, 9)	0.2649(4, 9)
	D^+	20% CH_3CN in D_2O	1.4×10^7	5	2.123(4, 9)	0.2649(4, 9)
1-Naphthol	H^+	H_2O	7.5×10^8	8	2.202(5, 8)	0.1644(5, 8)
	D^+	D_2O	4.6×10^8	8	2.202(5, 8)	0.1644(5, 8)
1-Methoxynaphthalene	H^+	20% CH_3CN in H_2O	1.1×10^9	3	2.202(5, 8)	0.1644(5, 8)
	D^+	20% CH_3CN in D_2O	5.1×10^8	3	2.202(5, 8)	0.1644(5, 8)

a) The proton-induced quenching rate constants for the excited neutral species at 300 K. b) The two reactive positions were selected for determinatoin of the P^*_Σ(or S^*_Σ) value. For details see the text. c) The reactive state of all aromatic compounds in polar media is the lowest excited singlet state (^1L_a). The reactive positions are shown in parentheses.

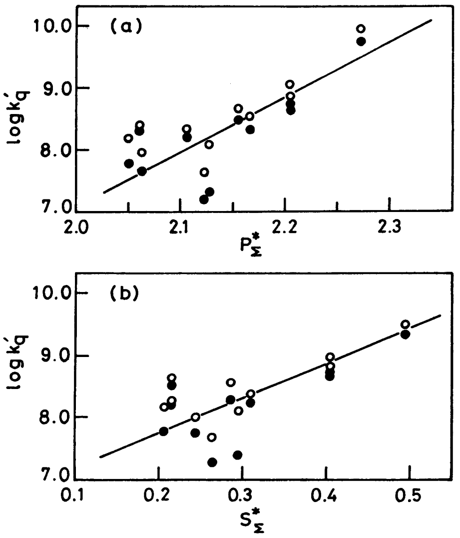

Fig. 1. Plots of (a) log k'_q *vs.* P^*_Σ and (b) log k'_q *vs.* S^*_Σ. ○: The H_2SO_4/H_2O system, ●: the D_2SO_4/D_2O system. The reactive positions were selected for determination of the P^*_Σ (or S^*_Σ) value. For details see the text.

coefficient $r=0.713$). However, lack of linear relation between log k'_q and $S^*_{\max}$ ($r=0.403$) was obtained. It is experimentally shown that the excited 1-methoxynaphthalene, for example, is attacked by protons mainly at the position 5 and slightly at the position 8.[3] Therefore, two reactive positions having larger P^* (or S^*) values in the lowest excited singlet state were selected from the carbon atoms as listed in Table 1. Figure 1 shows the plots of (a) log k'_q *vs.* P^*_Σ and (b) log k'_q *vs.* S^*_Σ, where P^*_Σ and S^*_Σ denote the summation values of charge densities and superdelocalizabilities at the two carbon atoms in the excited state, respectively. From Fig. 1, the following relations are obtained by the least squares method:

$$\log k'_q = 8.84 P^*_\Sigma - 10.59 \qquad (r = 0.792), \qquad (1)$$

and

$$\log k'_q = 5.54 S^*_\Sigma + 6.68 \qquad (r = 0.737). \qquad (2)$$

A plot of log k'_q *vs.* P^*_Σ (or S^*_Σ) where the reactive positions were expanded to three carbon atoms was also examined, and a straight line similar to that in Fig. 1 was obtained: $\log k'_q=8.01 P^*_\Sigma-17.20$ ($r=0.785$); $\log k'_q=5.13 S^*_\Sigma+8.12$ ($r=0.729$). From these results, the two reactive positions of the aromatic ring in the excited state may be adequate for determination of the P^*_Σ (or S^*_Σ) value. The linear relation in Fig. 1 strongly supports the mechanism that the proton-induced quenching is caused by electrophilic attack at one of carbon atoms of aromatic compounds.[3] Thus, one can approximately estimate the k'_q values for the proton-induced quenching of other aromatic compounds using Eq. 1 or 2.

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