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Proton Transfer Reactions in the Excited Electronic States of Aromatic Molecules

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Proton transfer reactions involving electronically excited aromatic molecules are examined and the methods for the determination of the acidities of aromatic molecules in various electronic excited states are discussed and compared. The proton phototransfer reactions in protic and aprotic solvents and in the solid phase as well as intramolecular proton phototransfer are considered separately. Particular attention is devoted to the degradation of the electronic excitation energy in proton phototransfer reactions.
The bibliography includes 186 references.

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I. INTRODUCTION

Considerable advances have been achieved during the last two decades in studies on the chemical reactions of electronically excited molecules. Many important characteristics of the reactions occurring in excited electronic states have been elucidated[1,2]. Photoexcitation of molecules leads to a significant change of their electronic structure and reactivity. Among the reactions of excited molecules, the acid–base processes involving the addition or elimination of a proton are of particular interest. Proton phototransfer is the simplest example of a heterolytic reaction and is extremely convenient for the investigation of the general characteristics of the reactions of electronically excited molecules. Phototransfer reactions are used in lasers and masers[3,4] and in photochromic materials[5,6].

Two types of proton transfer reactions are known. Proton transfer via a system of hydrogen bonds (between two heteroatoms) proceeds both in the ground and in the excited electronic states almost without activation energy and with very high rate constants—up to 10^{10}–10^{11} litre $mole^{-1}$ s^{-1}. In the absence of a hydrogen bond (when at least one of the reactants is a CH acid or a C base), a considerable activation energy is characteristic of the proton transfer reactions and the rate constants are less

than 10^7 litre mole^{-1} s^{-1}. The mechanisms of these two types of proton transfer reactions are significantly different[7]. In the excited electronic states, proton transfer via a system of hydrogen bonds usually takes place with retention of the electronic excitation (adiabatically). In proton phototransfer reactions involving CH acids and C bases, electronic excitation is lost. This review is devoted to reactions involving the phototransfer of a proton via a system of hydrogen bonds. The acid–base properties of electronically excited organic molecules, proton transfer reactions in liquid and solid solutions, and processes involving the degradation of the electronic excitation energy in proton phototransfer are considered.

II. THE ACID–BASE PROPERTIES OF THE EXCITED ELECTRONIC STATES

When an organic molecule absorbs light and passes to an excited state, the electron density is redistributed. In particular, in molecules containing an N, O, or S heteroatom, the density of the lone electron pair at the heteroatom increases or decreases, which causes a change in the acid–base properties of the organic molecule.

The change in acid–base properties occurring on photoexcitation was observed comparatively long ago. As early as 1931, Weber[8] observed a change in the fluorescence spectrum of 1-naphthylamine-4-sulphonate as the acidity of the solution was altered, although the absorption spectrum remained unchanged. Förster[9-11] attributed this phenomenon to a change in the acid–base properties of the molecules in the excited state. Later, the problem of the acid–base properties of electronically excited molecules and of proton phototransfer was investigated in detail by Weller[12-14]. Terenin and Karyakin observed proton phototransfer in solid layers in 1947[15]. The pK values corresponding to the excited states of numerous compounds have now been determined and are listed in Table 1.

The pK of the excited states are determined by various spectroscopic methods. Some of these will now be briefly considered.

1. The method based on the so called Förster cycle[10] can be called the thermodynamic method. The attainment of protolytic equilibrium in the excited state is not necessary in this method; it is sufficient to know the spectroscopic characteristics of the starting materials and the final products of the photoprotolytic dissociation.

By considering the diagram in Fig. 1, where ΔH and ΔH^* are the enthalpies of dissociation in the ground and excited states respectively and ΔE_{AH} and ΔE_{A^-} are the differences between the energies of the two states of the undissociated and dissociated forms respectively, one can write

$$\Delta H - \Delta H^* = \Delta E_{AH} - \Delta E_{A^-}. \quad (1)$$

Assuming further that the entropies of protolytic dissociation in the ground and excited states are equal, we obtain

$$\ln \frac{K^*}{K} = \frac{\Delta E_{AH} - \Delta E_{A^-}}{RT}, \quad (2)$$

where K and K^* are the equilibrium constants for protolytic dissociation in the ground and excited states respectively. If the energy difference is expressed in terms of the difference in wavenumbers ($\Delta\nu$, cm^{-1}) and the numerical value of R is substituted, then we have at room temperature (T = 298 K)

$$pK = pK^* + 2.1 \cdot 10^{-3} \Delta\nu. \quad (3)$$

Table 1. The acid dissociation constants of organic compounds in various electronic states in aqueous solutions.

Compound	p$K(S_0)$	p$K(S_1)$	Δp$K(S_1)$	Method	Refs.	p$K(T)$	Method	Refs.
1	2	3	4	5	6	7	8	9
OH Acids								
Phenol	10.0	4.1	—	1c	30*	8.5	1d	29*
	—	5.7	—	1c	28*	—	—	—
Phenol (in ethanol)	11.97	6.3	—	1a	70*	10.5	—	70
p-Bromophenol	9.36	3.1	—	1c	29	7.7	1d	29
	—	2.9	—	1c	30	—	—	—
	—	3.1	—	1c	20**	—	—	—
p-Cresol	10.3	4.3	—	1c	20**	8.6	1d	29
p-Methoxyphenol	10.24	5.7	—	1c	30	8.4	1d	29
p-Phenoxysulphonate	8.97	2.3	—	1c	30	7.5	1d	29
	—	2.4	—	1c	20**	—	—	—
1-Naphthol	9.23	2.0	—	1a	98	—	—	—
	10	2.68	—	2a	86	—	—	—
	—	—	7.65	1c	86	—	—	—
	9.6	0.7	—	1a	91	—	—	—
	—	2.37	—	2a	91	—	—	—
2-Naphthol	9.49	2.81	—	2a	98	8.1	2c	83
	—	2.5	—	1a	98	—	—	—
	—	3.0	—	2a	103	—	—	—
	—	3.2	—	2a	104	—	—	—
	—	3.4	—	1a	104	—	—	—
	—	3.0	—	1a	30	—	—	—
	—	3.07	—	1c	91	—	—	—
2-Naphthol-5-sulphonate	9.18	0.73	—	2a	12**	—	—	—
2-Naphthol-6-sulphonate	9.10	1.66	—	2a	98**	—	—	—
1-Naphthol-2-sulphonate	9.58	0.4	9.2	2b	77*	7.9	1d	77
Naphthalene-1-sulphonic acid	−10.6	−3.7	—	2b	52*	—	—	—
2,7-Dihydroxynaphthalene	9.37	8.20	—	1a	91*	—	—	—
	—	−1.0	—	1b	91	—	—	—
	—	3.37	—	1c	91	—	—	—
	—	2.65	—	2a	91	—	—	—
	—	2.46	—	2a	86	—	—	—
1-Hydroxypyrene	8.7	3.2	—	1a, 1b	84	—	—	—
3-Hydroxypyrene-5,8,10-trisulphonate	7.10	1.0	—	1a	98**	—	—	—
Benzoic acid	4.16	9.5	—	1c	30*	—	—	—
(Benzoic acid) H$^+$	−7.3	0	—	2a	99	—	—	—
	−7.26	1.62	—	1a	35*	—	—	—
	—	−2.0	—	1a	53**	−4.9	1d	53
Salicylic acid								
-COOH	—	—	−1.5	1a	87*	—	—	—
-OH	—	—	−0.2	1a	87*	—	—	—
Methyl salicylate (-OH)	—	—	6.1	1a	87	—	—	—
2-Naphthoic acid	4.21	11.5	—	1c	30*	—	—	—
	4.2	6.6	—	1a	82*, 83*	—	—	—
(2-Naphthoic acid)H$^+$	−6.9	1.5	—	2a	99*	—	—	—
	−8.0	1.4	—	2b	48*	—	—	—
Anthracene-1-carb xylic acid	3.7	6.9	—	1a	82*	5.6	2c	82*
(Anthracene-1-carboxylic acid)H$^+$	−8.5	1.7	—	2b	75*	—	—	—
(Anthracene-9-carboxylic acid)H$^+$	−7.4	−3.1	—	1c	73**	—	—	—
Pyrene-1-carboxylic acid	4	8.1	—	1a, 1b	84	5.2	2c	84
1-Hydroxyanthraquinone	9.3	—	—	—	—	8.8	2c	56*
1-Hydroxyfluorene	9.3	—	—	—	—	8.4	2c	56*
(Anisole)H$^+$	−6.8	−5	—	1a	38	—	—	—
(Acetophenone)H$^+$	−6.15	7.02	—	1a	35	—	—	—
	−6.0	1.0	—	2a	99	—	—	—
(Benzophenone)H$^+$	−5.7	−3.6	—	1c	45*	−0.4	1d	45*
	—	—	—	—	—	1.5	***	78**
p-Hydroxybenzophenone	6.5	−4	—	****	72	3.5	****	72
Flavone (basicity)	−1.33	−5.4	—	1c	44*	—	—	—
(Xanthone)H$^+$	−4.1	0.96	—	2b	55**	3.0	2d	55
(Coumarin)H$^+$	—	−5.3	—	1b	57*	—	—	—
	—	−7.4	—	1a	57	—	—	—
Tyrosine (-COOH)	2.3	—	5	1a	42	—	—	—
NH Acids								
2-Aminopyridine	—	12.0	—	1b	66*	—	—	—
(2-Aminopyridine)H$^+$	6.86	8.95	—	1c	64*	—	—	—
(2-Aminopyridine)H$_2^{2+}$	−7.6	−19.8	—	1a	66*	—	—	—
(2-*trans*-Styrylpyridine) H$^+$	4.98	11.4	—	1c	51*	—	—	—
(Quinoline)H$^+$	4.9	—	−5.0	1a	23	6.0	2c	83
(Quinoline)H$^+$ (in ethanol)	4.12	9.5	—	****	70	4.8	—	70
(Isoquinoline)H$^+$	5.14	7.5	—	1c	91*	—	—	—
2-Aminoquinoline	—	12.7	—	2b	62*	—	—	—
(5-Aminoquinoline)H$^+$	—	10.9	—	1c	59*	—	—	—
(6-Aminoquinoline)H$_2^{2+}$	1.2	−11.2	—	1a	58*	—	—	—
(Acridine)H$^+$	5.45	10.3	—	1a	102**	5.6	2c	83
(Acridone)H$^+$	−0.6	0.92	—	2a	101**	—	—	—
(1-Azaphenanthrene)H$^+$	5.2	11.5	—	1a, 1b	84*	7.0	2c	84**
	4.75	10.5	—	1c	49*	7.4	1d	49*
(2-Azaphenanthrene)H$^+$	4.6	9.4	—	1a, 1b	84	4.6	2d	84
(3-Azaphenanthrene)H$^+$	5.38	9.5	—	1c	49	7.2	1d	49
(4-Azaphenanthrene)H$^+$	4.2	11.0	—	1a, 1b	84	5.7	2c	84**
(9-Azaphenanthrene)H$^+$	4.6	9.6	—	1a, 1b	84	5.7	2c	84**
(5,6-Diazaphenanthrene)H$^+$	2.2	−0.07	—	2b	100	—	—	—
(*o*-Phenanthroline)H$^+$	4.85	12.7	—	1b	34**	6.7	1d	43
(*o*-Phenanthroline)H$_2^{2+}$	−1.4	−2.2	—	1b	34**	−3.8	1d	43
1-Naphthylamine	—	13.5	—	1c	95	—	—	—
(1-Naphthylamine)H$^+$	3.9	−4	—	1a	91	—	—	—
(2-Naphthylamine)H$^+$	4.07	−1.5	—	2a	11, 94	3.3	2c	83*

Table 1 cont'd.

Compound	$pK(S_0)$	$pK(S_1)$	$\Delta pK(S_1)$	Method	Refs.	$pK(T)$	Method	Ref.
1	2	3	4	5	6	7	8	9
2-Naphthylamine	—	12.2	—	2a	11	—	—	—
	—	12.3	—	1c	95	—	—	—
	14	11.86	—	2b	50*	—	—	—
(1-Aminoanthracene)H^+	3.3	−5.5	8.8	1a	85	3.5	1c	85**
(2-Aminoanthracene)H^+	3 45	−5.4	8.8	1a	85	3.0	1d	85**
(9-Aminoanthracene)H^+	2.7	−6.1	8.8	1a	85	3.0	1d	85
(1-Aminopyrene)H^+	2.8	−5.8	—	1a, 1b	84	3.5	2d	84
(4-Aminopyrene)H^+	—	—	−2	2a	96	—	—	—
3-Acetamidopyrene-5,8,10-trisulphonate	13.9	6.9	—	2a	97**	—	—	—
Indole	—	12.3	—	2b	90	—	—	—
	—	—	7.5	1c	68	—	—	—
(Indole)H^+	−3.5	2.1	—	2b	90	—	—	—
(1-Methylindole)H^+	−2.32	1.8	—	2b	90*	—	—	—
(Benzimidazole)H^+	—	—	−6.3	1c	68	—	—	—
(Indazole)H^+	—	—	−5.0	1c	68	—	—	—
(Benzotriazole)H^+	—	—	−2.4	1c	68	—	—	—
Carbazole	21.1	11.9	—	2b	92	—	—	—
(Carbazole)H^+	—	−1.3	—	2b	92	—	—	—
(ArN = NPh)H^+	−3.00	13.62	—	1a	35*	—	—	—
(Phenazine)H_2^{2+}	−4.3	4.1	—	1c	79	—	—	—
(Phenazine)HMe^{2+}	−3.5	3.3	—	1c	79	—	—	—
(Phenazine)H_2^+	3.8	8.5	—	1c	79	—	—	—
(Phenazine)HMe^+	5.7	10.4	—	1c	79	—	—	—
(1-Amino-2-naphthol)H^+	4.0	0.6	—	****	60*	—	—	—
(Quinoline-2-carboxylic acid) H_2^{2+}	—	−6.4	—	2b	76*	—	—	—

*The acidities of related compounds are also quoted in the relevant paper.

**The acidities determined by other methods are also quoted in the relevant paper.

***pK was determined from data on the variation of the rate constants for the destruction of triplet states with the acidity of the medium.

****The method of determination is not indicated.

There are literature data for the acidity constants of naphthols [111], hydroxyquinolines [36,39,40,61,65,67,74,88,93], 8-mercaptoquinoline [69], aminoquinolines [108], nitroquinolines [43], aminoanthracenes [109], nitrobenzene [70], azo- and azoxy-benzenes [33], 5,6-diazaphenanthrene [89], indolizidine [37], lumiflavin [63], thionine [54,71,80], warfarin [106], riboflavin [107], azures [54], fluoroscein and dichlorofluorescein [41], purines [46], and many other compounds [110,112-115].

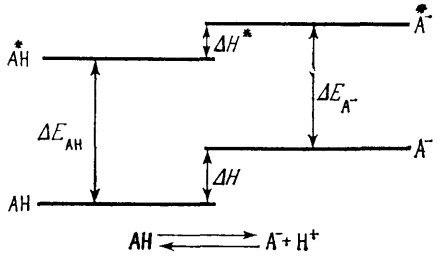
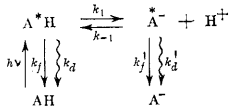


Figure 1. A simplified energy level diagram for acid dissociation in the ground and excited electronic states.

In this equation $\Delta\nu$ is determined experimentally. It is noteworthy that, first, the above equation is applicable only when the entropies of protolytic dissociation in the ground and excited states are equal. The discrepancy between the values of pK^* measured by this method and the values obtained by other procedures is sometimes attributed to the failure of precisely this condition [16]. Secondly, $\Delta\nu$ refers to purely electronic transitions between the zero vibrational sublevels of the corresponding electronic levels (0–0 transition). Since it is difficult to determine the frequency of the 0–0 transition (and hence also its shifts) for compounds in solutions, one usually measures the shift of the maxima in the absorption spectra of the acid and basic forms (method 1a) or in the fluorescence spectra of these forms (method 1b). The average shift in the absorption and fluorescence spectra (method 1c) is also frequently used. This procedure can be applied to determine the pK of triplet states. In this case, the shift of the short-wavelength maximum in the phosphorescence spectrum is determined experimentally assuming it to be the shift of the frequency of the 0–0 transition (method 1d).

2. The method based on the measurement of the intensity or quantum yields of the fluorescence under steady-state conditions has been developed in detail by Weller [12]. Consider the mechanism of the photoprotolytic dissociation of an acid AH:



(4)

Using the method of steady-states, the following expressions can be obtained for this mechanism:

$$\frac{\varphi}{\varphi_0} = \frac{1 + k_{-1}\tau_0'[H^+]}{1 + k_{-1}\tau_0'[H^+] + k_1\tau_0}, \quad (5)$$

$$\frac{\varphi\,\varphi_0'}{\varphi'\varphi_0} = \frac{1}{k_1\tau_0} + \frac{k_{-1}\tau_0'}{k_1\tau_0}[H^+], \quad (6)$$

where φ is the quantum yield of the fluorescence of the undissociated form for certain specific pH values. φ' the quantum yield of the fluorescence of the dissociated form at the same pH values, φ_0 the quantum yield of the fluorescence of the undissociated form in the absence of the protolytic reaction, φ_0' the quantum yield of the fluorescence of the dissociated form in an alkaline solution, k_1 and k_{-1} are the rate constants for the forward and reverse reactions, k_f and k_f' the rate constants for the processes involved in the fluorescence of the undissociated and dissociated forms, k_d and k_d' the rate constants for the monomolecular non-radiative deactivation processes for the undissociated and dissociated forms, and $\tau_0 = 1/(k_0 + k_d)$ and $\tau_0' = 1/(k_f' + k_d')$ the decay times of the fluorescence of the undissociated and dissociated forms respectively.

Having plotted $\varphi\varphi_0'/\varphi'\varphi_0$ against $[H_3O^+]$, it is possible to obtain the rate constants k_1 and k_{-1} as well as the photoprotolytic dissociation equilibrium constant $K^* = k_1/k_{-1}$ (method 2a). A necessary condition for the applicability of method 2a is the establishment (at least partially) of the acid–base equilibrium in the excited state. In certain cases, it is necessary to allow for the contribution of the deviation from the steady state to the kinetics of the protolytic dissociation. Eqn. (6) then assumes the form

$$W\frac{\varphi\,\varphi_0'}{\varphi'\varphi_0} - (1 - W) = \frac{1}{k_1\tau_0} + \frac{k_{-1}\tau_0'}{k_1\tau_0}[H^+], \quad (7)$$

where $1 - W$ is the fraction of molecules reacting immediately after excitation before the establishment of the steady state. W can be calculated from the changes in the relative fluorescence quantum yields as a function of the

pH of the solution by the method of successive approximations, provided that the corresponding diffusion coefficients are known[17].

The method in which the pH of the solution at the point of inflection in the plot of the relative fluorescence quantum yield against pH is adopted as pK^* (method 2b) is sometimes used. However, it has been shown[18,19] that this method frequently does not yield the true value of pK^*. According to Eqn. (5), the pH at the point of inflection ($pH_{\frac{1}{2}}$) in the φ/φ_0–pH plot is†

$$pH_{1/2} = \lg \frac{k_{-1}\tau_0'}{|1 + k_1\tau_0|}. \quad (8)$$

When $k_1\tau_0 \gg 1$, we have in this case

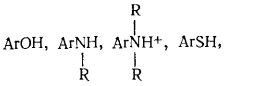
$$pH_{1/2} = pK^* + \lg \frac{\tau_0'}{\tau_0}. \quad (9)$$

Thus $pH_{\frac{1}{2}} \simeq pK^*$, provided that $\tau_0 \simeq \tau_0'$, but in this case it is better to use the more accurate method 2a. Method 2b is used when one of the forms (AH or A^-) does not fluoresce, but under these conditions the error is particularly large. Suppose that A^- does not fluoresce. This implies that $\varphi_0' < 10^{-4}$ and $\tau_0' < 10^{-12}$ s and if $\tau_0 = 10^{-8}$ s, then $pH_{\frac{1}{2}} < pK^* - 4$. The point of inflection method is used to determine the pK values for triplet molecules, since during the lifetime of the triple state there is sufficient time for the establishment of the protolytic equilibrium. The pH at the point of inflection in the plot of the intensity of the triplet–triplet absorption (method 2c) or phosphorescence (method 2d) against the pH of the solution is adopted as the value of p$K(T)$.

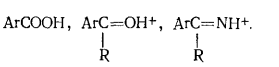
Measurements of the pK^* for aromatic hydroxy-compounds led to the conclusion[20] that methods 2b and 1c usually yield similar results, which do not agree with the results obtained by method 1a, the difference being outside the limits of experimental error. It is assumed that the difference is caused by the relaxation of the solvent molecules during the lifetime of the excited molecule. The frequencies of the 0–0 transitions in the absorption and fluoresence spectra will then differ. This is confirmed by measurements of the pK^* in solid solutions[20], where solvent relaxation is hindered. In this case, all three methods yield similar results.

The difference between pK values for the ground and excited states can reach several orders of magnitude. According to the charge-transfer theory[21], such a jump in acidity is a consequence of the mixing of the configuration of the corresponding electronically excited state with the possible configuration of the charge-transfer (CT) state, which has a higher energy. The degree of mixing is greater the smaller the difference between the energies of the two states, so that $\Delta pK\,(S_0 - S_1) > \Delta pK\,(S_0 - T)$. However, when this theory is used, one cannot explain the similarity of the pK values for the ground and triplet states found experimentally. The resonance theory predicts[22] that the relative contribution of the CT structure compared with that of the biradical structure should be greater in the S_1 state than in the triplet state. This theory readily explains small changes in the pK^* values for the singlet states of aromatic carboxylic acids on the grounds that these compounds have only one resonance structure incorporating the C=O bond. It has also been shown theoretically[23,31,32] that acidity can both increase and decrease on photoexcitation.

Examination of Table 1 shows that the acidity of excited singlet states increases for compounds in which the dissociated proton is in the α-position:



and decreases for compounds where the dissociated proton is in the β-position:



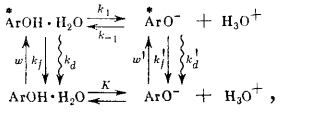
The basicity of amines of the aniline type decreases in the singlet excited state, while that of amines of the acridine type increases. A similar tendency has been observed for the triplet state, but is less pronounced.

Many interesting results may be obtained using the Hammett equations. It has been noted for phenol derivatives, 2,4-dinitrophenylhydrazones, and other benzene derivatives[24-28] that there is a linear relation between $\Delta\nu$ (in the absorption spectrum) and the σ constant for the substituent (in the ground state). Hence it follows[16] that, since the variation in the pK for the ground states of these compounds obeys the Hammett equation, the pK^* should also obey this equation. Such correlation has been obtained for a series of *meta*- and *para*-substituted phenols[29]. The change in ρ for these compounds relative to the ground state indicates[16] a change in the electronic interaction in the excited state.

For many compounds, the pK^* of the deuterated form is smaller than the value of the non-deuterated form[30].

III. PROTON PHOTOTRANSFER REACTIONS IN PROTIC SOLVENTS

Proton phototransfer reactions were first discovered and investigated in aqueous solutions. Förster[10,11] investigated similar reactions for solutions of hydroxy-derivatives of pyrene and naphthalene in water. The sharp increase in the acidity of these compounds on excitation leads to their dissociation during the lifetime of the excited state with formation of the excited ions of the conjugate base and the hydronium ion. These systems were investigated in detail by Weller[47,97,98,102,116], who studied the fluorescence spectra of many aromatic hydroxy-compounds, aromatic amines, and heterocyclic bases over a wide pH range. In many cases, the equilibrium in the excited state is not established completely owing to the competition of radiative and non-radiative deactivation processes involving the excited molecules. A typical curve for the pH dependence of the fluorescence of the dissociated and undissociated forms is illustrated in Fig. 2 (for 2-naphthol). The general mechanism of all dark and photochemical processes occurring in aqueous solutions of hydroxy-derivatives of aromatic compounds may be formulated as follows:



(10)

where w and w' are the rates of light absorption by the undissociated molecules and ions respectively. The variation of the relative fluorescence quantum yields of the dissociated and undissociated forms with hydrogen ion

†At the point of inflection, φ/φ_0 is equal to half the sum of the relative quantum yields of the AH fluorescence in acid and alkaline media.

concentration is described by Eqns. (5) and (6). A similar variation of the relative fluorescence quantum yields of the protonated and non-protonated forms with hydroxide ion concentration has been observed for bases whose proton-accepting properties are more marked in the excited state than in the ground state (for example, in the case of acridine).

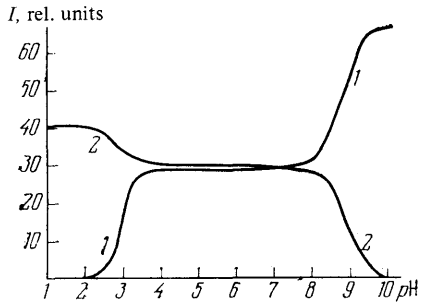


Figure 2. pH dependence of the fluorescence intensity (I) of the dissociated (curve *1*) and undissociated (curve *2*) forms of 2-naphthol in aqueous solution [176].

We shall consider in greater detail the 2-napthol–water system. The rate of protolytic dissociation of excited 2-napthol is fairly low compared with the rates of fluorescence and non-radiative deactivation and the majority of the excited 2-napthol molecules are deactivated without dissociating. In the pH range 3–8, the equilibrium in the excited state of this system is therefore not fully established. The activation energy for the dissociation of excited 2-napthol molecules is 16.8 kJ mol^{-1}. The rate-limiting stage in the proton transfer in this system is probably the reorientation of the water molecules of the solvation shell, which requires an activation energy. The rate of the reverse reaction is probably limited by diffusion. In the dissociation of excited 2-napthol, an appreciable kinetic isotope effect is observed [103]. The dissociation rate constants are 5.29×10^7 and 1.3×10^7 s^{-1} in H_2O and D_2O respectively, while the corresponding rate constants for the reverse reactions are 5.5×10^{10} and 3.5×10^{10} litre mol^{-1} s^{-1}. The influence of isotope substitution is significantly greater for the forward reaction than for the reverse reaction, where the effect can be to a large extent accounted for by the difference between the diffusion coefficients of the ions in H_2O and D_2O. It is still not clear whether the decreased rate constant for the dissociation of excited 2-napthol in D_2O is associated with an increase in the activation energy owing to the smaller vibrational energy of the zero level of the O–D bond compared with the O–H bond or with the decrease of the pre-exponential factor. The influence of isotope substitution on the protolytic dissociation equilibrium constants of excited aromatic hydroxy-compounds has been investigated [30].

The proton-accepting properties of water as well as its ability to give up a proton are fairly weak, so that the stronger bases and acids present in solution may compete with water in the reaction with excited proton donors and acceptors:

$$Ar^*OH + B \underset{k_A}{\overset{k_B}{\rightleftarrows}} Ar^*O^- + BH^+. \qquad (11)$$

The variation of the fluorescence quantum yields of the protonated and non-protonated forms with hydrogen ion (or hydroxide ion) concentration and with the concentration of the added base (or acid) can be described as follows [174]:

$$\frac{\varphi}{\varphi_0} = \left(1 + \frac{k_1\tau_0 + k_B[B]\tau_0}{1 + k_{-1}\tau_0'[H_3O^+] + k_A[BH^+]\tau_0'}\right)^{-1}, \qquad (12)$$

$$\frac{\varphi'}{\varphi_0'} = \left(1 + \frac{1 + k_{-1}\tau_0[H_3O^+] + k_A[BH^+]\tau_0'}{k_1\tau_0 + k_B[B]\tau_0}\right)^{-1}. \qquad (13)$$

Table 2. The rate constants for the proton phototransfer reactions in protic solvents.

Acid	Base	Solvent	T, °C	$10^{-8}\,k^{**}$ litre mole^{-1} s^{-1}	Refs.
2-Naphthol*	H_2O	H_2O	20	0.44 (1)	86
H_3O^+	2-Naphthoxide*	H_2O	20	490 (2)	86
1-Naphthol*	H_2O	H_2O	20	0.81 (1)	86
H_3O^+	1-Naphthoxide*	H_2O	20	390 (2)	86
1,2-DHN*[a]	H_2O	H_2O	20	1.8 (1)	86
H_3O^+	1,2-DHN ion*[a]	H_2O	20	400 (2)	86
1,5-DHN*[a]	H_2O	H_2O	20	0.4 (1)	86
H_3O^+	1,5-DHN ion*	H_2O	20	320 (2)	86
1,7-DHN*[a]	H_2O	H_2O	20	0.32 (1)	86
H_3O^+	1,7-DHN ion*[a]	H_2O	20	430 (2)	86
1,8-DHN*[a]	H_2O	H_2O	20	0.5 (1)	86
H_3O^+	1,8-DHN ion*[a]	H_2O	20	360 (2)	86
2,3-DHN*[a]	H_2O	H_2O	20	0.28 (1)	86
H_3O^+	2,3-DHN ion*[a]	H_2O	20	470 (2)	86
2,6-DHN*[a]	H_2O	H_2O	20	0.16 (1)	86
H_3O^+	2,6-DHN ion*[a]	H_2O	20	410 (2)	86
2,7-DHN*[a]	H_2O	H_2O	20	1.25 (1)	86
H_3O^+	2,7-DHN ion*[a]	H_2O	20	310 (2)	86
(Acridine)H^{+*}	OH^-	H_2O	25	185 (2)	102
(Acridine)H^{+*}	NH_3	H_2O	25	0.25 (2)	102
H_3O^+	2-Naphthoxide*	H_2O	25	480 (2)	98
2-Naphthol*	$C_2H_5COO^-$	H_2O	25	28.6 (2)	98
2-Naphthol*	$C_3H_7COO^-$	H_2O	55	27.6 (2)	98
2-Naphthol*	CH_3COO^-	H_2O	25	29.0 (2)	98
H_3PO_4	2-Naphthoxide*	H_2O	25	29.1 (2)	116
2-Naphthol*	$HCOO^-$	H_2O	25	24.0 (2)	98
2-Naphthol*	$H_2PO_4^-$	H_2O	25	6.0 (2)	116
HCOOH	2-Naphthoxide*	H_2O	25	0.33 (2)	98
H_3O^+	1-Cyano-2-naphthoxide*	H_2O	25	210 (2)	116
NH_4^+	Acridine*	H_2O	25	5.7 (2)	102
H_3BO_3	Acridine*	H_2O	25	3.8 (2)	116
$Mg(H_2O)_n^{2+}$	Acridine*	H_2O	25	0.94 (2)	116
2-Naphthol*	H_2O	H_2O	25	0.53 (1)	103
2-Naphthol*	D_2O	D_2O	25	0.13 (1)	103
H_3O^+	2-Naphthoxide*	H_2O	25	550 (2)	103
D_3O^+	2-Naphthoxide*	D_2O	25	350 (2)	103
H_2O	Benzoquinoline*	H_2O	25	0.07 (1)	117
(Benzoquinoline)H^{+*}	H_2O	H_2O	25	120 (2)	117
2-Naphthol*	H_2O	H_2O	25	0.45 (1)	118
2-Naphthol*	CH_3COO^-	H_2O	20	24.0 (2)	119
3-Acetamidopyrene-5,8,9-trisulphonate*	OH^-	H_2O	25	1.48 (2)	97
"	$(CH_3)_2NH$	H_2O	25	0.45 (2)	97
"	CH_3NH_2	H_2O	25	0.46 (2)	97
"	$(CH_3)_3N$	H_2O	25	0.22 (2)	97
"	NH_3	H_2O	25	0.23 (2)	97
2-Naphthol	CH_3COO^-	Methanol	20	8.1 (2)	119
2-Naphthol	CH_3COO^-	Ethanol	20	5.0 (2)	119

*Excited molecule.
**(1) The rate constant for a pseudounimolecular reaction (s^{-1}); (2) the rate constant for a bimolecular reaction (litre mol^{-1} s^{-1}).
[a] DHN = Dyhydroxynaphthalene.

Table 2 lists the rate constants for proton phototransfer in protic solvents determined by different investigators. It shows that the rate constants for the proton phototransfer reactions involving oppositely charged ions are of the order of 10^{10}–10^{11} litre mole^{-1} s^{-1} and depend only slightly on the

chemical nature of the reacting ions. This is evidence in support of the view that the rates of such reactions are diffusion limited. The slight differences between the rate constants are probably caused by the differences between the diffusion coefficients and steric factors.

The rate constants for the dissociation of excited hydroxy-derivatives of aromatic compounds have a wide range of values and depend on the nature of the hydroxy-compound. Weller [122] and Derkacheva [86] noted a linear relation between log k_1 and pK_a^* for a series of hydroxy- and dihydroxy-derivatives of naphthalene. The rate-limiting step in these reactions is apparently the actual proton transfer to the polar solvent accompanied by the dielectric relaxation of the latter. The water molecule is a weak proton acceptor and the dissociation of excited aromatic compounds in aqueous solutions proceeds exclusively by virtue of the high polarity of water and the specific solvation of the ions formed. The absence of any appreciable dissociation of excited 2-naphthol molecules in absolute ethanol [123], which is less polar than water, may serve as a confirmation of this hypothesis. Compounds which are more acid, such as excited ammonium derivatives of pyrene, dissociate also in alcoholic solutions [96]. In a study of the dissociation of compounds whose acidity changes in the excited state within the limits of four orders of magnitude (in methanol, ethanol, 1-propanol, and 1-butanol), Weller [96] showed that the ionisation rate constants are almost independent of the nature of the aromatic compound and depend only on temperature and the nature of the solvent. This is direct proof that the rate-limiting stage of proton phototransfer in such systems is the reorientation of the polar solvent molecules. The reactions of excited aromatic hydroxy-compounds with proton acceptors, which are much more powerful than water and alcohols, namely carboxylate anions, proceed at much higher rates than dissociation and their rates are probably limited by diffusion. The rate constants for the reactions of excited 2-naphthol with these bases are almost independent of the basicity of the anions, which varies over a factor of ten, and are equal to $(2.5 - 3.0) \times 10^9$ litre mole^{-1} s^{-1}. Proton phototransfer from excited 2-naphthol to the acetate ion proceeds also in alcoholic solutions [119].

The study of the proton phototransfer reaction in protic solvents involves a large class of protolytic reactions, ranging from fairly slow, whose rate is limited by the reorientation of the polar solvent molecules, requiring an activation energy, to rapid reactions, whose rate is limited by diffusion. On photoexcitation, certain compounds dissociate so rapidly that the fluoresence of the undissociated molecules in neutral aqueous solutions is not observed and only the dissociated form fluoresces. As an example, one may quote the 2-naphthylammonium cation [94,124] and 1-naphthol in aqueous solutions [47,86]. The absence of the fluorescence of these compounds in conjunction with the usual emission rate constants (approximately 10^8 s^{-1}) shows that the rate constant for the dissociation of the excited molecules $k \geqslant 10^{11}$ s^{-1}.

The high rate constant for proton phototransfer in principle enables this process to compete successfully with the deactivation reactions of the highest excited states and other relaxation processes. Analysing the kinetics of the onset of the fluorescence of the naphthoxide ion following the excitation of 2-naphthol in aqueous solution, Ofran and Feitelson [118] observed that a proportion of the excited 2-naphthol molecules, namely 5%, are dissociated during a period less than 1 ns, i.e. the rate of dissociation of some of the molecules is much higher than that of the others. Since the quantum yield in the formation of excited 2-naphthoxide ions is independent of the wavelength of the exciting light, the rate-limiting stage of such rapid dissociation is probably the rearrangement of the solvent molecules in the solvation shell. Consequently two processes were observed for 2-naphthol—rapid dissociation in the non-relaxed state and fairly slow dissociation in the state corresponding to thermal equilibrium.

In studies on the possibility of photoprotolytic reactions in the higher excited states, Hochstrasser [147] and Shablya [148] showed that the fluorescence quantum yields of the acridinium cation are different on excitation to the first and higher singlet states. The difference disappears when the fluorescence of the acridinium cation is quenched by hydrochloric acid, but persists on quenching by potassium chloride. In order to account for this phenomenon, it has been suggested [147,148] that, on excitation of the acridinium cation to the first (S_1) and higher (S_2) singlet states, the following equilibria occur:

$$S_1\ C_{13}H_9^*NH^+ \rightleftarrows C_{13}^*H_9N + H^+; \quad (14)$$

$$S_2\ C_{13}H_9^*NH^+ \rightleftarrows C_{13}^*H_9N + H^+. \quad (15)$$

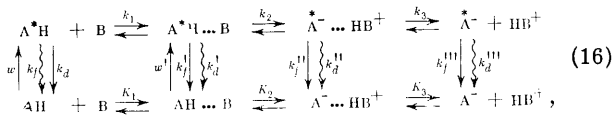
On excitation to the highest singlet states, the fluorescence quantum yield of the protonated form should then be smaller than for excitation to the S_1 state in consequence of dissociation and should increase when this process is suppressed, i.e. at a fairly high concentration of H^+ ions the quantum yields should be equal on excitation to different electronic states if the main deactivation process of the S_2 state is the internal transition $S_2 \rightarrow S_1$. However, the authors of the present review have shown [149] that the equalisation of the fluorescence quantum yields is observed only simultaneously with the quenching of the fluorescence and is not observed when acids such as perchloric, formic, and acetic are used. Furthermore, the equalisation of the fluorescence quantum yields on excitation of different electronic states is observed in systems where acid–base interaction is ruled out, for example on quenching the fluorescence of 2-naphthylamine by ethyl bromide in ethanol. The observed phenomena are probably associated with a change in the probabilities of the intercombination transitions from the highest singlet states to the highest triplet states and not with the shift of the protolytic equilibrium in the highest excited states.

Thus proton phototransfer in protic solvents (water, alcohols) proceeds via a protolytic mechanism with formation of solvated ions as the reaction products. The rate constants for such reactions are in the range 10^7 to 10^{11} s^{-1}. In most cases, the proton phototransfer proceeds in the excited singlet state corresponding to thermal equilibrium. However, in some instances rapid proton transfer occurs in the non-relaxed state. The proton phototransfer reactions may be accompanied by non-radiative deactivation of the excited molecules. This phenomenon is examined below.

IV. PROTON PHOTOTRANSFER REACTIONS IN APROTIC SOLVENTS

The interaction of aromatic hydroxy- and amino-compounds with acids and bases in the ground electronic state in aprotic solvents results in the formation of hydrogen-bonded complexes and ion pairs in which the ions are or are not separated by solvent molecules (depending on the strength of the acid and base and the

polarity of the solvent) [170]. This is manifested clearly in the infrared and near ultraviolet absorption spectra [125,126]. As in the ground state, in the excited state there is a possibility of the formation of excited hydrogen-bonded complexes, excited ion pairs, and excited solvated ions. The general mechanism of the processes occurring in the ground and excited states in aprotic solvents can be represented as follows:



(16)

where k_f, k'_f, k''_f, and k'''_f are the fluorescence rate constants, k_d, k'_d, k''_d, and k'''_d are the rate constants for the non-radiative deactivation of the free form of the fluorescent species, the excited hydrogen-bonded complex, the excited ion pair, and the excited ion respectively, and K_1, K_2, and K_3 are the equilibrium constants for the formation of the hydrogen-bonded complex, the ion pair, and the ion in the ground electronic state respectively. If the base B is fairly weak, proton transfer in the excited hydrogen-bonded complex does not occur and a new complex formation equilibrium is established in many cases during the lifetime of the excited state.

The fluorescence spectra of the hydrogen-bonded complexes differ insignificantly from those of the free molecules (the shift of the maximum is of the order of 500 cm^{-1}). The fluorescence of hydrogen-bonded complexes was first observed by Mataga et al. for complexes of 2-naphthol with methyl acetate, ethyl acetate, n-butyl acetate, and ethyl chloroacetate in hexane [127]. When the excited hydrogen-bonded complex fluoresces, it is possible to determine the complex-formation equilibrium constant in the excited state from the fluorescence data (Table 3). Mataga et al. [173] derived the following equation for the concentration dependence of the fluoroscence intensity subject to the conditions that equilibrium is established in the excited state, that there are no induced deactivation processes, and that the fluorescence spectra of the free form and the complex are identical:

$$\frac{1-I_0/I}{[B]} = -K^* + \alpha K^* I_0/I, \qquad (17)$$

where α is the ratio of the fluorescence quantum yields of the hydrogen-bonded complex and the free molecule. In those cases where the excited hydrogen-bonded complex does not fluoresce, it is possible to determine only the rate constant for the quenching of the free molecules. It is then convenient to use the formula taking into account the attainment of equilibrium in the ground state:

$$\frac{\varphi_0/\varphi}{1+K[B]\,\varepsilon_1/\varepsilon} = 1 + k_1\tau_0[B]\ , \qquad (18)$$

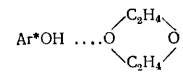
where ϵ and ϵ_1 are the extinction coefficients of the free form and the hydrogen-bonded complex at the wavelength of the exciting light. A similar situation is observed in the interaction of naphthols and 3-hydroxypyrene with pyridine and α-chloropyridine. Weller [122] identified the rate constants for the dynamic quenching of the fluorescence of these compounds by nitrogen-containing heterocycles with the rate constants for the formation of hydrogen-bonded complexes between the excited molecules of the hydroxy-compounds and those of the bases. This is confirmed by the finding that pyridine does not quench the fluorescence of 2-methoxynaphthalene. The quenching effect of pyridine on the fluorescence of 2-naphthol depends significantly on the solvating capacity and polarity of the solvent [120]. The reverse dissociation reaction of the excited hydrogen-bonded complex is usually neglected. The complex formation equilibrium constant in the ground state is as a rule of the order of 10^2 litre mol^{-1} and increases by 1–2 orders of magnitude on photoexcitation. Since the rate constant for the formation of the hydrogen-bonded complex does not exceed 10^{10} litre mol^{-1} s^{-1}, the rate constant for the reverse reaction is of the order of 10^6 s^{-1}, i.e. dissociation cannot compete with the radiative and non-radiative deactivation reactions of the excited hydrogen-bonded complex.

Table 3. The equilibrium constants for the formation of hydrogen-bonded complexes in the ground (K) and excited (K*) states.

Proton-donating molecule	Proton-accepting molecule	Solvent	K, litre mol^{-1}	K^*, litre mol^{-1}	Refs.
2-Naphthol	Pyridine	Benzene	41	84	168
2-Naphthol	Diethylamine	Cyclohexane	184	4620	123
2-Naphthylamine	Pyridine	Benzene	0.2	60	168
2-Naphthylamine	Pyridine	Cyclohexane	12	250	121
2-Naphthylamine	Ethyl acetate	Benzene	0.26	1.8	168
2-Naphthylamine	Butyl acetate	Benzene	0.1	1.8	168
2-Naphthylamine	Butyl acetate	Cyclohexane	1.1	9.8	121
2-Naphthylamine	Triethylamine	Cyclohexane	1.1	10	121
Carbazole	Pyridine	Cyclohexane	14	200	121
Carbazole	Butyl acetate	Cyclohexane	9.4	66	121
Carbazole	Triethylamine	Cyclohexane	5.5	100	121
3-Hydroxypyrene	Pyridine	Benzene	58	270	129
3-Hydroxypyrene	Pyridine	Methylcyclohexane	220	980	129
3-Hydroxypyrene	Pyridine	*o*-Chlorotoluene	78	430	122
3-Hydroxypyrene	α-Chloropyridine	Benzene	7	18	122
3-Hydroxypyrene	α-Chloropyridine	*o*-Chlorotoluene	8	23	122
3-Hydroxypyrene	α-Chloropyridine	Methylcyclohexane	18.5	60	122

Strong bases such as aliphatic amines interact with excited aromatic hydroxy-compounds, the process involving proton transfer from the excited molecule to the base. This is manifested experimentally by the anomalously large shift of the fluorescence maximum of the proton transfer product relative to the fluorescence maximum in the spectra of hydrogen-bonded complexes. In 1962 Mataga et al. attributed this long-wavelength maximum to the fluorescence of the excited ion pair in which the counterions are joined by a hydrogen bond [171]. Similar phenomena involving an anomalous fluorescence shift have been described by 2-naphthol–aliphatic amine, 3-hydroxy-pyrene–aliphatic amine, 1-naphthol–aliphatic amine, and aromatic aza-compound–carboxylic acid systems [117,123,130–132,172].

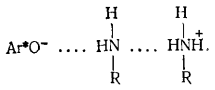
The excited ion pair can be formed in two ways: by the reaction of the excited fluorescent molecules with the base (dynamic pathway) and on excitation of the hydrogen-bonded complexes if the latter are already formed in the ground state (the static pathway). Comparison of the positions of the fluorescence maxima of the photoproduct, the initial excited molecule, and its conjugated base (acid) permits the identification of the proton phototransfer products. In a study of the dependence of the position of the maxima in the fluorescence spectra of 2-naphthol and 3-hydroxypyrene in various solvents (methylcyclohexane, dioxan, triethylamine, and n-butylamine), Weller [130] showed that the fluorescent species are the hydrogen-bonded complex



in dioxan, the contact hydrogen-bonded ion pair

$$Ar^*O^- \ldots HN\overset{+}{R}_3$$

in triethylamine, and the excited ion pair, in which the counterions are separated by hydrogen bonds with a solvent molecule,



in n-butylamine. Nakamizo[117] attributed the long-wavelength band in the fluorescence spectra of the complexes of benzoquinolines with acetic and trichloroacetic acids to emission by the protonated cation of the heterocycle, since the long-wavelength fluorescence spectrum coincided with the fluorescence spectrum of the cation in aqueous solution. In the 2-naphthol–diethylamine system in various solvents, the authors of the review observed the formation of an excited hydrogen-bonded complex, an excited ion pair, and an excited ion (Fig. 3)[123,134,145]. In a study of the temperature variation of the fluorescence spectra of the same system in methylcyclohexane, Krasheninnikov and Shablya[133] found that, when the temperature is reduced, bands with maxima at 365, 392, and 410 nm appear successively; these were assigned to the excited hydrogen-bonded complex, the excited contact ion pair, and the excited naphthoxide ion respectively. The lifetime of the excited ion pairs is in many cases shorter than the lifetime of the excited ions. This difference has been used as a method for the identification of the proton phototransfer products[134].

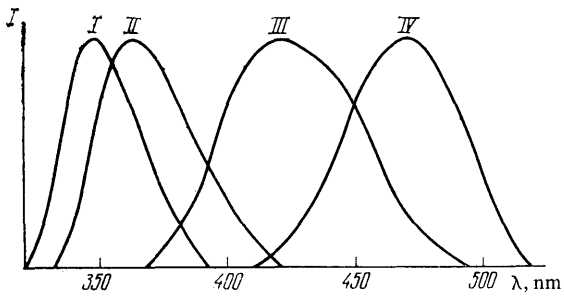
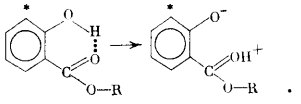


Figure 3. The fluorescence spectra of 2-naphthol in hexane (*I*), the hydrogen-bonded complex of 2-naphthol with triethylamine in hexane (II), the 2-naphthol–triethylamine ion pair in toluene (III), and the naphthoxide ion in dimethylformamide (IV).

The nature of the proton phototransfer product depends to a considerable degree on the solvent. For example, in aromatic solvents (benzene, toluene, and *o*-chlorotoluene) the interaction of excited 2-naphthol and 3-hydroxypyrene molecules with triethylamine and diethylamine leads to the formation of excited ion pairs[123,130]. A different situation is observed in cyclohexane solutions[123]. When excited 2-naphthol interacts with diethylamine at low concentrations of the latter, an excited hydrogen-bonded complex is formed, an increase of the concentration of the amine results in marked quenching of the fluorescence, and a new fluorescence band, which has been attributed to the fluorescence of the ion pair, appears only at very high concentrations. When excited 2-naphthol interacts with triethylamine, a broad fluorescence spectrum is observed and is regarded[130] as resulting from the superposition of the fluorescence spectra of the hydrogen-bonded complex and the ion pair, which are in equilibrium. The shift of the equilibrium towards the formation of the ion pair in aromatic hydrocarbons is evidence that these solvents stabilise the ion pair to a greater extent, despite the fact that their dielectric constants hardly differ from those of aliphatic hydrocarbons. The polarisation of the π-electron system of the aromatic solvent, leading to partial delocalisation of the charges of the ion pair, probably also has a stabilising influence.

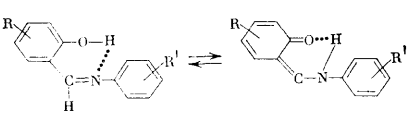
V. INTRAMOLECULAR PROTON PHOTOTRANSFER REACTIONS

Proton phototransfer can occur not only between two separate molecules of an acid and a base but also between the parts of a single molecule joined by a hydrogen bond. These reactions are observed both in liquid solutions and in the solid phase. The first intramolecular proton phototransfer reaction, involving salicylic acid and its esters, was observed in 1955 by Weller, who subsequently investigated this phenomenon in detail[122,130,138,139]. On excitation, proton transfer occurs in these systems from the hydroxy-group to the carbonyl group with formation of an excited product:

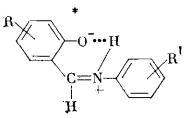


The fluorescence spectra of salicylic acid and its esters consist of two bands—a short-wavelength band corresponding to the emission by the excited initial molecule and the long-wavelength band corresponding to the emission by the form with proton transfer. It is assumed that equilibrium between the two forms is fully established in the excited state. Estimates showed that the energy barrier between the two forms in the excited state of methyl salicylate does not exceed 0.12 kcal mole^{-1}. The enthalpy of the reversible interconversion of the two forms is very sensitive to the nature of the substituent in the aromatic ring. The loss of electronic excitation by the form with proton transfer is accompanied by the rapid reverse proton transfer and the regeneration of the initial compound.

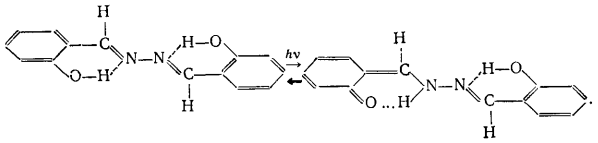
Intramolecular proton phototransfer has been observed in the hydrogen-bonded complex of 2-hydroxy-3-naphthoic acid and pyridine. When this complex is excited, a proton is transferred from the hydroxy-group to the carboxy-oxygen[140-142]. The proton phototransfer reaction occurring with retention of electronic excitation in azomethines with an *ortho*-hydroxy-group in the aldehyde ring has been investigated in detail by Knyazhanskii et al.[186] In solutions of these compounds, there is a tautomeric equilibrium between the benzenoid and quinonoid forms, the equilibrium constant depending on the polarity and proton-donating properties of the solvent:



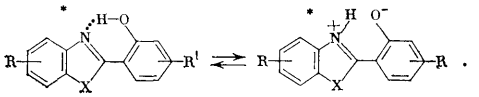
Photoexcitation of the benzenoid form leads to proton phototransfer with formation of an excited ionic form:



which is responsible for the luminescence of the system. A similar intramolecular proton transfer reaction in the salicylaldehyde molecule has been observed by Fassler et al.[6]:

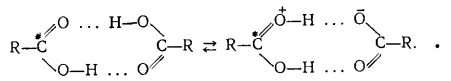


Williams and Heller examined proton phototransfer in 2-hydroxy-derivatives of benzoxazoles, benzothiazoles and benzimidazoles[167]:

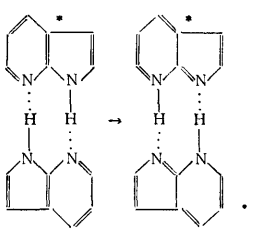


The majority of investigators believe that the form with proton transfer is dipolar and not quinonoid, but the problem has not been finally elucidated.

Proton transfer in dimers can be regarded by convention as intramolecular transfer Hochstrasser[135] observed an appreciable bathochromic shift of the fluorescence of the 1-naphthoic acid dimer in a methylcyclohexane solution at 77 K relative to room temperature. This shift was attributed to the formation of an ion pair as a result of proton transfer in the dimer owing to the sharp increase of the basicity of the carbonyl group:



Solutions of 7-azaindole in solvents incapable of forming hydrogen bonds exhibit two emission bands. Their relative intensities depend on the 7-azaindole concentration, temperature, and the excitation wavelength[136]. It has been suggested that the long-wavelength fluorescence band is due to the emission by the excited tautomeric form of the dimer with double proton transfer via the mechanism



VI. PROTON PHOTOTRANSFER IN THE SOLID PHASE

Bimolecular processes requiring the migration of the reactants are inhibited in the solid state. Cases of proton phototransfer within hydrogen-bonded complexes[131,132] in 1-naphthol–aliphatic amine systems have been noted. According to the authors, proton phototransfer within the complex is very rapid and leads to the formation of an ion pair in the excited singlet state, which is manifested by the fact that a band, identical with that in the fluorescence spectrum of the naphthoxide ion, appears in the emission spectrum of this system. The phosphorescence spectra of the systems then coincide with the phosphorescence spectrum of 1-naphthol, which shows that the reverse proton transfer takes place after the intercombination transition in the triplet state of the ion pair.

Interesting results were obtained by Terenin and coworkers in studies on the reversible proton phototransfer reactions in frozen solutions of acridine derivatives[145,146]. When 3,6-diaminoacridinium, 3-aminoacridinium, Acridine Orange, and trypaflavinium cations are irradiated with light, the cations dissociate in tetrahydrofuran and toluene at 77 K with formation of the free bases. This photochemical reaction is reversible on raising the temperature. A study of the dependence of the steady-state concentration of the ionic form and of the base on light intensity led the authors to the conclusion that the photochemical reaction proceeds in both directions and that photodeprotonation of the cation is a two-photon process and occurs on excitation to one of the highest triplet states; the reverse reaction, involving the regeneration of the ionic form, is a one-photon process. The quantum yields of both the forward and reverse reactions are low.

The proton phototransfer at 77 K in solid layers obtained by the sublimation of aminoacridines together with various organic acids has been investigated in fair detail. In these systems, protonated forms of the aminoacridines are formed in the ground state, their photolysis resulting in the elimination of a proton and the formation of the base. In this case, the reaction has a one-quantum mechanism[148].

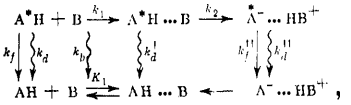
VII. DEGRADATION OF THE ELECTRONIC EXCITATION ENERGY IN PROTON PHOTOTRANSFER REACTIONS

The deactivation of the excited molecules, associated with the acid–base interaction, was observed for the first time by Mataga et al. in 1957[177] and by Feitelson in 1964[42]. Photochemical acid–base reactions, leading to isotope exchange in C acids and bases, proceed with loss of electronic excitation and lead to the formation of products in the ground state. Induced non-radiative deactivation, competing with the isotope exchange reaction and leading to the loss of excitation without the formation of products, is also observed[151].

For heteroatomic acids and bases, proton phototransfer proceeds in many cases adiabatically, i.e. with retention of electronic excitation. However, in these reactions too non-radiative deactivation of the excited molecules, induced by the acid–base interaction, is observed. Since the proton transfer process involves many stages, non-radiative deactivation can occur at different stages of the reaction. Firstly, the deactivation can proceed when the molecules of the acid and base interact in the step involving the formation of an excited hydrogen-bonded complex. Secondly, there is a possibility of deactivation in the proton transfer stage, where the excited hydrogen-bonded complex is converted into an excited pair. Finally, there is a possibility of the deactivation of the excited ion pair owing to the interaction of the counterions. We shall consider each of the above deactivation pathways in greater detail.

The kinetic mechanism of the proton phototransfer reaction, taking into account the deactivation processes,

is of the following form for systems where the reverse reactions may be neglected[134]:



(19)

where k_q is the rate constant for the induced non-radiative deactivation in the stage involving the formation of the excited hydrogen-bonded complex. On steady-state excitation at the isosbestic point, the dependence of the quantum yields and the fluorescence quenching times for the initial compound and the proton phototransfer product on the reactant (acid or base) concentration can be expressed as follows taking into account complex formation in the ground state:

$$\frac{\varphi_0}{\varphi}\frac{1}{1+K_1[B]} = 1+(k_1+k_q)\tau_0[B], \tag{20}$$

$$\frac{\tau_0}{\tau} = 1+(k_1+k_q)\tau_0[B], \tag{21}$$

$$\frac{\varphi_0\varphi''}{\varphi[B]} = \varphi_1''\frac{\varphi_0}{\varphi}\frac{K_1}{1+K_1[B]} + \varphi_1''k_1\tau_0, \tag{22}$$

$$\frac{\varphi_0}{\varphi}\left(1-\frac{\varphi''}{\varphi_1''}\right) = 1+k_q\tau_0[B], \tag{23}$$

$$\frac{\varphi_1''\tau_0}{\varphi_0\tau_0''} = \frac{k_f''}{k_f}\frac{k_2}{k_2+k_d'}, \tag{24}$$

where φ_0 and φ are the fluorescence quantum yields of the initial compound in the absence and presence of the reactant, φ'' is the fluorescence quantum yield of the photochemical reaction product, φ_1'' the fluorescence quantum yield of the photochemical reaction product extrapolated to infinite concentration of the reactant where the entire initial compound is in the ground state in the form of the hydrogen-bonded complex, $k_2/(k_2 + k'_d)$ a quantity characterising the efficiency of the adiabatic proton transfer within the complex, τ_0 and τ are the lifetimes of the excited initial compound in the absence and presence of the quenching agent, and τ_0'' is the lifetime of the excited product of the photochemical reaction (ion pair). The authors of the present review have shown[134] that, in the 2-naphthol–aliphatic amine systems in polar aprotic solvents (dimethylformamide and acetonitrile), the induced non-radiative deactivation of the excited 2-naphthol molecules by the amine molecules in the stage involving the formation of the excited hydrogen-bonded complex competes to a large extent with the adiabatic reaction [the rate constant k_q for non-radiative deactivation is of the order of 10^9 litre mol^{-1} s^{-1} (Table 4)]. In solvents of low polarity (benzene, toluene, and dichloroethane), induced non-radiative deactivation was not observed at this stage. In polar solvents, diethylamine and triethylamine also quench the fluorescence of 2-methoxynaphthalene (which is incapable of forming hydrogen bonds with amines), which suggested a donor–acceptor mechanism of the induced non-radiative deactivation.

A study of proton phototransfer from 2-naphthol to various bases in protic solvents showed[119] that the ratio of the rate constants for the reaction and the induced deactivation depends on the type of base‡. Thus the rate constant for the induced non-radiative deactivation in the 2-naphthol–sodium acetate system is negligibly small compared with the rate constant for the adiabatic proton phototransfer. If triethylamine and dimethylhydrazine are used as the bases, the rate constants for proton transfer are comparable to the rate constants for the induced non-radiative deactivation. In the system with potassium benzoate and dimethylaniline, whose molecules contain an aromatic ring, only the quenching of the fluorescence of the neutral form of 2-naphthol is observed. The absence of the fluorescence of the naphthoxide ion in such cases is evidence that the non-radiative deactivation process predominates over the adiabatic proton transfer. It is noteworthy that potassium benzoate and dimethylaniline quench the fluorescence of not only 2-naphthol but also of 2-methoxynaphthalene, the rate constant for the quenching of the fluorescence of 2-methoxynaphthalene by potassium benzoate being close to the corresponding constant for 2-naphthol.

Table 4. The rate constants for the formation of excited ion pairs and ions (k_1) and for the non-radiative deactivation (k_q) of 2-naphthol in the presence of various bases[119,162].

Base	Solvent	$10^{-8}(k_1+k_q)$, litre mole^{-1} s^{-1}	k_1, litre mole^{-1} s^{-1}	$10^{-8}k_q$, litre mole^{-1} s^{-1}
Triethylamine	Benzene	20±2	20±4	<4
Diethylamine	Benzene	41±4	41±8	<8
Triethylamine	Toluene	23±2	23±2	<2
Diethylamine	Toluene	34±3	34±8	<8
Piperidine	Toluene	40±6	40±6	<6
Triethylamine	Dichloroethane	46±5	46±10	<10
Triethylamine	Acetonitrile	11±1	1.6±0.6	9±3
Diethylamine	Acetonitrile	12±1	3.0±0.7	9±3
Piperidine	Acetonitrile	19±2	7±2	13±4
Triethylamine	Dimethylformamide	3.3±0.3	1.0±0.1	2.2±0.2
Triethylamine	Ethanol	2.0±0.1	0.8±0.1	1.2±0.1
Dimethylhydrazine	Ethanol	6.0±0.6	2.8±0.3	3.2±0.3
NN-Dimethylaniline	Ethanol	44±4	<0.4	44±4
Potassium benzoate	Methanol	19.5±2.0	<0.2	19.5±2.0
Sodium acetate	Ethanol	5.0±0.5	5.0±0.5	<0.5

In the above systems, excited 2-naphthol molecules behave both as the acid (proton donor) and the electron acceptor. The donor–acceptor interaction can lead to the deactivation of excited molecules[154]. The relative rate constants for the adiabatic proton transfer and the deactivation depend on the relative basicity of the base and on its ionisation potential (its electron-donating properties). On passing from triethylamine (I = 7.8 eV) and dimethylhydrazine (I = 7.75 eV) to dimethylaniline (I = 7.3 eV), the proton transfer rate constant decreases and the deactivation rate constant increases. Similarly, the reaction

‡In protic solvents, where the acid and base form hydrogen-bonded complexes with the solvent, it is impossible to separate experimentally the deactivation processes at various stages, so that the deactivation rate constants determined from the equation

$$\frac{\varphi_0}{\varphi}\left(1-\frac{\varphi''}{\varphi_0''}\right) = 1+\left[k_q+k_1\frac{k_d'}{k_2+k_d'}\right][B]\tau_0 \tag{25}$$

may refer to a combination of processes of different types: deactivation at the stage involving the formation of the excited complex and in the proton transfer step itself.

with the benzoate ion leads to the deactivation of excited 2-naphthol molecules, in contrast to the reaction with the acetate ion, which proceeds adiabatically and leads to proton transfer (the ionisation potentials of acetic and benzoic acids are 10.7 and 8.5 eV respectively). Thus, non-radiative deactivation at the stage involving the formation of the excited hydrogen-bonded complex in the above systems apparently proceeds as a result of the donor–acceptor interaction of the components and competes with the reaction proper.

The quenching of the fluorescence as a result of the formation of hydrogen-bonded complexes has been observed by Cooke and Solomon in a study of the interaction of excited 1- and 2-methoxynaphthalenes with benzoic acid[156]. The introduction of a compound capable of forming a hydrogen bond with benzoic acid, for example, dioxan, reduces the efficiency of the quenching and, at high dioxan concentrations, the quenching vanishes altogether. It is of interest that only monomers and linear (but not cyclic) benzoic acid dimers can quench the fluorescence of methoxynaphthalenes.

Table 5. The relative quantum yields for the formation of excited ion pairs on excitation of the hydrogen-bonded complexes of 2-naphthol with aliphatic amines[134].

Solvent	Triethylamine	Diethylamine	Piperidine	Benzylamine	t-Butylamine
Toluene	1.0	0.8±0.1	0.6±0.1	0.4±0.1	0.6±0.1
Dichloroethane	1.0	0.8±0.1	0.8±0.1	—	—

A number of experimental data, which are treated as proof of the occurrence of non-radiative deactivation in the proton transfer step itself, have been obtained recently. In the excitation of hydrogen-bonded complexes of 2-naphthol with aliphatic amines in aprotic solvents of low polarity, the quantum yield in the formation of the excited ion pair is in many instances less than unity[134] (Table 5). This shows that the degradation of the electronic excitation energy can occur directly in the proton transfer step itself and not as a result of subsequent or competing electron transfer processes.

Förster showed[124] that the excitation of the 2-naphthylammonium cation in aqueous sulphuric acid solutions to the fluorescence of 2-naphthylamine, which is a result of proton transfer to the solvent. At sulphuric acid concentrations where the fluorescence of both forms is observed, the overall fluorescence quantum yield is very low (0.002). The fluorescence quantum yields of 2-naphthylamine in the H_2SO_4–H_2O and D_2SO_4–D_2O systems at low acid concentrations approach a common limit of 0.26. Both values decrease with increase of acid concentration, but the quantum yield in the deuteriated system decreases much more slowly. In the range of acid concentrations where the fluorescence of the cation may be observed, the fluorescence quantum yield in the deuteriated system is much higher than in the non-deuteriated system. With increase of acidity, the fluorescence quantum yields of the cation increase in both systems and approach one another. In the deuteriated system, the equalisation of the fluorescence quantum yields of the cation and the molecular base occurs at a somewhat lower acid concentration than in the non-deuteriated system. Förster[124] believes that the proton transfer from the excited cation to the solvent makes possible non-radiative deactivation, which is not observed either for the neutral molecule or the cation separately.

However, there are other explanations of the above experimental facts. Schulman and Liedke[143] suggest the existence of at least one non-emitting intermediate complex. This may be a stoichiometric intermediate complex of the naphthylammonium ion and one water molecule. Such a complex may be virtually non-fluorescent owing to the intense internal transition to the ground state. Förster[124] believed that the deactivation could be also caused by the protonation of the aromatic ring of 2-naphthylamine in the singlet state. The excited amine is more sensitive to electrophilic attack by the proton than the cation. The rate of this process should increase with increased acidity of the solution and with increase of the fraction of the neutral amine obtained in the excited state.

Deactivation processes in excited ion pairs have been observed in 2-naphthol–aliphatic amine systems. In particular, the deactivation is manifested by a decreased lifetime of the excited ion pairs compared with the 2-naphthoxide ion in the same solvent and by the marked dependence of the fluorescence quantum yields and the lifetimes of the excited ion pairs on temperature[133,134,161]. In those cases where the molecules of the polar protic solvent quench the fluorescence of the aromatic acid or base, it is difficult to isolate the stage in which the electronic energy is degraded. It has been observed that excited 1-naphthol[162] and indole and its derivatives[178] are effectively quenched by water molecules. In both cases, a decrease of solution temperature and deuteriation of the solvent lead to an appreciable decrease in the rate constant for the non-radiative deactivation. The fluorescence quantum yield and the lifetime of the excited 1-naphthol molecules in aqueous solution increase in the presence of an electrolyte (guanidinium chloride) and a non-electrolyte (sucrose) at high concentrations (of the order of several mole litre^{-1}).[169] A similar influence of added salts on the fluorescence of organic compounds has been found for sodium 1-naphthol-4-sulphonate and the ionised forms of indole and its derivatives[179,180]. The authors explain this effect by a decrease in the activity of water when its molecules are bound in the solvation shells of the added salts. The mechanism of the quenching of the fluorescence by water molecules has not been completely elucidated. It is suggested that, when the excited molecule of an aromatic acid or base interacts, there is a possibility of the formation of forms with charge transfer (complete or partial) due to proton or electron transfer[179]. The quenching of the fluorescence of organic molecules by water is probably a general phenomenon.

The study of the temperature variation of the lifetimes of excited ion pairs led to the conclusion that the rate constant for non-radiative deactivation k''_d [see Eqn. (19)] is the sum of two terms, of which the first (k''_{d_1}) depends only slightly on temperature and is comparable to the rate constant for the non-radiative deactivation of the 2-naphthoxide ion, while the second component, of the type $k_T = k''_{d_2} \exp(-E/RT)$, is determined by the interaction of the counterions and depends markedly on the nature of the amine and the solvent (Table 6).

Two possible mechanisms of such deactivation have been proposed. In the first, each cycle of the reversible proton transfer in the ion pair is accompanied by the deactivation of some of the molecules[161]. In this case the measured activation energy (of the order of 5–10 kcal

mole^{-1}) should correspond approximately to ΔH^* for the reversible reaction

$$A^*H \ldots B \rightleftarrows \dot{A}^- \ldots\ldots HB^+,$$

and the pre-exponential factor for the deactivation rate constant is equal to the product of the proton transfer rate constant and the probability of the degradation of the energy in the excited hydrogen-bonded complex. The decrease of the activation energy for the quenching processes in ion pairs and the decrease of the pre-exponential factor following the replacement of hydrogen by deuterium are evidence in support of this model. According to another model, the electronic excitation energy is degraded by the donor–acceptor interaction of the counterions in the excited ion pair [133,161]. In this case, the activated quenching mechanism may be associated with the fact that the counterions must overcome an energy barrier (possibly the dissociation of the $-O^-\ldots H-\overset{+}{N}\lessgtr$ hydrogen bond is necessary) in order to achieve a configuration ensuring the maximum probability of rapid electron transfer. The activation energy for the electronic excitation energy degradation processes can then include the dissociation energy of the hydrogen bond between the ions. Such energy degradation in the products of the proton phototransfer reaction leads to the usual quenching via the electron transfer mechanism.

Table 6. The kinetic characteristics of the deactivation processes in excited ion pairs formed by the 2-naphthoxide anion with alkylammonium ions [182].

Cation	Solvent	lg k_T (20° C)	E_{act}, kcal mole^{-1}	lg k_{d_0}
$(C_2H_5)_3\overset{+}{N}H$	Toluene	8.9±0.1	6.4±0.5	13.6±0.5
	Triethylamine	8.7±0.1	5.2±0.5	12.5±0.5
	Tetrahydrofuran	7.5±0.2	4.7±0.7	11.0±1.0
	Butyronitrile	8.0±0.1	5.0±0.5	11.7±0.5
$(C_2H_5)_2\overset{+}{N}H_2$	Toluene	8.7±0.1	10.0±1.0	16.0±1.0
	Diethylamine	8.4±0.1	9.3±0.7	15.0±1.0
	Tetrahydrofuran	7.9±0.2	6.3±0.5	12.5±1.0
$(C_2H_5)_2\overset{+}{N}D_2$	Toluene	8.2±0.1	6.6±1.0	13.0±1.0
	Deuterated diethylamine	7.4±0.2	—	—
$(CH_2)_5\overset{+}{N}H_2$	Toluene	8.6±0.1	10.0±1.0	16.0±1.0
	Tetrahydrofuran	7.9±0.2	6.7±0.5	13.0±0.5
$C_6H_5CH_2\overset{+}{N}H_3$	Toluene	8.2±0.1	8.0±1.6	14.0±1.0
	Tetrahydrofuran	7.9±0.2	5.0±1.0	12.0±1.0
t-$C_4H_9\overset{+}{N}H_3$	Toluene	7.9±0.2	6.5±1.0	12.0±1.0
t-$C_4H_9\overset{+}{N}H_3$	Tetrahydrofuran	8.3±0.1	4.0±0.8	—

A similar deactivation mechanism, including proton transfer to the hydrogen-bonded complex followed by the donor–acceptor interaction of the counterions, one of which is excited, has been proposed by Ermolaev and coworkers [157,159,182] to explain the complete absence of the fluorescence and phosphorescence of the hydrogen-bonded complexes where both the proton donor and acceptor possess a π-electron system directly linked to the acid and basic functional groups. The hydrogen-bonded complexes of aromatic hydroxy-derivatives with aromatic heterocycles are examples of such systems [120,122,164,183]. It is suggested that, in the excited hydrogen-bonded complex, there is a fairly high probability of the formation of species with proton transfer, which exhibit electron-donating and electron-accepting properties favourable for electron transfer from the anion to the cation when one of them is in the excited state and the partners have a conjugated π-electron system. Electron transfer results in the formation of a pair of radicals, which, being unable to move apart in the time available, recombine with formation of a hydrogen-bonded complex in a non-excited state. Proton transfer in the complex is much slower (10^{-12} s) than electron transfer (10^{-15} s). Furthermore, proton transfer is retarded by a potential barrier, whose presence is due to a small difference between the acid–base properties of the partners in the complex, so that it is quite likely that proton transfer is the rate-limiting stage in the quenching process. Apparently these stages are not significantly separated during their occurrence, so that it is impossible to isolate one from the other.

The transfer of a proton and an electron is equivalent to the transfer of a hydrogen atom. In a study of the interaction of 2-naphthol with pyridine in cyclohexane solution by flash photolysis, it was shown [128] that the excitation of the hydrogen-bonded complex did not lead to the formation of any intermediate products, while the reaction of free 2-naphthol molecules in both the first singlet state and the triplet state led to the formation of naphthoxy-radicals, i.e. the fluorescence is quenched via the abstraction of a hydrogen atom from 2-naphthol by pyridine. A similar mechanism of the quenching of fluorescence by the transfer of a hydrogen atom in hydrogen-bonded complexes has been proposed for the benzacridine–phenol system [158]. Mataga and coworkers [184] showed by laser photolysis that, apart from the formation of the excited ion, in the carbazole–triethylamine system in acetonitrile there is a competing process involving the abstraction of a hydrogen atom and the formation of the carbazyl radical. However, the quenching of the carbazole fluorescence by pyridine is not accompanied by the appearance of any unstable intermediate products.

A study of the quenching process in hydrogen-bonded complexes at low temperatures permitted certain conclusions concerning the rate-limiting deactivation stage [159]. When the temperature is reduced from 77 to 4K, the quenching of the fluorescence in 2-naphthol–pyridine and carbazole–pyridine complexes in frozen toluene solutions is found to be diminished. The rate-limiting stage of the deactivation process in such complexes is apparently proton transfer from the acid to the base (pyridine) by tunnelling.

All the processes considered above refer to the singlet excited state. The study of the deactivation processes in the triplet state is complicated by the fact that the latter is formed from the singlet state as a result of an intercombination transition. All the deactivation processes leading to the quenching of the singlet state can therefore decrease the quantum yield of the triplet state. However, this difficulty may be overcome if the triplet state is populated by means of a triplet–triplet energy transfer. Using the method of the triplet–triplet energy transfer from the toluene glassy matrix to the luminescent compound investigated, it has been shown [164] that the phosphorescences of carbazole, 2-naphthol, pyrazine, benzophenone, and anthraquinone are quenched by pyridine and phenol. In contrast to the latter, triethylamine does not quench the phosphorescence of carbazole and 2-naphthol. In those cases where the system components do not form a hydrogen bond and the functional groups forming a hydrogen bond

with the π-systems of the aromatic molecules are not conjugated, there is no quenching of the phosphorescence and hence no deactivation of the triplet state.

When processes involving the deactivation of the singlet excited state in proton phototransfer reactions are examined, it is of interest to consider the problem of which process (internal conversion or intercombination transition) is influenced to a greater extent by the acid–base interaction§. It has been stated that proton transfer within 2-naphthol–aliphatic amine complexes [162] increases the degree of internal conversion.

Non-radiative degradation of the electronic excitation energy has also been observed in intramolecular proton transfer reactions in salicylate esters [185]. This is manifested by a sharp increase of the intensity of the fluorescence of the species with proton transfer as the temperature is reduced. The absence of any influence by isotopic substitution on the kinetic characteristics of the deactivation processes is evidence that the latter are not associated with the proton phototransfer reaction. This is the essential difference between the mechanisms of the degradation of the electronic excitation energy in intramolecular and intermolecular proton transfers.

The available data are insufficient to decide whether the deactivation processes in one of the species involved in interconversion play a dominant role or whether deactivation proceeds with a high efficiency in both species.

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§We are not concerned here with the numerous studies devoted to the influence of the formation of hydrogen-bonded complexes on the relative positions of the $n\pi^*$ and $\pi\pi^*$ levels and the associated change in the relative probabilities of the internal and intercombination transitions.

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