EXCITED STATE pK_a* VALUES OF AROMATIC AMINES BY DYNAMIC ANALYSES

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Determination of the proton dissociation constant in the excited state pK_a* is well established; the Förster cycle [1 - 3], fluorescence titration [2, 3] and $T_n \leftarrow T_1$ absorption [4] methods are well known. In a preliminary paper [5] it has been shown that for α- and β-naphthylamines simple acid–base equilibria in the excited singlet state cannot be accomplished since proton-induced quenching of neutral amines is involved. Therefore the pK_a* values of napthylamines cannot be determined directly from the Förster cycle and fluorescence titration curve, and dynamic analyses by means of nanosecond time-resolved spectroscopy with fluorimetry must be employed in order to determine the correct pK_a* values [5].

In the present work, we should like to report that the dynamic method involving proton-induced quenching k'_q is generally applicable to other aromatic amines (N,N-dimethyl-α-naphthylamine (DMNA), 1-aminoanthracene (1-AA), and 1-aminopyrene (1-AP)) in the presence of protons. The isotope effects on the proton dissociation k_1, association k_2 and quenching k'_q rate constants were also examined.

The experimental procedures and analyses were the same as reported previously [5]. The k'_q (or k_1) value can be determined by fluorimetry. The convolution method [6] was applied to the analyses of fluorescence response functions, and the values of k_1 (or k'_q) and k_2 were obtained. The reaction scheme of the excited states of aromatic amines in the presence of protons is shown in Fig. 1. The static quenching mechanism involving hydration of the naphthylamine cations in the ground state was recently
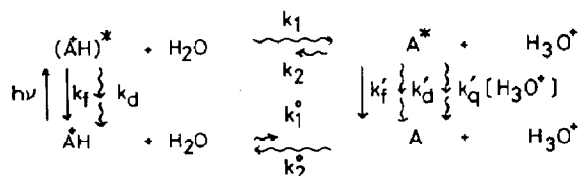

Fig. 1. Reaction scheme of excited state naphthylamines in the presence of protons [5].

TABLE 1

Proton dissociation k_1, protonation k_2 and quenching k'_q rate constants in the S_1 state and pK_a* of aromatic amines at 300 K

	Quencher	$k_1(10^8\,s^{-1})$	$k_2\,(10^8\,M^{-1}s^{-1})$	$k'_q\,(10^8\,M^{-1}s^{-1})$	pK_a*
DMNA	H⁺	0.096 ± 0.005	30 ± 3	41 ± 4	2.5 ± 0.2
	D⁺	0.017 ± 0.004	11 ± 2	10 ± 2	2.8 ± 0.1
1-AA	H⁺	3.5 ± 0.4	0.8 ± 0.1	1.2 ± 0.1	−0.64 ± 0.03
	D⁺	0.97$_5$ ± 0.01	0.24 ± 0.03	0.2 ± 0.03	−0.61 ± 0.02
1-AP	H⁺	42 ± 2	2.7 ± 0.2	0.36$_8$ ± 0.02	−1.2 ± 0.1
	D⁺	34 ± 2	2.3 ± 0.2	0.14$_4$ ± 0.02	−1.1$_2$ ± 0.1

proposed by Schulman and Sturgeon [7]. The mechanism was based on the observation that the fluorescence decay times T_0 of the cations were unchanged at various concentrations of protons as the apparent quantum yield of fluorescence increased with increasing [H$^+$] (α-NA, T_0 = 4.1 ns; β-NA, T_0 = 5.0 ns) [7]. However, the constant lifetimes such as T_0 were never observed in our repeated experiments of naphthylamines [5] and also in the present work. The apparent lifetimes τ_{AH} increased with increasing [H$^+$] to give a maximum value of τ_{AH} at higher acid concentrations. Therefore, the static quenching mechanism is not acceptable for the present work.

From k_1 and k_2 values the correct pK_a* values were determined, which were different from those obtained from the Förster cycle and also the fluorescence titration curve. These data are summarized in Table 1.

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THE PRIMARY PROCESSES IN THE Cd(^{3}P$_1$)–C$_2$H$_6$ REACTION AT 265 °C

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A detailed analytical investigation of the Cd(^{3}P$_1$)–C$_2$H$_6$ reaction at 265 °C in the gas phase has been made with a gas chromatograph (GC) and a mass spectrometer. The reaction has a well-defined induction period, the length of which decreases with an increase of the incident light intensity, cadmium concentration in the cell or of the reactant pressure. During the induction period no products could be detected (the lower detectibility limit of the GC is 5 × 10^{-9} mol l^{-1} of hydrocarbons in the reaction cell). The major products detected are H$_2$, n-C$_4$H$_{10}$ and C$_2$H$_4$, while the minor products are CH$_4$, C$_3$H$_8$, C$_3$H$_6$, C$_4$H$_8$-1, C$_5$H$_{10}$-1 and n-C$_6$H$_{14}$. The major products and methane were estimated and they were found to form at accelerated rates with conversion after the induction period. It was noted that the hydrogen and ethylene were formed by the primary and secondary processes, while n-butane and methane were formed entirely by the secondary processes. The initial rates of hydrogen and of ethylene were found to be approximately equal at a given reactant pressure. It has been suggested that the primary processes are

$$Cd(^3P_1) + C_2H_6 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Cd(^3P_0) + C_2H_6 \tag{1, 2}$$

$$Cd(^3P_1) + C_2H_6 \xrightarrow{k_3} Cd(^1S_0) + H_2 + C_2H_4 \tag{3}$$

$$Cd(^3P_0) + C_2H_6 \xrightarrow{k_4} Cd(^1S_0) + H_2 + C_2H_4 \tag{4}$$