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KINETIC ANALYSIS OF THE ABNORMAL FLUORIMETRIC TITRATION BEHAVIOUR OF NAPHTHYLAMINES

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The fluorimetric titration behaviour of naphthylamines is abnormal in that the sum of the reduced quantum yields of conjugated acid and base passes through a minimum. Based on fluorescence quantum yield and lifetime measurements, we explain this behaviour by two independent mechanisms: A diabatic quenching of the excited base by protons and a decrease of the excited cation's protolytic dissociation in the hyperacidic region. Though apparently independent processes, their rate constants can be shown to be related to each other by a quasi-thermodynamical equation.

1. Introduction

In the investigation of the behaviour of acid–base reactions in the excited singlet state, the application of stationary and time-dependent fluorescence measurements is well established [1]. Normally the sum of the reduced quantum yields of the acidic form AH^+ and the neutral form A is unity,

$$\Phi_{AH^+}/\Phi_{AH^+}^{max} + \Phi_A/\Phi_A^{max} = 1, \qquad (1)$$

which is a consequence of adiabaticity ("conservation of excitation") in the excited-state protolytic reactions. One famous exception to this relation is the fluorescence change of naphthylamine and its derivatives, first investigated by Forster [2,3] and Schulman [4]. Whereas in systems obeying eq. (1) the fluorescence decrease of the basic component is accompanied by a concomitant increase of the acid component, in the case of the naphthylamines the fluorescence change of either component occurs in its own region of pH or H_0, respectively.

As an explanation those authors suggested that a non-fluorescent intermediate should be involved in the proton-transfer reaction, opening a channel of effective radiationless deactivation and thus causing a drastic decrease in the sum of reduced quantum yields in moderately acidic solutions. As possible non-fluorescent intermediate, an exciplex between hydronium ion and naphthylamine [3,4] or a ring-protonated species [3], as suggested by Weller, were considered.

Tsutsumi and Shizuka (TS) [5] analyzed the quantum yield and lifetime of the amine fluorescence in the pH region $1 \leqslant pH \leqslant 3$ in terms of proton-induced quenching, which was shown to dominate the adiabatic protonation of the amine. These authors were not interested in the increase of the fluorescence intensity of the protonated form AH^+ in the hyperacidic region ($-3 \geqslant H_0 \geqslant -6$).

Schulman and Surgeon [6] recently reinvestigated the fluorescence change of naphthylamines. According to their measurements the lifetime of the excited AH^+ is independent of the acid concentration. Therefore, to explain the change of the cationic fluorescence quantum yield, they had to assume a static quenching mechanism for which they suggested the following ground-state hydration equilibrium:

$$(AH^+)(H_2O)_n \rightleftharpoons AH^+ + nH_2O, \qquad (2)$$

where only the unhydrated species (present in concentrated acid) was assumed to be fluorescent.

Measurements in our laboratory have shown that the lifetime of the excited AH^+ changes with acid concentration in the same way as the quantum yield. We are able to explain the quenching of the neutral form as well as the increase of the fluorescence in-

tensity of the cationic species in the highly acidic region. Furthermore we can show that the cationic and neutral base fluorescences, though kinetically apparently independent, are related to each other by a quasi-thermodynamic relation.

2. Experimental

1-naphthylamine (Merck, reagent grade) was used without further purification 2-naphthylamine (Merck) was purified via its hydrochloride and by subsequent sublimation. Reagent-grade H_2SO_4 (Merck) and deionized and doubly distilled water were used, the actual acid contents determined by titration. The amine concentrations were 2×10^{-4} M (1-naphthylamine) and 8×10^{-4} M (2-naphthylamine). The investigations were carried out with solutions showing cationic absorption spectra. Only freshly prepared solutions were investigated in order to avoid chemical reactions of the naphthylamines.

The measurements were made on air-saturated solutions, since control experiments with degassed solutions showed that oxygen does not influence the quantum yields and lifetimes.

Fluorescence spectra were recorded with a Hitachi–Perkin–Elmer (MPF-3L) spectrophotometer. Slit widths smaller than 8 nm were used. For determination of absolute fluorescence quantum yields indole in ethanol ($\Phi_F = 0.36$ [7]) was used as a quantum standard for the cationic fluorescence and quinine bisulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.54$ [8]) for the amine fluorescence. Lifetime measurements were performed on a single photon counting apparatus (Ortec), with a half width of the exciting flash of 2.5 ns.

3. Results and discussion

Quantum yields and fluorescence decay constants of 1- and 2-naphthylamine are given in tables 1 and 2 for various concentrations of H_2SO_4 where the quan-

Table 1
Fluorescence quantum yields and decay constants of 1-naphthylamine (free base RNH_2 and cation RNH_3^+) at various acid concentrations

RNH_3^+				RNH_2			
$c_{H_2SO_4}$ (mol/ℓ)	Φ_{AH^+}	λ_2 (10^6 s^{-1})	k_f (10^6 s^{-1})	$c_{H_2SO_4}$ (mol/ℓ)	Φ_A	λ_2 (10^6 s^{-1})	k'_f (10^6 s^{-1})
9 9	0 24	20	4 8	0 001	0 28	56	15 6
8 6	0 20	23	4 6	0 005	0 15	109	16.4
7 7	0.15	34	5 1	0 009	$0\ 10_2$	160	16 3
7 1	$0\ 12_5$	36	4.5	0 013	0 079	200	15 8
5 7	0 072	64	4 6	0 018	0 061	256	15 6
5 1	0 046	100	4 6	0 031	0 041	392	16 0

Table 2
Fluorescence quantum yields and decay constants of 2-naphthylamine (free base RNH_2 and cation RNH_3^+) at various acid concentrations

RNH_3^+				RNH_2			
$c_{H_2SO_4}$ (mol/ℓ)	Φ_{AH^+}	λ_2 (10^6 s^{-1})	k_f (10^6 s^{-1})	$c_{H_2SO_4}$ (mol/ℓ)	Φ_A	λ_2 (10^6 s^{-1})	k'_f (10^6 s^{-1})
10 2	0 060	40.1	2 40	0.001	0.39	57 0	22 2
9.7	0 059	42 2	2 49	0 103	0 27	83.1	22 4
8 7	0 042	59.0	2.48	0 205	0 20	108	21.6
7 55	0 019	132	2 51	0.423	0 13	176	22 8
6 7	$0\ 010_5$	240	2 52	0 63	0 092	245	22 5
6.0	$0\ 006_4$	395	2 53	0 86	0 065	336	21.8

tum yields are high enough to allow accurate lifetime measurements In the intermediate acidity range only the quantum yields were determined. The results obtained for these are in fair agreement with TS (see fig. 1 of ref. [5]).

We first discuss the fluorescence behaviour of the neutral compounds, which at $pH \leqslant 3$ is observed on excitation of the cationic forms. As already described by TS the corresponding fluorescence decay curves, as measured by single photon counting technique, can be fitted by convolution of the exciting pulse with the following fluorescence response function $I_A(t)$ to δ-pulse excitation·

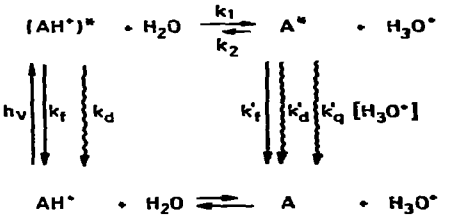
$$I_A(t) \propto (e^{-\lambda_1 t} - e^{-\lambda_2 t}). \qquad (3)$$

For 1- and 2-naphthylamine the slow time constants, describing the decay at long times, can be determined with good accuracy. They are given in tables 1 and 2 for various acid concentrations. In each case the product of decay constant and quantum yield results in a constant value for the rate constant of fluorescence (k_f'), independent of the *pH* of the solution.

The fast time constant could be determined by single photon technique with reliable accuracy for 1-naphthylamine only It was found to be 8.5×10^8 s^{-1} at *pH* 2 7. In the case of 2-naphthylamine the time resolution of the single photon apparatus was not sufficient to resolve the fast time constant, which, according to eq. (3), determines the rise of the fluorescence of A. If the excited A is formed from the fluorescent cationic species the fast decay of AH^+ must be identical with the rise of A-fluorescence. Unfortunately the cationic fluorescence, though detectable whenever AH^+ is excited, is too weak for accurate lifetime measurements in the acidity region where lifetime measurements of the neutral base fluorescence are feasible. However, using the rate constant of fluorescence of AH^+ (4.8×10^6 s^{-1} for 1-naphthylamine and $2\,5 \times 10^6$ s^{-1} for 2-naphthylamine) measured in the hyperacidic region where the quantum yield of AH^+ is high, and using the quantum yield of AH^+ at *pH* 3 (0.006 for 1-naphthylamine and 0.0007 for 2-naphthylamine), fluorescence decay constants at this *pH* are calculated to be 8.0×10^8 s^{-1}, respectively. The value for 1-naphthylamine is in good agreement with the fast time constant obtained from the single photon counting measurement on the amine fluorescence. The rate constant for 2-naphthylamine is indeed of an order of magnitude not resolvable by this experimental technique and so far in accord with the experimental findings. We consider these results as evidence that the *fluorescent* species $(AH^+)^*$ is the direct precursor of A^*, when formed via excitation of AH^+.

This conclusion is in direct contradiction to the paper of Schulman and Surgeon [6] who attributed the formation of A^* to the dissociation of a *non-fluorescent* hydrated cation and assumed the cationic fluorescence to be emitted by a non-hydrated cation. These conclusions are based, however, on an erroneous experimental result concerning the acidity dependence of the lifetime of the cationic fluorescence, which is disproved by our measurements.

If, as we conclude from our results, there is only one kind of excited cation, the decrease of lifetime and quantum yield of the neutral fluorescence with increasing acid concentration cannot be explained by an adiabatic protonation of A^*, since this would be indicated by a corresponding increase of the cationic fluorescence intensity. At a *pH*, however, where the neutral fluorescence has dropped to one percent of its initial value, the cationic fluorescence has increased to less than 1% of its maximal value (cf. also fig. 1 of TS [5]). In agreement with TS we conclude therefore that there is a diabatic quenching process by protons, the rate constant (k_q') of which exceeds by far the rate constant of the adiabatic association process (k_2). In the following we make use of the kinetic scheme of TS, adopting the same symbols for the rate constants. We show, that with some modifications this scheme can account for all the features of the abnormal fluorimetric titration curves (see scheme I)



Scheme I

For the *pH*-region where lifetime measurements of A^* are feasible (see tables 1 and 2), the results described so far can be summarized by the relations:

$$k_1 \gg k'_q[H_3O^+] \gg k_2[H_3O^+], \quad k_1 \gg k_0 \approx k'_0$$

$$(k_0 = k_f + k_d, k'_0 = k'_f + k'_d). \tag{4}$$

With these conditions the following expression can be derived for the fluorescence quantum yield of A (cf. eq. (2) of TS [5])

$$\Phi_A = \Phi_A^{max} k'_0/(k'_0 + k'_q[H_3O^+]). \tag{5}$$

For the two rate constants of fluorescence of A (and AH^+) one obtains

$$\lambda_{1,2} = \tfrac{1}{2}\{k_0 + k_1 + k'_0 + (k'_q + k_2)[H_3O^+]$$
$$\pm (k_0 + k_1 - k'_0 - (k'_q + k_2)[H_3O^+])$$
$$\times \{1 + 4k_1 k_2[H_3O^+]$$
$$\times (k_0 + k_1 - k'_0 - (k'_q + k_2)[H_3O^+])^{-2}\}^{1/2}\}, \tag{6}$$

which, under the condition (4) valid at small values of $[H_3O^+]$ and using the approximation $(1+x)^{1/2} \approx 1 + x/2$ (for $x < 1$), can be simplified to

$$\lambda_1 = k_0 + k_1 + k_2[H_3O^+], \tag{7}$$

$$\lambda_2 = k'_0 + k'_q[H_3O^+]. \tag{8}$$

From (5) and (8) it follows immediately that for the slow time constant λ_2, evaluated from the single photon experiments, the following relation must hold

$$\lambda_2 \Phi_A = k'_0 \Phi_A^{max} = k'_f = \text{const.}, \tag{9}$$

which is confirmed experimentally (see tables 1 and 2). Both equations (5) and (8) are Stern–Volmer relations, yielding linear plots in the limit of low H^+-concentration. From either of these k'_q can be calculated. Our values of 5.8×10^9 M^{-1} s^{-1} and 1.9×10^8 M^{-1} s^{-1} for 1- and 2-naphthylamine, respectively, are in fair agreement with those obtained by TS As for k_2, it is clear from eqs. (7) and (8) that under the conditions, indicated in eq. (4), information can be only obtained from the fast time constant λ_1 This requires, however, that λ_1 is measured with an accuracy of better than 1% which, in our opinion is outside the scope of a nanosecond technique, since $\lambda_1 \geqslant 10^9$ s^{-1}. Therefore one cannot obtain kinetically determined pK_a^* values for the naphthylamines.

In the hyperacidic region ($5 < c_{H_2SO_4} < 10$ mol/ℓ corresponding to approximately $-2.5 > H_0 > -6$) the fluorescence of AH^+ increases strongly with the acid concentration (see tables 1 and 2) and lifetime measurements can be performed by the single photon technique. The fluorescence decay curves are monoexponential and the product of decay constant and quantum yield is constant, indicating that k_f is constant This justifies our assumption that in the region where the lifetime of $(AH^+)^*$ is too short to be determined experimentally, k_f is still unchanged, allowing the determination of the decay time from the quantum yield.

Based on our experimental results, we explain the increase of the cationic fluorescence in the strongly acidic region as follows The single-exponential decay of this fluorescence is in accord with the assumption $k_2 \ll k'_q$ [cf. eq. (4)]. Therefore the kinetic problem is that of a single, directly excited species, in which case we have

$$\Phi_{AH^+} = k_f/(k_f + k_d + k_1). \tag{10}$$

Since k_f is constant, as demonstrated in tables 1 and 2, and since for low proton concentrations, where Φ_{AH^+} is very small, $k_1 \gg (k_f + k_d)$, an increase of Φ_{AH^+} with increasing acid concentration can only be due to a decrease of k_1.

To understand this behaviour it is important to note, that in the hyperacidic region, where the increase of the cationic fluorescence begins, the activity of the proton acceptor water becomes markedly reduced. We do not give a mechanistic interpretation of the decrease of k_1 here, but instead point out that a quasi-thermodynamic relation exists between k_1 and the quenching constant k'_q. This rate parameter, again, is not a true constant, but increases as the acidity of the solution increases. This was also observed by TS.

Since the character of the solvent is changed when proceeding from dilute aqueous to highly acidic solutions, one cannot expect the rates of protonation or quenching of A^* to be described correctly by $k_2[H_3O^+][A^*]$ or $k'_q[H_3O^+][A^*]$, respectively, if k_2 and k'_q are regarded as true rate constants. Therefore we generalize these expressions by introducing the $[H_3O^+]$-dependent rate "constants" $\tilde{k}_2$ and $\tilde{k}'_q$, with the only assumption that their ratio is constant:

$$\tilde{k}_2/\tilde{k}'_q = c. \tag{11}$$

The rate parameter $\tilde{k}'_q$ can be calculated from the quantum yield of the free base Φ_A by use of eq. (5):

$$\tilde{k}'_q = (\Phi_A^{max}/\Phi_A - 1)k'_0/[H_3O^+]. \quad (12)$$

We also use $\tilde{k}_1$ instead of k_1 in order to express the $[H_3O^+]$-dependence of this rate constant. It can be calculated by the equation:

$$\tilde{k}_1 = k_0(\Phi_{AH^+}^{max}/\Phi_{AH^+} - 1). \quad (13)$$

We now consider the hypothetical case that all rate constants of scheme I are zero except $\tilde{k}_1$ and $\tilde{k}_2$. Then a true thermodynamic equilibrium between A^* and $(AH^+)^*$ would be established in the excited state, which in the hyperacidic region would be determined by the pK_a^* and the Hammett acidity function H_0 [9]:

$$\log[A^*/(AH^+)^*] = H_0 - pK_a^*, \quad (14)$$

if we assume that the H_0 function, valid for the ground state, can also be applied to the excited state.

On the other hand, for kinetic reasons, the following equation would hold:

$$[A^*]/[(AH^+)^*] = \tilde{k}_1/\tilde{k}_2[H_3O^+] = \tilde{k}_1 c/\tilde{k}'_q[H_3O^+]. \quad (15)$$

Hence from eqs. (14) and (15) we obtain:

$$\log\tilde{k}_1 \log(\tilde{k}'_q[H_3O^+]) = H_0 - pK_a^* - \log c. \quad (16)$$

Substituting $\tilde{k}_1$ and $\tilde{k}'_q$ by the corresponding quantum yield expressions (12) and (13) leads to:

$$\log(\Phi_{AH^+}^{max}/\Phi_{AH^+} - 1) - \log(\Phi_A^{max}/\Phi_A - 1)$$
$$= H_0 - pK_a^* - \log(k_0/k'_0) - \log c. \quad (17)$$

Thus we have arrived at a quasi-thermodynamic relation between functions of the fluorescence quantum yields of excited acid and base and the acidity function H_0, though different mechanisms affect these quantum yields. The plots of the left hand side of eq. (17) versus H_0 are shown in fig. 1. For both amines

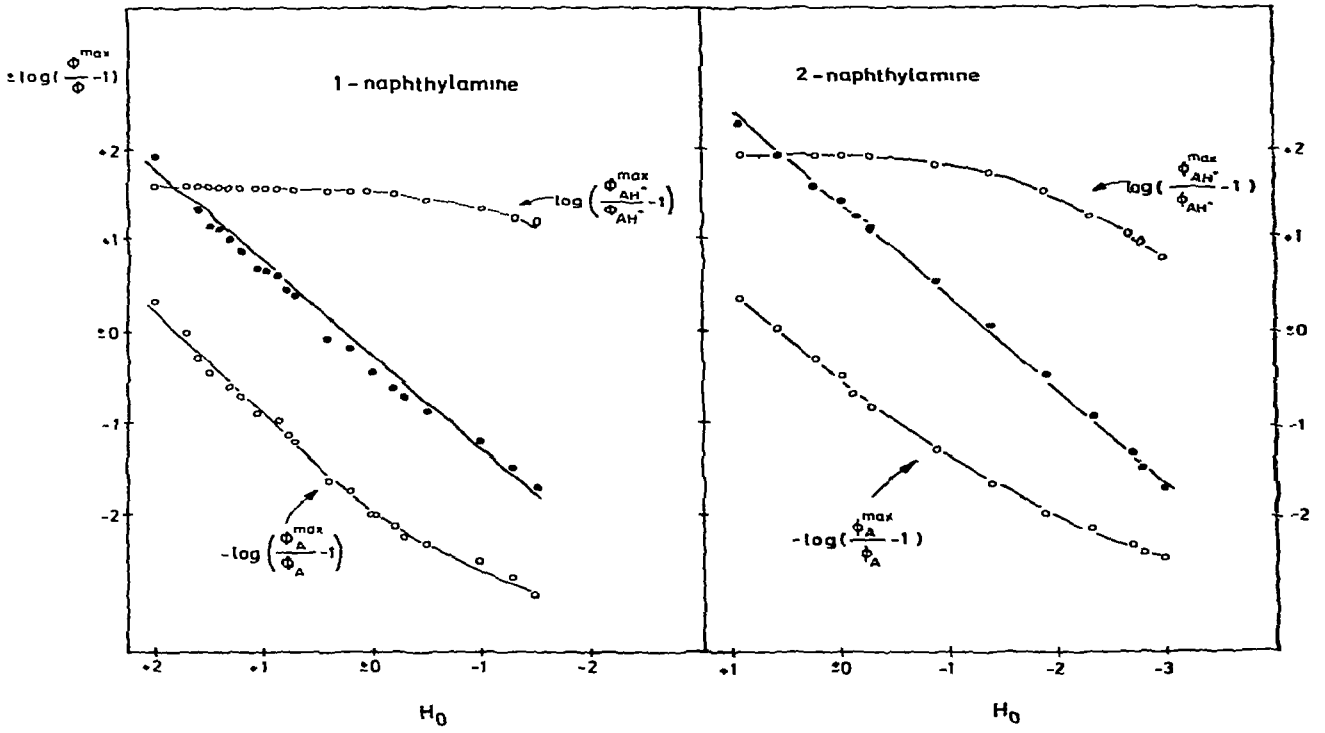


Fig. 1. Plot of left-hand side terms of eq. (17) versus Hammett acidity function H_0 (conversion of H_2SO_4-concentration to H_0 according to ref. [10]). Open circles: individual contributions of cationic and neutral amine fluorescence. Full circles: difference of the respective contributions

straight lines are obtained with almost theoretical slopes (1 02).

4. Conclusions

Our experimental results on the acidity dependence of the fluorescence quantum yield and lifetime of 1- and 2-naphthylamine and their respective cations lead us to the following explanation of the exceptional fluorescence behaviour of these compounds in the spectral turnover region: The *fluorescence of the excited bases*, formed upon adiabatic dissociation of the excited cations, *decreases* (equally in quantum yield and lifetime) with increasing acidity *due to a diabatic quenching* of the excited bases by protons The *fluorescence of the excited cations increases* with acidity in the hyperacidic region (equally in quantum yield and lifetime) not because of a reprotonation of the excited bases, but *because of a decrease of the protolytic dissociation rate constant* (k_1). The latter has to be explained by a decreasing activity of water, the proton-accepting species in the system. The adiabatic reprotonation of the excited base (k_2) is negligible compared to the diabatic quenching by protons $(k'_q)^{\ddagger}$. A quasi-thermodynamic relation between k_1 and k'_q has been established, even though the corresponding reactions do not compose a chemical equilibrium.

‡ For cases where k'_q and k_2 are comparable see ref [11].

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