

EXCITED STATE PROTON TRANSFER IN FLUORESCIN CATION

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THIS note is part of the extensive program undertaken to understand the complex nature of proton transfer in the excited state of the fluorescein cation depending upon the nature of excitation and temperature¹. The results of the preliminary work are reported in respect of the excited state proton transfer at 295 K where the process is simpler as no wavelength dependence or red edge excitation (REE) effect is observed.

Rozwadowski² noted that the change in the emission spectrum of fluorescein cation on changing the pH does not occur simultaneously with the change in the absorption spectrum. He attributed this phenomenon to the excited state proton transfer in the cation. Moderate acidic solutions ($\leq 4\text{N H}_2\text{SO}_4$) show proton transfer and it is found that although the absorption spectrum remains the same, the emission spectrum shows two peaks ($\lambda_{\text{max}} \sim 480\text{ nm}$ corresponding to the cation and $\lambda_{\text{max}} \sim 515\text{ nm}$ corresponding to the neutral species)³. The latter gains intensity in more dilute solutions ($2\text{N H}_2\text{SO}_4$).

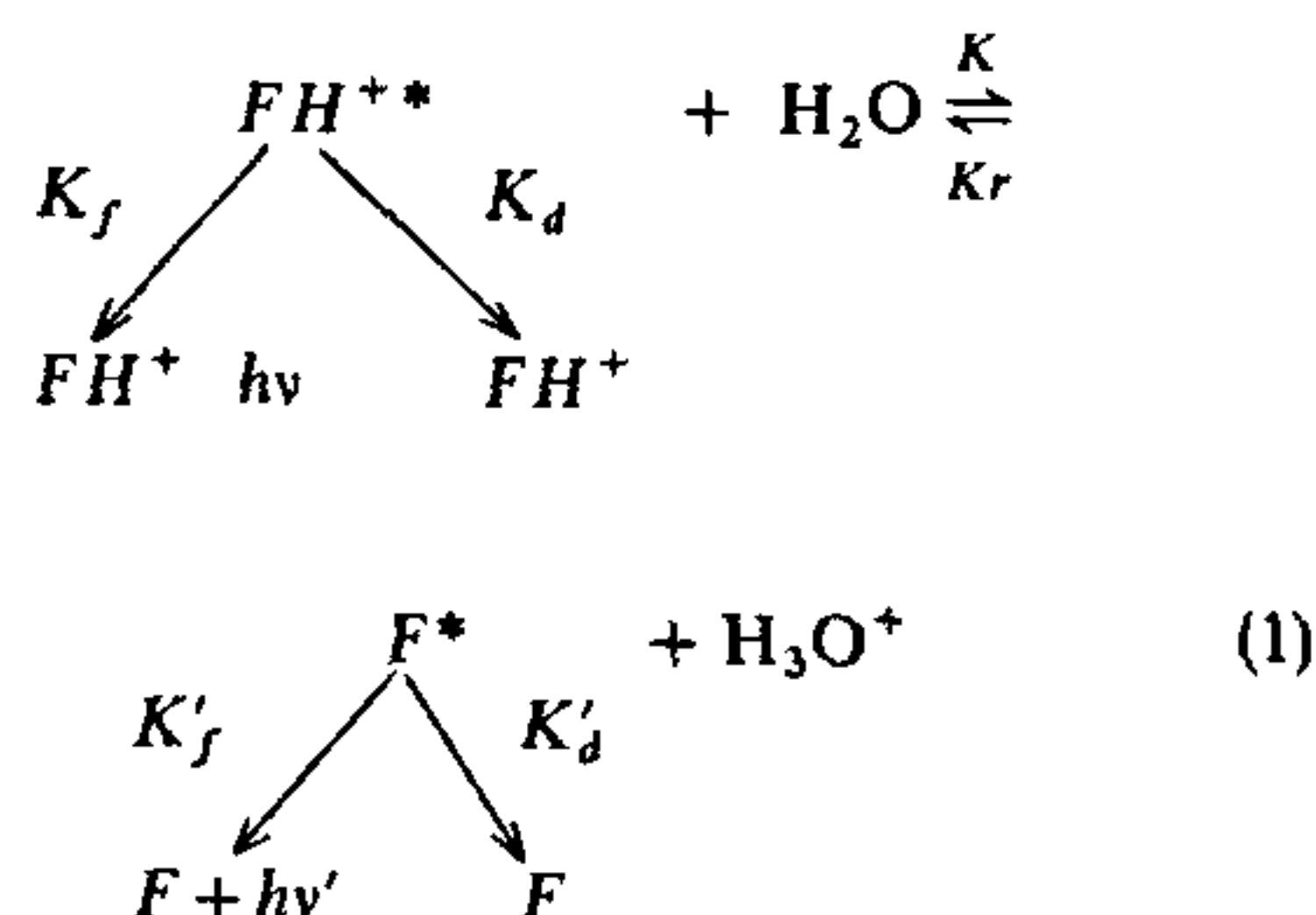
Rozwadowski reported that both the quantum yields and lifetimes of total fluorescence (which included the emissions due to cation and neutral species) decrease on dilution. However, Lindqvist *et al.*'s⁴ lower value for the lifetime for cation casts some doubt about the accuracy of the values measured by Rozwadowski. In our studies we have been able to resolve the two emissions and have measured the lifetimes of each one separately at three dilutions. To avoid complications due to overlap of emissions, the lifetimes have been measured using long wavelength part of the spectrum for the neutral emission and short wavelength part for

Table 1 The observed values of lifetimes and rate constant for proton transfer reaction.

Solvent	Emission wavelength nm	Fluorescence lifetime (nanosecond)	Reaction rate constant
20 N H ₂ SO ₄	480	3.40	
2 N H ₂ SO ₄	480,	2.1,	
	515	2.3	
0.1 N H ₂ SO ₄	480,	1.8,	$2.6 \times 10^8 \text{ sec}^{-1}$
	515	2.3	

the cation. Data are reported in table 1. The instrument was SLM phase fluorimeter and calibrated by measuring the lifetime of the double negative fluorescein ion (pH ~ 8). The measured value of 4.2 nsec agreed reasonably with the reported value 4.02 nsec⁵.

The kinetic scheme for the protolytic reaction in aqueous solutions is given below



where K_f , K_d and K'_f and K'_d are the rate constants of fluorescence and deactivation processes for cation (FH^+) and neutral species (F) respectively and K and K_r are the rate constants for forward and reverse proton transfer reaction.

The rate equation that describes the above kinetic scheme is given by

$$-\frac{d}{dt}[\text{FH}^{+*}] = (K_f + K_d + K)[\text{FH}^{+*}] - K_r[\text{F}^*][\text{H}_3\text{O}^+], \quad (2)$$

and

$$-\frac{d}{dt}[\text{F}^*] = (K'_f + K'_d + K_r[\text{H}_3\text{O}^+])[\text{F}^*] - K[\text{FH}^{+*}], \quad (3)$$

for $\text{pH} \ll \text{pK}^*$, no proton transfer occurs and (2) reduces to (4)

$$-\frac{d}{dt}[\text{FH}^{+*}] = (K_f + K_d)[\text{FH}^{+*}]. \quad (4)$$

This equation describes the fluorescence decay of the cation with lifetime $\tau = 1/(K_f + K_d)$. As the hydrogen ion concentration decreases, the second term on the right side of (2) becomes negligible and equation becomes

$$-\frac{d}{dt}[\text{FH}^{+*}] = (K_f + K_d + K)[\text{FH}^{+*}]. \quad (5)$$

The fluorescence lifetime τ' is now $1/(K_f + K_d + K)$.

Assuming K_d to be independent of the hydrogen ion concentration, the value of K obtained from the difference between the reciprocals of the lifetimes, comes out to be $2.6 \times 10^8 \text{ sec}^{-1}$.

K can also be separately calculated⁶ by (6)

$$\frac{1}{(\phi_0/\phi)-1} = \frac{1}{K\tau} + \frac{K_r\tau'}{K\tau} [\text{H}_3\text{O}^+], \quad (6)$$

where ϕ_0 is the fluorescence yield of cation when no proton transfer takes place and ϕ is the fluorescence yield of cation in more dilute acid solution. However, the rate constant calculated on this basis, works out to be an order of magnitude larger than calculated by lifetime measurements. This discrepancy cannot be attributed to the presence of various other anions like HSO_4^- or HS_2O_7^- . However, such anomalies are related to a 'configuration quenching' of the cation superimposed on the proton transfer reaction⁷. Those cations in the effective volume of which a water molecule or HSO_4^- ion is present at the moment of absorption, are supposed to transfer the proton immediately. Since this is assumed to be a very fast reaction, this will be reflected as a rapid decrease in the intensity measurements whereas the lifetime will remain unaffected resulting in a discrepancy in the two methods of calculation.

The neutral species has three modifications viz. quinonoid form, lactonic form and the amphi-ion. The lactonic form does not absorb in the visible or near ultraviolet and, therefore, does not contribute in the emission. The amphi-ion seems to be converted into the quinonoid form (4). The lactonic form is present mostly in organic non-ionic solvent but in aqueous solutions the dominant neutral form is the quinonoid form. It is not possible to determine the dissociation constant for the excited state in fluorescein cation because of the lactonic form occupying intermediate position between the cations and anions. However, taking into account the emission and absorption of the quinonoid form only, the excited state pK value of the cation was calculated for the quinonoid form by the Forster cycle

$$pK - pK^* = \frac{0.615}{T} (v_{FH^+} - v_F).$$

The value of pK^* comes out to be -1.3 . The ground state pK being 2.2^2 , the cation becomes more acidic in the excited state.

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SYNTHESIS OF α -METHYLARYLAMIDO- β -NAPHTHYL-(1-METHYLAMINO-2-METHYLBENZIMIDAZOLYL)-ETHERS

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THE antifertility activity of various substituted ethers has been shown by many schools of research¹⁻⁴. Tiwari and Subodh Kumar⁵ reported the effectiveness of a few benzofuran derivatives containing ether linkage. It has been shown that these derivatives might get hydrolysed by enzymes in the human system to produce phenols which may act as biological carriers for the introduction of toxic residues for cellular metabolism^{6,7}. In order to achieve more favourable therapeutic results, the authors synthesized a few ether derivatives containing benzimidazole nucleus.

N-hydroxymethylbenzamide, *N*-hydroxymethylphthalimide and *N*-hydroxymethylnicotinamide were condensed with β -naphthol in the presence of con. H_2SO_4 to yield α -methylarylamido- β -naphthol (I) which on condensation with 2-chloromethylbenzimidazole (II) gave α -methylarylamido- β -naphthyl benzimidazolyl-2-methyl ethers (III) in yields ranging from 40 to 50%. A mixture of III, formaldehyde solution and secondary amines on heating under reflux in methanol, afforded α -methylarylamido- β -naphthyl-(1-methylamino-2-methylbenzimidazolyl)-ethers (IV) in about 30% yields.

α -Methylarylamido- β -naphthols (I): *N*-hydroxymethylamides/imides were obtained following the procedure of Buc⁸. A mixture of β -naphthol (0.1 mol) and amidoalcohol (0.1 mol) was dissolved in minimum