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General Kinetics of Reversible Reactions in the Excited State. Application to Excited Singlet pK Determination of Acridone, Xanthone and Thioxanthone*

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From steady state kinetics of a general excited state reversible reaction scheme, a linear relation between the total luminescence and the concentration of one reactant is derived, showing that the equilibrium constant of certain excited state reactions can be determined from the total fluorescence spectra without the separation of the components and irrespective of the ground state equilibrium. The relation is checked by comparison with published results, and it is applied to the determination of excited state acidity constants of acridone, xanthone and thioxanthone in ethanol-water (1:1).

Aus der „steady state“-Kinetik eines allgemeinen Schemas reversibler Reaktionen angeregter Zustände wird eine lineare Beziehung zwischen der totalen Lumineszenz und der Konzentration eines Reaktanten abgeleitet. Sie zeigt, daß die Gleichgewichtskonstante gewisser Reaktionen angeregter Zustände aus dem totalen Fluoreszenz-Spektrum ohne Separation der Komponenten und ohne Rücksicht auf das Gleichgewicht im Grundzustand abgeleitet werden kann. Die Beziehung wird durch Vergleich mit veröffentlichten Ergebnissen geprüft und wird dann auf die Bestimmung von Säurekonstanten im angeregten Zustand von Acridon, Xanthon und Thioxanthon angewandt.

The kinetic treatment of excited state acid-base reactions developed mainly by the extensive studies of WELLER [1] constitute a complementary approach and a good test of the experimental ap-

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plicability of FÖRSTER's elegant thermodynamic method [2]. The fundamental and experimental limitations of "Förster's cycle" have been discussed by various authors [3—6].

In the following, a kinetic calculation based on a general scheme of excited state reversible reactions, leading to a simple relation which allows determination of equilibrium constant from total fluorescence spectra, without separation of the components and irrespective of the ground state equilibrium, is presented. The validity of this relation is checked by comparison of excited state acid-base equilibrium constants of some compounds with those obtained by other workers. Finally, a new excited state acid-base reaction involving thioxanthone is reported and its equilibrium constant determined. A tentative correlation between the possible structures and the magnitudes of the excited state equilibrium constants, as well as the spectral characteristics of acridone, xanthone and thioxanthone, is presented at the end of the paper.

Experimental

All measurements were performed in ethanol-water (1:1 v/v) at 25°.

The various solutions were prepared from stock solutions of the reagents in ethanol (Merck G.R.) to which water was added in equal proportion. The pH was adjusted with sulfuric acid 98% (Merck G.R.) or sodium hydroxide (0.4 M) and measured by a Metrohm E 500 digital pH-meter with Metrohm glass electrode. It should be pointed out that even in the very low pH range the meter readings were in accord with the values calculated from the added acid amounts.

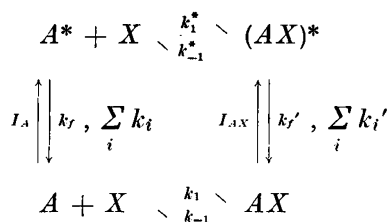
Acridone (Fluka) was recrystallized from ethanol-water (m.p. 354°); xanthone (Fluka puriss. m.p. 173—174°) and thioxanthone (Fluka purum) were used without further purification.

Spectra and luminescence measurements were taken on Aminco-Bowman and Hitachi-Perkin Elmer MPF-2A spectrofluorimeters and a Beckman DB-G spectrophotometer.

Results and discussion

Kinetics

The following reaction sequence is adopted as being a most general representation of a reversible reaction occurring in ground and excited states:



where I_A, I_{AX} are the intensities (einstein. s⁻¹) absorbed by A and AX ; $I = I_0 (1 - e^{-\epsilon c l})$, I_0 : intensity of incident beam; k_f, k_f' : luminescence (fluorescence) rate constants;

$\sum_i k_i, \sum_i k_i'$: sum of rate constants of all photophysical processes of A and AX , other than luminescence;

$k_1, k_{-1}, k_1^*, k_{-1}^*$: rate constants of forward and reverse reactions at ground and excited states.

In the above reaction scheme, it is assumed that the species $(AX)^*$ is the same, whether it is formed by reaction of A^* with X or by direct excitation of AX . This is very probably so, when X is a hydronium ion [7]. This assumption may be incorrect when X is another molecule of A , or some other reactant (metal ion or another organic species) which is photoinactive at the same wavelength as A . Indeed, in differentiating between the encounter complex $(A^* - X)$ and the excited complex $(AX)^*$, the general mechanism as presented here, assumes that in the sequence $A^* + X \rightleftharpoons (A^* - X) \rightleftharpoons (AX)^*$ the diffusion controlled equilibrium relaxation is rate determining when compared to intramolecular energy partition.

From the reaction scheme, the total emission intensity can be expressed as:

$$F_{\text{total}} = k_f (A^*) + k_f' (AX^*) \tag{1}$$

and if

$$k_1^* \tau_0 (X) \gg 1$$

and

$$k_{-1}^* \tau_0' \gg 1$$

where

$$\tau_0 = (k_f + \sum_i k_i)^{-1}$$

and

$$\tau_0' = (k_f' + \sum_i k_i')^{-1}$$

a stationary state kinetic treatment yields:

$$(A^*) = \frac{\tau_0 \tau_0' (I_A + I_{AX})}{\beta^* \tau_0 (X) + \tau_0'} \quad (2)$$

$$(AX^*) = \frac{\tau_0 \tau_0' \beta^* (X) (I_A + I_{AX})}{\beta^* \tau_0 (X) + \tau_0'} \quad (3)$$

where

$$\beta^* = \frac{k_1^*}{k_{-1}^*}$$

is the excited state equilibrium stability constant.

Upon substitution of (2) and (3) into (1) and with the additional experimental conditions such as:

$$I_a = I_0 (1 - e^{-\epsilon cl}) \approx I_0 \epsilon cl$$

$$F = \Phi I_a \approx \Phi I_0 \epsilon cl$$

c : concentration of A or AX

Φ : fluorescence efficiency

I_a : absorbed intensity

one gets:

$$\Phi = \frac{(\beta^*)^{-1} \varphi_0 \tau_0' + \tau_0 \varphi_0' (X)}{(\beta^*)^{-1} \tau_0' + \tau_0 (X)} \quad (4)$$

with the limiting values:

$$\lim_{(X) \rightarrow 0} \Phi = \varphi_0$$

and

$$\lim_{(X) \rightarrow \infty} \Phi = \varphi_0'$$

where

$$\varphi_0 = \frac{k_f}{k_f + \sum_i k_i}$$

and

$$\varphi_0' = \frac{k_f'}{k_f' + \sum_i k_i'}$$

Dividing (4) by φ_0 (or φ_0') and rearranging, the following linear relations are derived:

$$\frac{1}{\frac{\Phi}{\varphi_0} - 1} = \frac{1}{\beta^*} \frac{\tau_0'}{\tau_0} \left(\frac{1}{\frac{\varphi_0'}{\varphi_0} - 1} \right) \frac{1}{(X)} + \left(\frac{1}{\frac{\varphi_0'}{\varphi_0} - 1} \right), \quad (5)$$

$$\frac{1}{\frac{\Phi}{\varphi_0'} - 1} = \beta^* \frac{\tau_0}{\tau_0'} \left(\frac{1}{\frac{\varphi_0}{\varphi_0'} - 1} \right) (X) + \left(\frac{1}{\frac{\varphi_0}{\varphi_0'} - 1} \right). \quad (6)$$

Both relations (5) and (6) are applicable at the wavelengths where φ_0 and φ_0' are not zero. If $\varphi_0' = 0$ at the wavelength of measurement, relation (5) is applicable; if, on the contrary, $\varphi_0 = 0$ then (6) may be used. In such cases (5) and (6) reduce to STERN-VOLMER type relations (7) and (8) respectively:

$$\frac{\Phi_0}{\Phi} = 1 + \beta^* \frac{\tau_0}{\tau_0'} (X), \tag{7}$$

$$\frac{\Phi_\infty}{\Phi} = 1 + \frac{1}{\beta^*} \frac{\tau_0'}{\tau_0} \frac{1}{(X)}. \tag{8}$$

The intercept divided by the slope gives the product of the excited state equilibrium constant with the ratio of the lifetimes of the species involved.

Experimentally, it is sufficient to record the fluorescence intensities at the chosen wavelength, as a function of (X) . Indeed, it can easily be shown that in the present case $\frac{\Phi}{\Phi_0} = \frac{F}{F_0}$.

The general expressions (5) and (6) were tested in the particular case of excited state acid-base reactions. The data published by other workers (Table 1) gave linear plots and the values of $(pK^* - \log \frac{\tau_0'}{\tau_0})$ derived from the slopes were in good agreement with the previously reported ones.

Table 1. Comparison of published and calculated acidity constants

	$pK^* - \log \frac{\tau_0'}{\tau_0}$	
	lit.	calc.
α -naphthol	2.50 [9]	2.48
β -naphthol	2.82 [9]	2.33
	2.5 [1]	2.31
2-naphthol-5-sulfonic acid	1.36 [9]	1.55
acridone	0.92 [8]	0.93
		0.96
xanthone	0.96 [10]	1.0 ^a
		0.52 ^b
thioxanthone	—	0.54
		0.52

^a in water, with HClO₄, ionic strength 1.0 M. (Ref. [10]).

^b in ethanol-water (1:1) with H₂SO₄.

Excited state acid-base reactions of acridone xanthone and thioxanthone

The excited state acid-base reactions of acridone in water-ethanol (1:1) were studied by KOKUBUN [8] who determined an increased basicity for the first excited singlet state. Our spectral observations of two similar heterocyclic ketones, xanthone and thioxanthone, in

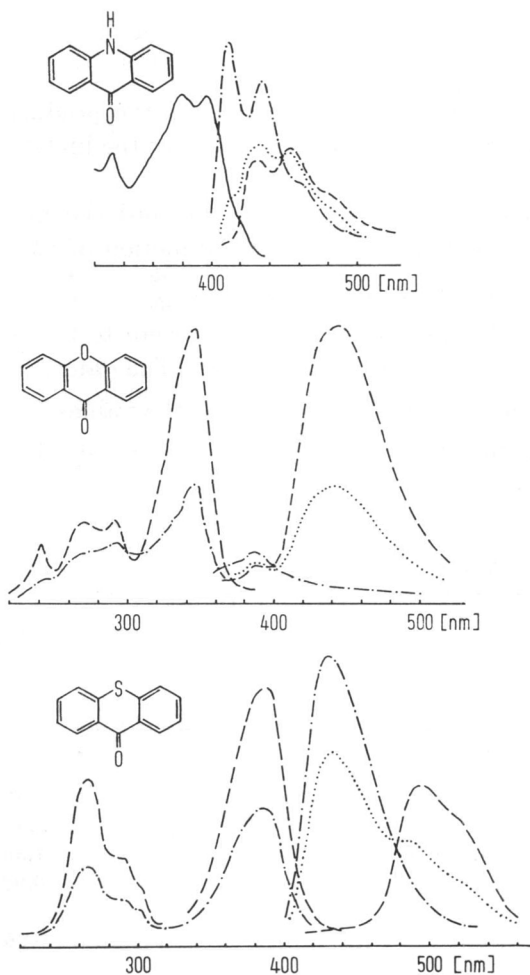


Fig. 1. Uncorrected fluorescence excitation and emission spectra of acridone (1.7×10^{-5} M), xanthone (2.5×10^{-6} M) and thioxanthone (10^{-5} M) in: (— · — · —) ethanol-water (1:1); (····) at pH 0.6, 0.7, 0.8 respectively; (---) ethanol- H_2SO_4 (7 N) (1:1)

the same solvent system, showed also increased basicities for these molecules in their S_1 states. A higher basicity was determined by IRELAND and WYATT for xanthone S_1 in water alone [10] (Table 1).

The excitation-fluorescence spectra of Fig. 1 show variations of the fluorescence spectra with increasing H_3O^+ concentration while excitation spectra remain unchanged, indicating a proton exchange which is effective only in the excited state. It is also apparent from the bathochromic shift that the protonated forms have a lower

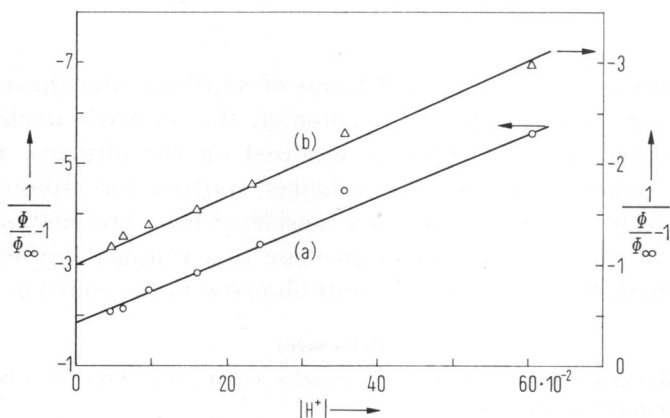


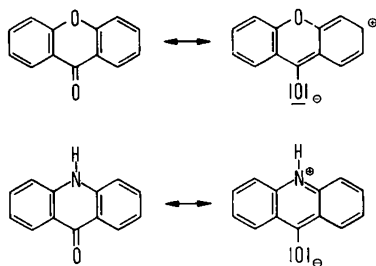
Fig. 2. Plots of $\left(\frac{\Phi}{\Phi_\infty} - 1\right)^{-1}$ as a function of $(H_3O)^+$ for thioxanthone: a) at 484 nm; b) at 520 nm

$(S_1 - S_0)$ energy gap. This shift is very distinct in the case of xanthone and thioxanthone. The isoemissive points are at 448 nm for acridone, at 400 nm for xanthone and at 476 nm for thioxanthone.

The values of $\left(pK^* - \log \frac{\tau_0'}{\tau_0}\right)$ obtained from the slopes of linear plots for xanthone and thioxanthone are presented in Table 1. In Fig. 2, the linear plots for thioxanthone at 484 nm and at 520 nm, show an intercept equal to unity at this latter wavelength, implying that the protonated form is the only emitter, while a different value at 484 nm corresponds to both protonated and unprotonated species as emitters. The acidity constants derived are the same in both experiments.

The values obtained for xanthone and thioxanthone are very close to each other, whereas for acridone it is almost twice as large. A tentative explanation for this difference may be proposed if it is

considered that the contributions of the charged canonical forms, as shown below, are greater in the excited singlet state.



It appears that the excited forms of xanthone and thioxanthone are similar, with the positive center on the aromatic nucleus. For acridone the positive charge is localized on the nitrogen, and the excited singlet state contains a higher contribution from a larger conjugate system. From the cases considered here, protonation on the oxygen of the carbonyl should give rise to a conjugate system compatible with the bathochromic shift observed in the emission spectra.

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