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Fast dynamic excited state proton transfer (ESPT) reaction of weak oxoaromatic bases. Aminocoumarins with fixed amino group

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Abstract

The excited state protonation of the carbonyl group of 7-aminocoumarins, containing a 7-amino group fixed in the yulolidine fragment, is an irreversible diffusion-limited process in protic solvents and proceeds by a dynamic mechanism. The effect of the non-stationary diffusion of reagents contributes significantly to fluorescence quenching (25% in the presence of 0.1 M H_2SO_4 for **IIb** in EtOH). The limiting value (acid concentration → ∞) of the fluorescence quantum yield of the product of the excited state proton transfer (ESPT) reaction (ϕ'_∞) reaches 0.48. The quenching of 7-aminocoumarins in protic solvents is effected by the solvated proton. The dependence of k_q on the solvent is determined by the limiting proton conductance in the solvent. The activation energy of the decay of the encounter complex between the solvated base and proton is determined by two factors: (1) the energy of H–OR bond breakage in this complex; (2) the difference between the stabilization energies of the encounter complex and the transition state in the polar solvent.

Keywords: Excited state proton transfer; Aminocoumarins; Ground state

1. Introduction

Oxoaromatic compounds are weak organic bases. In the ground state, oxoaromatic compounds are protonated in strongly acidic media ($pK_a(S_0)$ for xanthone, −4.1) [1–4]. On excitation, the basicity of oxoaromatic compounds increases, and protonation in the excited state takes place at moderate acidity ($pK_a(S_1)$ for xanthone, 0.96) [4–8].

The study of the kinetics and mechanism of this reaction is hampered by the change in solvent properties at high acid concentration (approximately 5 M), which is required for protonation in the ground state. To carry out these investigations at lower acid concentrations, the basicity of the carbonyl group of the oxoaromatic compound must be increased. This can be done by the introduction of selected electron-donor substituents into the oxoaromatic compound, e.g. an amino group. This is corroborated by calculations of the proton affinity (P_A) of amino and carbonyl groups of acetamide, *N*-methylacetamide and *N*-methylformamide by ab initio calculations [9]. A supramolecular approach of the solvent effect shows that the oxygen and nitrogen basicities of these compounds are of the same order. Aromatic amines do not form hydrogen bonds even with strong proton donors [10]. Hence it is expected that the scheme of acid–base interaction of the oxoaromatic compounds in the excited state will remain unchanged if an amino group is introduced into the molecule. Therefore aminocoumarins have been chosen as the subject of our investigation.

In solution, aminocoumarins in the ground state are protonated at the amino group. The basicity of 7-aminocoumarins (**I**) in acetonitrile (MeCN) decreases as the 7-amino group is fixed in the rigid yulolidine fragment [11]. In addition, this promotes the photoprotonation of the C=O group. If excitation takes place at the absorption band of the cation protonated at the nitrogen atom of the 7-amino group, the photoprotonation of the C=O group by sulphuric acid has a low efficiency. The fluorescence quantum yield of the excited state proton transfer (ESPT) reaction product does not exceed 0.01 [11].

In this paper, the kinetics and mechanism of the excited state protonation of substituted 2,3,6,7-tetrahydro-1H, 5H,11H-[1]benzopyrano[6,7,8-ij]quinolizin-11-ones (**II**), which are 7-aminocoumarins with a fixed 7-amino group, were studied. The effect of the solvent and base structure on C=O group protonation was investigated. The structures of the aminocoumarins are given in Scheme 1. The study was carried out in methanol (MeOH), ethanol (EtOH), propanol (PrOH), isopropanol (i-PrOH), butanol (BuOH), sec-butanol (s-BuOH), ethylene glycol ($(CH_2OH)_2$) and water

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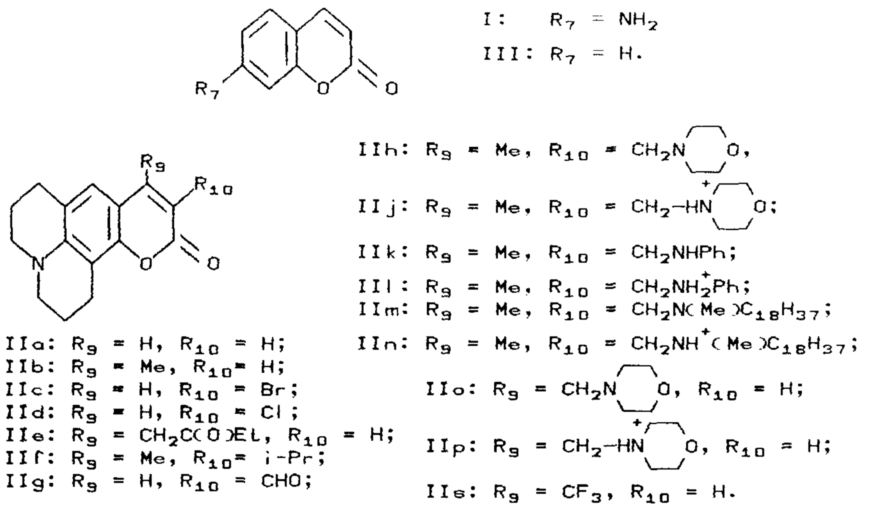


I: $R_7 = NH_2$
III: $R_7 = H$.

IIa: $R_9 = H$, $R_{10} = H$;
IIb: $R_9 = Me$, $R_{10} = H$;
IIc: $R_9 = H$, $R_{10} = Br$;
IId: $R_9 = H$, $R_{10} = Cl$;
IIe: $R_9 = CH_2C(O)Et$, $R_{10} = H$;
IIf: $R_9 = Me$, $R_{10} = i\text{-}Pr$;
IIg: $R_9 = H$, $R_{10} = CHO$;

IIh: $R_9 = Me$, $R_{10} = CH_2N$ O,
IIj: $R_9 = Me$, $R_{10} = CH_2\text{–}\overset{+}{H}N$ O;
IIk: $R_9 = Me$, $R_{10} = CH_2NHPh$;
IIl: $R_9 = Me$, $R_{10} = CH_2\overset{+}{N}H_2Ph$;
IIm: $R_9 = Me$, $R_{10} = CH_2N(Me)C_{18}H_{37}$;
IIn: $R_9 = Me$, $R_{10} = CH_2\overset{+}{N}H(Me)C_{18}H_{37}$;
IIo: $R_9 = CH_2N$ O, $R_{10} = H$;
IIp: $R_9 = CH_2\text{–}\overset{+}{H}N$ O, $R_{10} = H$;
IIs: $R_9 = CF_3$, $R_{10} = H$.

Scheme 1.

(H_2O) with sulphuric acid, and in EtOH and MeCN with trifluoroacetic acid.

2. Experimental details

The electronic structures of coumarin, 7-aminocoumarin and their cations protonated at the oxygen atom of the C=O group and at the nitrogen atom of the NH_2 group in the ground and excited states were calculated by the MNDO method [12]. The geometry of 7-aminocoumarin was optimized suggesting a planar structure for the molecule. The excited state electronic structure was calculated taking into account one singly excited configuration, related to the electron transition from the higher occupied to the lower unoccupied molecular orbital (MO). The absorption spectra were recorded with a UV-3100 spectrophotometer, the fluorescence spectra were recorded with an Elumin-2M spectrofluorometer and the fluorescence kinetics was recorded with an SP-70 nanosecond spectrometer. The fluorescence quantum yield was measured by comparing the areas under the corrected fluorescence spectra of the fluorophore and a solution of quinine bisulphate in 1 N sulphuric acid ($\phi_f = 0.546$ [13]). The fluorescence characteristics of the photoreaction products and the rate constants of the fluorescence quenching of the coumarins were determined using the home-generated programs *SPECTR* and *EQUILI*. The measurements were carried out at 20 °C. The cations **IIj**, **IIl**, **IIn** and **IIp** were prepared by the addition of 1×10^{-4} M H_2SO_4 to ethanolic solutions of the corresponding coumarins **IIh**, **IIk**, **IIm** and **IIo**. The concentration of the 7-aminocoumarins was equal to approximately 2×10^{-5} M. The solvents were purified and dried according to the methods given in Ref. [14].

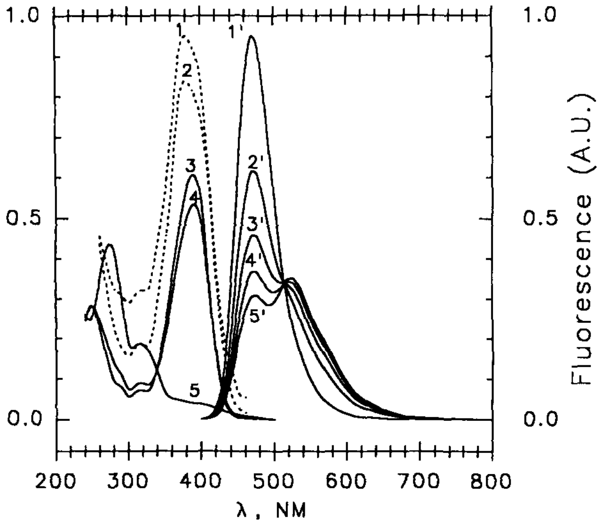


Fig. 1. Fluorescence excitation (1, 2), absorption (3–5) and fluorescence emission (1'–5') spectra of **IIb** in EtOH at 20 °C. H_2SO_4 concentrations: 0.330 (1, 2), 0 (3, 1'), 0.027 (2'), 0.053 (3'), 0.080 (4'), 0.106 (5'), 0.328 (4), 3.33 (5) M. Fluorescence wavelengths in the excitation spectra: 470 nm (1); 530 nm (2).

3. Results

The absorption spectrum of an ethanolic solution of **IIb** does not change on addition of H_2SO_4 (less than 0.1 M). In more acidic solutions, the short-wavelength band of the cation **IIb**$H_N{}^+$, protonated in the ground state at the nitrogen atom of the amino group, appears in the absorption spectrum (Fig. 1). In acidic solution ($[H_2SO_4] < 0.1$ M), the fluorescence of the neutral form of **IIb** (470 nm) is quenched and a new band in the long- wavelength region (530 nm), belonging to the cation **IIb**$H_O{}^+$ protonated at the C=O group, appears. The intensity of the latter band increases as the H_2SO_4 concentration increases (Fig. 1). The excitation of this system was carried out at the long-wavelength absorption band of the neutral form **IIb** (365 nm) where the cation **IIb**$H_N{}^+$ does not absorb. Under these conditions, an isoemissive point exists in the fluorescence spectra. The excitation spectra of both fluorescence bands are practically identical and similar to the absorption spectrum of the initial form. A limiting value

($[H_2SO_4] \rightarrow \infty$) of the fluorescence quantum yield of the ESPT product (ϕ'_∞) was determined according to the equation

$$\phi_\infty' = \frac{\phi_t - \phi}{1 - \phi/\phi_0}$$

where ϕ_0 and ϕ are the fluorescence quantum yields of **IIb** without and with acid respectively and ϕ_t is the total fluorescence quantum yield of the system in the presence of acid. The value ϕ'_∞ is independent of the acid concentration and is equal to 0.45. It is about 1.5 orders of magnitude higher than the fluorescence quantum yield of the ESPT product of the **IIb**–H_2SO_4 system in MeCN if the N-protonated form is excited (short-wavelength excitation) [11]. The value of ϕ'_∞ is dependent on the solvent and varies from 0.29 (H_2O) to 0.48 (PrOH). Other aminocoumarins of series **II** interact in the ground and excited states with sulphuric acid in protic solvents in a similar manner. The position of the fluorescence band of the FSPT product is independent of the solvent.

The fluorescence of the initial form **IIb** at the short- wavelength side of the spectrum (450 nm), during the time interval from the maximum (t_{max}) to the end of the fluorescence decay curve (when the excitation pulse has ended), decays monoexponentially at all acid concentrations used. In the presence of H_2SO_4, the fluorescence lifetime and quantum yield of the initial form decrease. Under the same conditions, the fluorescence kinetics of the product at the long-wavelength side of the spectrum (600 nm) is the sum of two exponents with equal modulus amplitudes ($|a_1| \approx |a_2|, a_1 < 0$)

$$I'(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}$$

The value of τ_1 decreases as the acid concentration increases, and τ_1 is equal to the fluorescence lifetime of the initial form. The value of τ_2 is independent of the acid concentration. The monoexponential decay of the fluorescence of **IIb** indicates that the precursor of the ESPT product is an excited initial form. This also agrees with Ref. [15], where the ESPT reaction kinetics of **IIb** in water was studied. Since the convolution of the fluorescence kinetics of the initial form with e^{-t/τ_2} is close to the fluorescence kinetics of the ESPT product, this conclusion is correct for any decay law (e.g. in the case of non-stationary fluorescence quenching) for the excited state of the initial form. These results indicate that the protonation of **IIb** in the excited state is irreversible.

Table 1
Fluorescence spectral maxima (λ_f), fluorescence quantum yields (ϕ_0) and lifetimes (τ_0) and rate constants for radiative (k_f) and radiationless (k_d) decay of the first excited singlet state of 7-aminocoumarins in EtOH at 20 °C

Coumarin	λ_f (nm)	ϕ_0	τ_0 (ns)	k_f (10^8 s^{-1})	k_d (10^8 s^{-1})
IIa	470	0.91	4.52	2.01	0.20
IIb	470	0.80	4.36	1.83	0.46
IIc	495	0.77	4.09	1.88	0.56
IId	495	0.78	5.35	1.46	0.41
IIe	480	0.71	4.94	1.44	0.58
IIf	475	0.84	4.35	1.93	0.37
IIg	505	0.85	4.35	1.95	0.35
IIh	475	0.74	3.90	1.90	0.66
IIj	480	0.80	4.36	1.83	0.46
IIk	475	0.74	4.15	1.78	0.63
IIl	480	0.79	4.34	1.82	0.48
IIm	475	0.35	2.54	1.38	2.56
IIn	485	0.74	4.27	1.73	0.61
IIo	485	0.91	5.01	1.82	0.18
IIp	510	0.65	3.92	1.66	0.89
IIq [a]	472	0.63	4.30	1.55	0.78
IIr [b]	468	0.61	3.90	1.64	0.92
IIs	536	0.54	3.40 [c]	1.59	1.30

[a] In MeCN, $R_{10} = CH_2COOH$, $R_9 = CH_3$ [16].
[b] In MeCN, $R_{10} = CH_2COO^-$, $R_9 = CH_3$ [16].
[c] τ_0 value from Ref. [17].

4. The effect of solvent and structure on the luminescence of 7-aminocoumarins

4.1. Intramolecular electrofluorochromy of 7-aminocoumarins

The maximum wavelengths (λ_f) and lifetimes (τ_0) of fluorescence, fluorescence quantum yields (ϕ_0) and rate constants of radiative (k_f) and radiationless (k_d) deactivation of the singlet excited state of 7-aminocoumarins in EtOH are given in Table 1. It can be seen that an increase in the electron-acceptor ability of the substituents (σ^* inductive Taft constants [18]) in positions 9 (in series **IIa**, **IIo**, **IIp** and **IIs**) and 10 (in series **IIa**, **IIh**, **IIj**, **IIc**, **IId** and **IIg**) results in a long-wavelength shift of the fluorescence spectrum. If the spectral effects of the substituents are additive, it is expected that the maximum frequency of the fluorescence spectrum (ν_f) will be related to the σ^* constants of the substituents in positions 9 ($\sigma_9{}^*$) and 10 ($\sigma_{10}{}^*$) by the following expression [11]

$$\nu_f = a - b\sigma_9{}^* - c\sigma_{10}{}^* \qquad (1)$$

The values of σ^* were taken from Ref. [19] and are equal to −0.19 ($CH(CH_3)_2$), 0.0 (CH_3), 0.49 (H), 0.50 (CH_2NH_2), 0.62 ($CH_2C(O)CH_3$), 2.15 (CHO), 2.24 ($CH_2NH_3{}^+$), 2.61 (CF_3), 2.84 (Cl) and 2.96 (Br). The linear correlation of ν_f with σ^* yields the following constants: $a = 21\,400 \pm 170$, $b = 840 \pm 110$ and $c = 380 \pm 100$ cm^{-1} (correlation coefficient $\gamma = 0.932$).

The location of a charged $+I$ electron-acceptor substituent in position 10 of molecule **II** results in an increase in ϕ_0 and τ_0 (compare **IIh** and **IIj**, **IIk** and **IIl**, **IIm** and **IIn**), but the location of the charged substituent in position 9 results in a decrease in ϕ_0 and τ_0 (compare **IIo** and **IIp**). Previously, we detected the effect of a charged substituent on the absorption and fluorescence spectra and fluorescence quantum yield of 7-diethylaminocoumarin derivatives [16,20]. This effect was explained by the influence of the electrostatic field of the

Table 2
Fluorescence spectral maxima and fluorescence quantum yields of **IIb** (λ_f, ϕ_0) and cation **IIb**H_O^+ (λ_f', ϕ_∞'), fluorescence lifetimes (τ_0), rate constants of radiative (k_f) and radiationless (k_d) deactivation of the first excited state of **IIb** and rate constants of **IIb** fluorescence quenching (k_q) by sulphuric acid in various solvents at 20 °C

Solvent	λ_f (nm)	λ_f' (nm)	ϕ_0	ϕ_∞'	τ_0 (ns)	k_f (10^8 s^{-1})	k_d (10^8 s^{-1})	k_q[a] (10^9 (M s)$^{-1}$)	k_q[b] (10^9 (M s)$^{-1}$)
MeOH	476	530	0.79	0.39	4.47	1.77	0.47	17.80	15.00
EtOH	471	530	0.80	0.45	4.36	1.83	0.46	4.79	3.64
				0.43[c]				2.08[c]	
PrOH	468	530	0.86	0.48	4.45	1.93	0.32	2.76	2.69
i-PrOH	463	530	0.80	0.41	4.24	1.89	0.47	3.28	2.85
BuOH	468	530	0.99	0.44	4.36	2.27	0.02	2.23	1.67
s-BuOH	460	530	0.87	0.39	4.17	2.09	0.31	1.69	1.40
$(CH_2OH)_2$	482	535	0.87	0.35	5.16	1.69	0.25	2.67	1.74
H_2O	491	535	0.99	0.29	5.04	1.26	0.72	29.90	27.60
MeCN[c]	460	520	0.67	0.42	4.2	1.59	0.79	2.16	–

[a] Error of the determination of k_q is 10%.

[b] With non-stationary effect; encounter complex radius is set to 9 Å.

[c] Proton donor is trifluoroacetic acid; excitation at 365 nm.

substituent, non-conjugated with the chromophore system of the molecule.

A comparison of the elementary constants of radiative (k_f) and radiationless (k_d) deactivation for the pairs **IIh** and **IIj**, **IIk** and **IIl**, **IIm** and **IIn**, **IIo** and **IIp** and **IIq** and **IIr** shows that the substituent field has a stronger influence on k_d than on k_f. A positively charged substituent in position 10 of molecule **II** results in a decrease in k_d (compare **IIh** and **IIj**, **IIk** and **IIl**, **IIm** and **IIn**), but a negatively charged substituent results in an increase in k_d (compare **IIq** and **IIr**). An analogous effect of an external electrostatic field on the rate constants of elementary photophysical processes in pyrimidine vapour has been described in Ref. [21]. The effect has been explained by a change in the singlet–triplet (S–T) interaction induced by the external field. We believe that the intramolecular electrofluorochromic effect in aminocoumarins can be explained in the same way. Indeed, as we go from a noncharged molecule to a charged molecule, the change in S–T splitting is determined by the difference between the interaction energy of the charged substituent with the delocalized charge of the chromophore part of the molecule in the excited singlet and triplet states. The sign of the effect changes as the sign of the substituent changes.

4.2. *Effect of the solvent on the luminescence properties of IIb*

The luminescence characteristics of **IIb** in protic solvents are given in Table 2. It can be seen that k_f increases as the length of the hydrocarbon chain in the alcohol molecule increases. This is caused by the change in Einstein's coefficient A of the spontaneous radiative transition. In this case, a linear correlation of ν_f and $(k_f n)^{1/3}$ in the series of solvents of the same type (aliphatic alcohols, ethylene glycol and water) should be observed if the transition dipole moment is constant. Here n is the refraction index of the solvent. This is indeed observed ($\gamma = 0.864$) with

$$\nu_f = (14\,280 \pm 1340) + (12.16 \pm 2.89) \times (k_f n)^{1/3}$$

A formal description of the solvent effect on the rate constants of certain processes was proposed by Kamlet, Taft and coworkers [22,23]. According to the Kamlet–Taft equation, the non-specific (parameter of polarity and polarizability π^*) and specific (parameters of acidity and basicity α and β) solvent–solute interactions are considered separately

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta \qquad (2)$$

where XYZ and XYZ_0 are the properties of interest in the given solvent and cyclohexane respectively. The values π^*, α and β were taken from Ref. [23] and are given in Table 4 (see Section 5.3.1). The logarithm of the k_f value ($\equiv XYZ$) correlates with the Kamlet–Taft parameters according to Eq. (2) ($XYZ_0 = 8.69 \pm 0.09$, $a = -0.499 \pm 0.098$; s and b values differ insignificantly from zero; $\gamma = 0.915$). The calculated value of logk_f in cyclohexane agrees with the experimental value (8.61 [17]) within experimental error. The value of logk_d does not correlate with the Kamlet–Taft parameters ($\gamma = 0.437$).

Thus the solvent effect on k_f of **IIb** can be explained by the solvent-induced shift of the emission spectrum, the integration of which gives the Einstein coefficient A. According to the Kamlet–Taft equation, this effect depends on the proton-donor ability of the solvent.

5. ESPT reaction of aminocoumarins

5.1. *Electronic structure and proton affinity of coumarins*

The relative basicity of the functional group in the series of compounds of the same type can be estimated indepen-

Table 3
Charges on the oxygen atoms of carbonyl group (q_O) and the nitrogen atoms of the amino group (q_N) and proton affinity of the amino (P_{An}) and carbonyl (P_{AO}) groups of coumarin and 7-aminocoumarin in the ground and excited states [a]

Compound	P_{AO} (kJ mol^{-1})	P_{AN} (kJ mol^{-1})	$-q_O \times 10^4$ (e)	$-q_N \times 10^4$ (e)
Coumarin	870.9 (880.1)	–	3025	–
Coumarin*	909.9 (912.3)	–	2861	–
7-Aminocoumarin	903.9 (911.5)	822.3	3096	3644
7-Aminocoumarin*	974.3 (983.5)	864.6	3016	2939

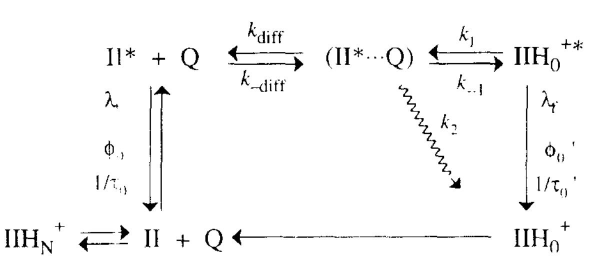
[a] Asterisk denotes the first excited state. The P_{AO} value is given for the molecule conformation having the oxygen atom of the pyrone ring and the proton in trans (cis) configuration relative to the C=O bond of the molecule.

dently from a comparison of the proton affinity (P_A) values and from a comparison of the reaction centre charge (q) values. The greater the P_A value [24] and the higher the absolute value of the negative charge q on the atom to be protonated [25], the more basic the functional group. The charges on the oxygen atom of the carbonyl group (q_O) and on the nitrogen atom of the amino group (q_N), calculated by the MNDO technique, and the proton affinities of the amino (P_{AN}) and carbonyl (P_{AO}) groups of compound **I** and parent coumarin (**III**) in the ground and excited states are given in Table 3. For the calculation of the proton affinity, the heat of proton formation was taken to be equal to the sum of one-half of the dissociation energy of the hydrogen molecule and the ionization potential of the hydrogen atom (1530.6 kJ mol^{-1}).

It can be seen from Table 3 that the use of these two methods of basicity estimation does not always give coincident results. If we compare the molecules in the same electronic state (compare **I** and **III** in the ground or first excited singlet state), according to both methods the basicity of the C=O group should increase if a 7-amino group is introduced into molecule **III**. A comparison of P_{AO} (P_{AN}) of the same molecule in various electronic states shows that, on excitation of compounds **I** and **III**, the basicities of these molecules at the C=O (NH_2) group should increase. An analogous comparison of q_O (q_N), however, gives the opposite conclusion. Thus these methods of estimation do not result in the same answer to the question regarding the character of the basicity change of the various functional groups of compounds **I** and **III** on excitation or the relative basicity of these groups. However, according to both methods, the basicity of the C=O group of compound **III** should increase strongly on introduction of a 7-amino group.

5.2. The kinetics and efficiency of IIb photoprotonation in EtOH

Scheme 2 shows the main processes taking place in **II**–H_2SO_4 systems during long-wavelength excitation (365 nm) where the cation protonated at the nitrogen atom of the 7-amino group ($IIH_N{}^+$) does not absorb



Scheme 2.

Here (**II*** · · · Q) is an encounter complex between **II** and the proton donor Q, τ_0 is the fluorescence lifetime of **II**, ϕ'_0 and τ'_0 are the fluorescence quantum yield and lifetime of the ESPT product $IIH_O{}^{+*}$ on excitation from the ground state, k_{diff} and k_{-diff} are the rate constants of formation and dissociation of the encounter complex, k_1 and k_2 are the rate constants of formation of the excited product and radiationless deactivation induced by the forward reaction and k_{-1} is the rate constant of the back reaction. The values of k_{diff} and k_{-diff} have been calculated according to Eqs. (3)–(5) [26–28]

$$k_{diff} = 4\pi r_c (D_Q + D_{II}) N_A \frac{\delta}{e^{\delta} - 1} \qquad (3)$$

$$k_{-diff} = \frac{4\pi r_c (D_Q + D_{II}) N_A}{V_q} \frac{\delta}{1 - e^{-\delta}} \qquad (4)$$

$$\delta = \frac{Z_Q Z_{II} e^2}{\epsilon r_c RT} N_A \qquad (5)$$

where r_c is the radius of the encounter complex, D_Q and D_{II} are the diffusion coefficients of Q and **II***, N_A is Avogadro's number, V_q is the volume of the encounter complex, Z_Q and Z_{II} are the charges of Q and **II***, e is the elementary charge, ϵ is the dielectric constant of the medium, R is the universal gas constant and T is the absolute temperature.

The diffusion coefficients of **II*** and H_2SO_4 (D_{H2SO4}) have been estimated according to the Othmer–Thakar relation [29]

$$D = \frac{14.0 \times 10^{-5}}{V^{0.6} \eta_s} \qquad (6)$$

where V is the molar volume (cm^3 mol^{-1}) of the compound and η_s is the solvent viscosity (cP) at 20 °C. For fluorescence quenching of **II** by H^+, the diffusion coefficient of the quencher (D_H) has been calculated according to the equation

$$D_H = \lambda_+ RT/F^2 \qquad (7)$$

where λ_+ is the limiting proton conductance of the solvent and F is the Faraday constant.

If the non-stationary quenching is accounted for, the fluorescence quantum yield of the initial form **II** can be calculated according to the equation [30]

$$\frac{\phi_0}{\phi} = (1 + k_q \tau_0 [Q]) e^{V_q [Q]} = \frac{\phi_0}{\phi_S} e^{V_q [Q]} \qquad (8)$$

where k_q is the rate constant for the stationary quenching of **II** fluorescence

$$k_q = \frac{k_{\mathrm{diff}}[k_1 + k_2(1 + k_{-1}\tau_0')]}{k_1 + (k_2 + k_{-\mathrm{diff}})(1 + k_{-1}\tau_0')} \tag{9}$$

The ratio of the fluorescence quantum yields of the cation $\mathbf{II}H_O{}^+$ and the initial form **II** is expressed as

$$\frac{\phi'}{\phi} = \frac{\phi_\infty'}{\phi_0} k_q \tau_0 [Q] \tag{10}$$

$$\phi^{\infty\prime} = \frac{k_1 \phi_0'}{k_1 + k_2(1 + k_{-1t0}')} \tag{11}$$

If the reaction is irreversible ($k_{-1} = 0$), then $\phi'_\infty = \phi_r \phi'_0$ [31]. The value of the total rate constant of proton transfer and induced deactivation (k_i) is determined by the following equation

$$k_i = k_1 + k_2 = \frac{k_{-\mathrm{diff}} k_q}{k_{\mathrm{diff}} - k_q} \tag{12}$$

If the non-stationary diffusion of reagents is accounted for, the following law of fluorescence decay is valid [32]

$$F(t) = F_0 \int_0^t \mathrm{e}^{-\theta x - \xi x^{1/2}} W(t-x)\, \mathrm{d}x \tag{13}$$

where $W(x)$ is the pump profile, $\theta = 1/\tau_0 + k_q[Q]$ and ξ is determined by (1) the diffusion coefficients of **IIb*** and the quencher, (2) the quenching sphere radius (r_c for the fluorescence quenching of the initial form) and (3) the quencher concentration. The analysis of the fluorescence kinetics of **IIb** in EtOH in the presence of H_2SO_4 shows that, at a time greater than t_{max}, the contribution of the second term in the exponent of Eq. (13) is negligible and the dispersion of ξ is comparable with ξ^2. In this case, the τ_1 and τ_2 values of **II*** and $\mathbf{II}H_O{}^{+*}$ fluorescence are determined by [33]

$$\frac{2}{\tau_{1,2}} = \frac{1}{\tau_0} + \frac{1}{\tau'} + k_i[Q] \pm \left[\left(\frac{1}{\tau_0} - \frac{1}{\tau'} + k_i[Q] \right)^2 + 4k_i k_{-1}[Q] \right]^{1/2} \tag{14}$$

where $1/\tau' = 1/\tau'_0 + k_{-1}$.

The dependence of ϕ_0/ϕ and τ_0/τ on the acid concentration for **IIb** in EtOH is shown in Fig. 2. It can be seen that, for $r_c = 0$ (stationary quenching), ϕ_0/ϕ and τ_0/τ do not coincide. This may be caused by the reversibility of the photoreaction, the static quenching effect or non-stationary quenching. The analysis of the fluorescence kinetics of **IIb** using Eq. (14) for the initial and protonated forms by the non-linear least-squares method gives the rate constant of the forward reaction $k_i = (4.15 \pm 0.16) \times 10^9$ s^{-1}; the product $k_1 k_{-1}$ differs insignificantly from zero and $\tau'_0 = 5.45$ ns. Thus the excited state protonation of the C=O group of **IIb** is dynamic and practically irreversible. Since the static quenching can be neglected because of the experimental conditions (excitation at the absorption band of the non-protonated form of **IIb**) and the irreversibility of the reaction is indicated by the analysis of the kinetic data, we can conclude that the difference between ϕ_0/ϕ and τ_0/τ values is caused by non-stationary quenching. The ratio ϕ_0/ϕ_S corrected for the non-stationary quenching effect by the equation

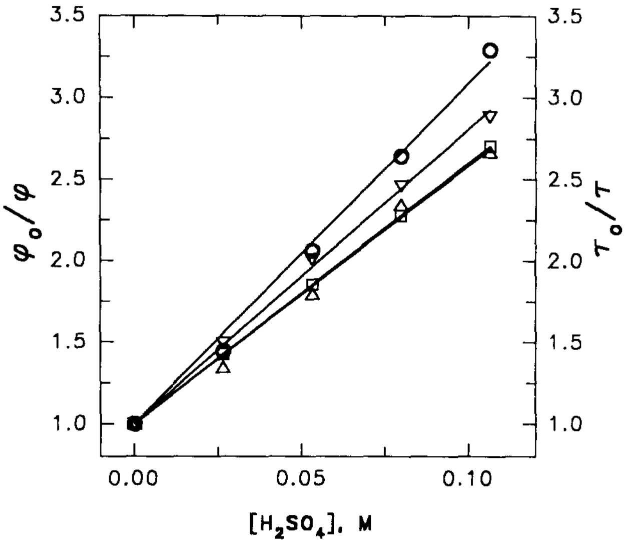


Fig. 2. Dependence of ϕ_0/ϕ (○), τ_0/τ (▽), ϕ_0/ϕ_S (□) and τ_0/τ_S (△) on the H_2SO_4 concentration for **IIb** in EtOH at 20 °C.

$$\phi_0/\phi_S = (\phi_0/\phi)\mathrm{e}^{-V_q[Q]}$$

coincides with the ratio τ_0/τ at $r_c = 9$ Å (Fig. 2). The corrected Stern–Volmer constant $k_q\tau_0$ is equal to 15.86 ± 0.42 M^{-1}. The same value of $r_c = 9$ Å was found in the analysis of the non-stationary perylene fluorescence quenching by oxygen in dodecane [34]. The non-stationary contribution to the total fluorescence quenching of the initial form **IIb** in EtOH, calculated according to the ratio

$$\frac{1 - \mathrm{e}^{-V_q[Q]}}{1 - \phi/\phi_0}$$

is equal to 25% for 0.1 M of acid. In Ref. [15], the non-stationary effect in the ESPT reaction kinetics of **IIb** in H_2O was not taken into consideration, although its contribution is rather high (18% at pH 1).

Thus the ESPT reaction of **IIb** with sulphuric acid in EtOH is an irreversible diffusion-limited process with a rate constant $k_i = (4.15 \pm 0.16) \times 10^9$ M^{-1} s^{-1} at 20 °C. The difference between ϕ_0/ϕ and τ_0/τ values is caused by non-stationary reagent diffusion. The radius of the quenching sphere is equal to 9 Å.

5.3. Effects of solvent and structure on the ESPT of 7-aminocoumarins

5.3.1. ESPT reaction of IIb in various solvents

The rate constants of the reactions in Scheme 2 are given in Table 2. The rate constants of the reaction of **IIb*** with CF_3COOH in EtOH and MeCN (similar to that of **IIb*** with H_2SO_4 in EtOH) are almost equal. The fluorescence quantum yield ϕ'_∞ of the ESPT reaction product with CF_3COOH in

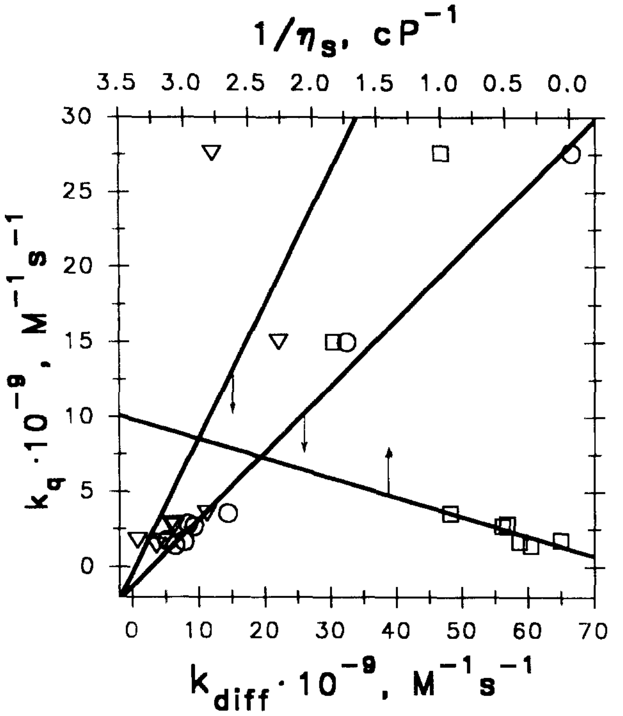


Fig. 3. Dependence of the rate constant k_q of coumarin **IIb** fluorescence quenching by sulphuric acid on the reciprocal solvent viscosity $1/\eta_s$ (□). The relation between the rate constant k_q of coumarin **IIb** fluorescence quenching by sulphuric acid and the rate constant k_{diff} of reagent diffusion for the interaction with the solvated proton (○) and with a molecule of H_2SO_4 (▽).

MeCN on excitation at long- wavelength (365 nm) and short-wavelength (320 nm [11]) absorption bands differ by approximately 1.5 orders of magnitude. In the first case, only initial form **IIb** is excited, but in the second case, the N-protonated form $\mathbf{IIbH_N}^+$ is excited (Fig. 1). In the second case, the formation of $\mathbf{IIbH_O}^{+*}$ takes place in two steps: (1) acidic dissociation of $\mathbf{IIbH_N}^{+*}$ into **IIb*** and H^+; (2) reaction of **IIb*** and H^+ to form the final product $\mathbf{IIbH_O}^{+*}$ according to Scheme 2. Since the quantum yield of $\mathbf{IIbH_O}^{+*}$ formation in the second step is high and depends only slightly on the solvent, the low value of ϕ'_∞ can be explained either by the greater time of $\mathbf{IIbH_N}^{+*}$ dissociation in comparison with the fluorescence lifetime, or by the effective radiationless deactivation induced by $\mathbf{IIbH_N}^{+*}$ dissociation.

It has been shown that the ESPT reaction of **IIb** in EtOH is a diffusion-limited irreversible process. Therefore, if the diffusion of the reagents obeys the Stokes–Einstein law, the value of k_q should be proportional to the reciprocal solvent viscosity (η_s). The dependence of k_q on $1/\eta_s$ is shown in Fig. 3. In viscous alcohols, k_q increases linearly as $1/\eta_s$ increases, but at low viscosities (MeOH and H_2O), large deviations from linearity are observed. This indicates that, at low viscosities, quencher diffusion may take place faster than expected from the Stokes–Einstein law. It seems that, in this case, the relay mechanism of proton transfer along the hydrogen bond chain [35] plays an important role.

The ESPT reaction of **IIb*** in the protic solvents studied occurs via a molecule of sulphuric acid or via a solvated proton. In order to determine the nature of the quencher in fast reactions, the dependence of k_{diff} on the medium viscosity for various quenchers can be used. The calculated values of the diffusion coefficients and kinetic rate constants at $r_c = 9$ Å are given in Table 4. The values of λ_+ and η_s necessary for the calculation were taken from Refs. [35–38] and are listed in Table 4. In Fig. 3, the measured k_q values are plotted against k_{diff} evaluated for different quenchers. A satisfactory correlation is observed for k_{diff} of the solvated proton, $\gamma = 0.994$. The correlation for k_{diff} of a molecule of acid is poor, $\gamma = 0.637$. Furthermore, it can be seen from Table 4 that the values of k_i in $(CH_2OH)_2$ and H_2O are negative if the quencher of **IIb** fluorescence is assumed to be a molecule of H_2SO_4. This indicates that **IIb** fluorescence quenching is

Table 4
Diffusion coefficients of **IIb*** (D_{II}), proton (D_H) and H_2SO_4 molecule ($D_{H_2SO_4}$) and kinetic rate constants (k_{diff} and k_i) of **IIb*** interaction with H_2SO_4 in different solvents at 20 °C

Solvent	D_{II}	D_H	$D_{H_2SO_4}$	k_{diff}[a]	k_{diff}[b]	k_i[a]	k_i[b]	π^*[c]	α[c]	β[c]	η_s[d] (cP)	λ_+ ($cm^2\ \Omega^{-1}\ mol^{-1}$)
	(10^{-6} $cm^2\ s^{-1}$)			(10^9 $M^{-1}\ s^{-1}$)		(10^9 s^{-1})						
MeOH	8.88	38.90	23.60	32.40	22.10	15.30	25.60	0.60	0.93	0.62	0.545	146.2 [e]
EtOH	4.47	16.60	11.90	14.30	11.10	2.58	2.84	0.54	0.83	0.77	1.083	62.4 [f]
PrOH	2.50	11.10	6.63	9.23	6.21	2.06	2.58	0.52	0.78	0.84	1.938	41.8 [f]
i-PrOH	2.33	9.98	6.18	8.34	5.79	2.35	3.05	0.48	0.76	0.95	2.080	37.5 [f]
BuOH	1.86	9.63	4.93	7.78	4.62	1.16	1.42	0.47	0.79	0.88	2.608	36.2 [f]
s-BuOH	1.43	8.01	3.80	6.40	3.55	0.97	1.26	–	–	–	3.382	30.1 [g]
$(CH_2CH)_2$	0.29	7.37	0.77	5.20	0.73	1.42	<0	0.92	0.90	0.52	16.60	27.7 [e]
H_2O	4.84	97.90	12.80	66.40	12.00	25.70	<0	1.09	1.17	0.47	1.000	349.8 [e]

[a] For the interaction of **IIb*** with H^+; encounter complex radius, 9 Å.
[b] For the interaction of **IIb*** with H_2SO_4 molecule; encounter complex radius, 9 Å.
[c] From Ref. [23].
[d] From Ref. [38].
[e] From Ref. [35].
[f] From Ref. [36].
[g] From Ref. [37].

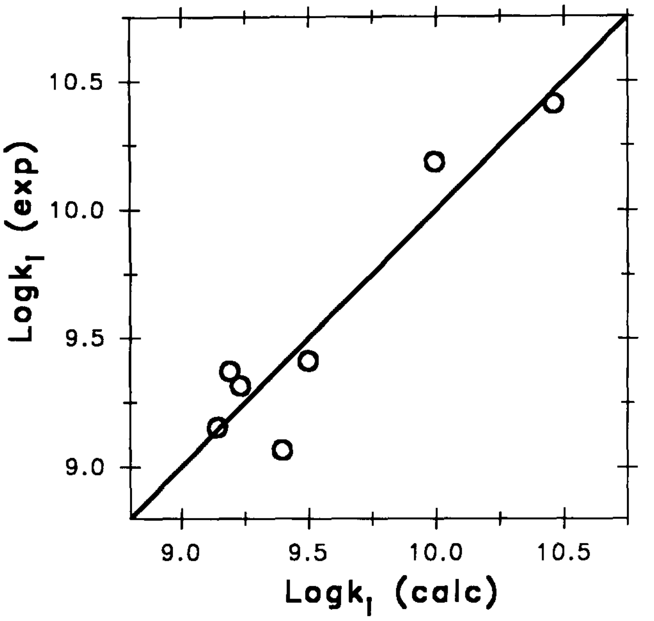
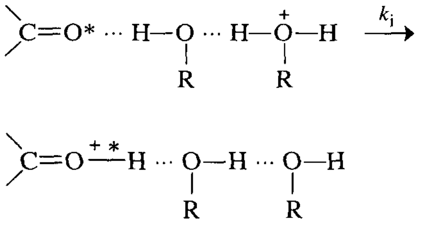


Fig. 4. Correlation between the experimental and calculated (according to Eq. (2)) log k_i values.

not caused by molecules of H_2SO_4, but by solvated protons. The deviation from the linear dependence of k_q on $1/\eta_s$ at low η_s values is attributed to the accelerated proton diffusion along the hydrogen bond chain.

The correlation between the experimental values of log k_i and similar values calculated according to Eq. (2) is given in Fig. 4. A linear correlation ($XYZ_0 = 5.48 \pm 0.78$, $s = -2.08 \pm 0.80$, $a = 6.19 \pm 1.38$, b differs insignificantly from zero, $\gamma = 0.938$) is observed. Thus the value of k_i is mainly influenced by the solvent proton-donor ability. An increase in solvent acidity results in an increase in the k_i value, but an increase in the solvent polarity and polarizability results in a decrease in the k_i value. Based on these results, it can be proposed that the activation energy of the monomolecular decay of the encounter complex between the solvated base and proton



$$>C{=}O^{*}\cdots H{-}\underset{R}{O}\cdots H{-}\overset{+}{\underset{R}{O}}{-}H \xrightarrow{k_i} >C{=}\overset{+*}{O}{-}H\cdots\underset{R}{O}{-}H\cdots\underset{R}{O}{-}H$$

is determined by two factors: (1) the energy of H–OR bond breakage; (2) the difference between the stabilization energies of the encounter complex and the transition state in the polar solvent (this energy is less for the transition state because of the greater delocalization of the positive charge). An increase in solvent acidity results in a decrease in the activation barrier of the reaction because of the first factor, but an increase in the solvent polarity results in an increase in the activation barrier of the reaction because of the second factor.

5.3.2. Effect of structure on ESPT of 7-aminocoumarins in ethanol

The wavelengths of the fluorescence maxima (λ'_f), fluorescence quantum yields of the cations $\mathbf{IIH_O}^+$ (ϕ'_∞), k_{diff} and k_q (with and without non-stationary quenching) of the coumarins and k_i for the reaction in the encounter complex with non-stationary quenching are given in Table 5. The value of ϕ'_∞ reaches 0.48. An increase in the electron-acceptor properties of the substituents in positions 9 and 10 results in a long-wavelength shift of the fluorescence spectrum and a decrease in ϕ'_∞ (compare $\mathbf{IIbH_O}^+$ with $\mathbf{IIaH_O}^+$, $\mathbf{IIeH_O}^+$ and $\mathbf{IIpH_O}^+$ for 9-substituted aminocoumarins and $\mathbf{IIbH_O}^+$ with $\mathbf{IIjH_O}^+$, $\mathbf{IIlH_O}^+$ and $\mathbf{IInH_O}^+$ for 10-substituted aminocoumarins). The maximum frequencies of the fluorescence spectra of the $\mathbf{IIH_O}^+$ cations correlate with the σ^* inductive constants of the substituents according to Eq. (1) ($a = 18\,900 \pm 150$ cm^{-1}, $b = 514 \pm 124$ cm^{-1} and $c = 136 \pm 70$ cm^{-1}; $\gamma = 0.829$). The substituent in position 9 influences the ν_f value of the $\mathbf{IIH_O}^+$ cations more than the substituent in position 10.

The introduction of an uncharged electron-acceptor substituent into positions 10 (**IIc** and **IId**) and 9 (**IIs**) results in a decrease in ϕ'_∞ and the rate constant of proton transfer k_i (see Table 5). The transition of the ESPT reaction from a diffusion to a kinetic regime is accompanied by a decrease in ϕ'_∞. The small value of ϕ'_∞ may be caused by the small value of ϕ_r and/or by the small value of ϕ'_0. The ESPT reaction of some 7-aminocoumarins (including **IIa**, **IIb** and **IIs**) on

Table 5
The wavelengths of the fluorescence spectral maxima (λ_f'), the limited fluorescence quantum yields of $\mathbf{IIH_O}^+$ (ϕ_∞') and kinetic (k_q, k_{diff} and k_i) characteristics of the ESPT reaction of 7-aminocoumarins in EtOH–H_2SO_4 at 20 °C

Coumarin	λ_f' (nm)	ϕ_∞'	k_q[a]	k_q[b]	k_{diff}	k_i (10^9 s^{-1})
			(10^9 M^{-1} s^{-1})			
$\mathbf{IIaH_O}^+$	533	0.38	5.77	4.33	14.43	3.06
$\mathbf{IIbH_O}^+$	530	0.45	4.79	3.64	14.30	2.58
$\mathbf{IIbH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIcH_O}^+$	552	0.18	2.44	1.86	13.95	1.17
$\mathbf{IIcH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIdH_O}^+$	554	0.19	1.91	1.74	14.20	1.08
$\mathbf{IIdH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIeH_O}^+$	543	0.29	5.16	3.59	14.00	2.62
$\mathbf{IIeH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIfH_O}^+$	542	0.35	12.76	10.71	14.15	24.00
$\mathbf{IIfH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIgH_O}^+$	530	0.04	5.01	3.66	14.47	2.66
$\mathbf{IIjH_O}^+$	539	0.28	2.26	1.97	42.90	–
$\mathbf{IIlH_O}^+$	541	0.24	3.25	2.81	42.93	–
$\mathbf{IInH_O}^+$	540	0.19	2.89	1.17	42.78	–
$\mathbf{IInH_O}^+$[c]	≈550	<0.01	–	–	–	–
$\mathbf{IIpH_O}^+$	567	0.12	5.56	5.03	42.95	–
$\mathbf{IIsH_O}^+$	590	0.05	2.02	1.46	13.95	0.887

[a] The error of the determination of k_q is 10%.

[b] Corrected for non-stationary fluorescence quenching; encounter complex radius set to 9 Å.

[c] In MeCN–H_2SO_4; short-wavelength excitation [11].

the carbonyl group has been studied and the reaction efficiency ϕ_r has been estimated [39]. According to Ref. [39], ϕ_r is less than unity for some systems (particularly **IIs**). Unfortunately, Ref. [39] does not give a description of the ϕ_r estimation technique in detail. Therefore, the ϕ_r values in Ref. [39] give rise to some doubt. The electrostatic field of the positively charged substituent in position 9 of the $\mathbf{II}\mathrm{H_O}^+$ cation results in a decrease in ϕ'_∞ and a fluorescence band shift to the long-wavelength region (up to 27 nm from $\mathbf{IIb}\mathrm{H_O}^+$ to $\mathbf{IIp}\mathrm{H_O}^+$). The field of the charged substituent in position 10 of the $\mathbf{II}\mathrm{H_O}^+$ cation results in a decrease in ϕ'_∞, but does not influence the spectral position of the fluorescence band (compare $\mathbf{IIf}\mathrm{H_O}^+$ and $\mathbf{IIj}\mathrm{H_O}^+$, $\mathbf{IIl}\mathrm{H_O}^+$ and $\mathbf{IIn}\mathrm{H_O}^+$).

The logarithm of the total rate constant of the proton transfer reaction and induced radiationless deactivation ($\log k_i$) correlates with the σ^* inductive Taft constants for coumarins **IIa–IIf** and **IIs**

$$\log k_i = a - b\sigma_9{}^* - c\sigma_{10}{}^*$$

The correlation parameters are $a = 8.58 \pm 0.04$, $b = 0.20 \pm 0.03$, $c = 0.18 \pm 0.02$, $\gamma = 0.977$. It is clear that the value of k_i decreases as the electron-acceptor ability of the substituent in positions 9 and 10 increases. The value of k_i for coumarins **IIj**, **IIl**, **IIn** and **IIp**, having charged substituents in positions 10 (**IIj**, **IIl**, **IIn**) and 9 (**IIp**), can be evaluated only with a large margin of error, since $k_q \approx k_{\mathrm{diff}}$.

The carbonyl group basicity changes ($\Delta \mathrm{p}K_a$) on excitation of the compounds of series **II**, calculated by the Förster cycle [40], are given in Table 5. For the majority of the compounds, $\mathrm{p}K_a$ increases by approximately 5 units on excitation. The aminocoumarin **IIg** is an exception, since in this case the $\mathrm{p}K_a$ value increases by approximately 2 units.

6. Conclusions

The ESPT reaction of 7-aminocoumarins at the carbonyl group in protic solvents proceeds by a dynamic mechanism and is an irreversible diffusion-limited process. The effect of non- stationary reagent diffusion contributes significantly (25% for **IIb** in EtOH in the presence of 0.1 M H_2SO_4) to fluorescence quenching. It was found that the quenching of 7-aminocoumarins in protic solvents is effected by solvated protons. The dependence of k_q on the solvent is determined by the limiting proton conductance in the solvent. The activation energy of monomolecular decay of the encounter complex between the solvated base and proton is determined by two factors: (1) the energy of H–OR bond breakage in the complex; (2) the difference between the stabilization energies of the encounter complex and the transition state in the polar solvent. The electrostatic field of the charged substituent in position 10 influences mainly k_d, but not k_f. This may be caused by a change in the S–T interaction. The solvent effect on k_f of **IIb** can be explained by the dependence of the Einstein coefficient A on the transition energy and, according to the Kamlet–Taft equation, is determined by the proton-donor ability of the solvent.

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