The Mechanism of the Photoprotolytic Reactions of Some Oxyazomethine Compounds

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The kinetic spectral study of the photoprotolytic reactions of oxyazomethine molecules was performed. It was established that the deprotonation reactions of oxyazomethines proceed with the participation of electronically excited molecules and are characterized by parameters which differ to basic state reactions.

Introduction

In recent years, luminescence spectroscopy has assumed a major role in analysis, particularly in the determination of trace contaminants in our environment, industries and medicine because for applicable compounds luminescence methods gives high sensitivity and high specificity. High sensitivity results from the difference in wavelength between the exciting and luminescence radiation. High specificity results from dependence on two spectra: the excitation and emission spectra. The phenomenon of fluorescence itself is subject to more rigorous constraints on molecular structure than is absorption [1-6]. This paper is concerned with new molecules with stereoelectronic parameters which possess specific chemical properties and reactivity. Main scientific interest of this work is the involvement of the excited state in the protolytic reaction which could be confirmed by the lifetime measurements.

A photoprotolytic equilibrium involving a new luminescent organic reagent should be defined by a specific equilibrium constant which permits to predict the direction and the completeness of a reaction and the mechanism of reaction. The mechanism of reactions is usually expressed in terms of a series of chemical equations which consider energy of excitation, condition of reaction and the participation of each molecul (deactivated or excited) in a reaction [1]. This study involves the spectrokinetic investigation of the mechanism of the photoprotolytic reactions of some oxyazomethine compounds.

Experimental

Reagents

Various oxyazomethine compounds as well as their derivates were synthetized. More details about the synthesis and chemical nomenclature are given in our previous paper [8,9]. In order to present the effects of the kinetic of photoprotolytic reactions, only two characteristic compound B_1 (2-oxybenzilidiene-4'-aminodifenylamine) and B_2 (2-oxybenzylidiene-4'- aminobenzanilide) were chosen and tested. The kinetic study of the photoreaction of deprotoning some luminescent reagents was performed using a nanosecond spectrometer SP-70 "Applied Photophysics" and "Ortec". By means of the single photon counting technique using an exciting flash length of 1.3 ns; the reaction rates of the processes shown in Table 1 were determined.

Table 1. Reaction rate nomenclature

Rate constant	Process description	Process reaction
Kf	-fluorescence of A	$A^\star \to A_0 + h\nu$
Kd	-radiationless transition	$A^\star \to A_0$
K_Q	-deactivation of A by Q	
K_a, K_a	-proton transfer by the excited coupled acid	$(R^\star H^\star) + H_2O \rightleftharpoons R^\star + H_3O^+$
K_a, K_a	-proton transfer by the excited acid	$ROH^\star + H_2O \rightleftharpoons (RO)^\star + H_3O^+$

The significance of the rate constant of the quenching of luminophore radiation (K_Q) by ions (H_3O^+) was approximated by the slope of the Stern-Volmer function $(I/I_0 - 1$ vs $[H_3O^+]$ or $\tau_0/\tau - 1$ vs $[H_3O^+])$, as well as the shape of the functions $1/\tau_Q - 1/\tau_R$ vs $[H_3O^+]$, according to refs [7,10], where t_Q and t_R are the fluorescence lifetimes in the absence and presence of a quencher respectively.

It was insured that $[H^+] > [R]$ by using 0.005-0.008% solutions of reagents in the photoprotolytic reactions. The rate constants for the diffusion of closer ions, $K_{diff}(dm^3 mol^{-1} s^{-1})$, with molar absorptivity, ε, were calculated according to Eq.1 [7,11].

$$K_{diff} = \frac{4n \cdot N \cdot a}{1000}(D_+ + D_-)(\frac{\delta}{e^\delta - 1}) \tag{1}$$

$$\delta = \frac{e_0^2}{\varepsilon_{act}} \cdot \left(\frac{1}{1 + \chi \cdot a}\right) \qquad \chi = \sqrt{\frac{8\pi e_0^2 NI}{1000 e KT}}$$

where: n-number of mols, a-the closest distance between ions, N- Avogadro's number, D_+, D_--diffusion coefficients of cations and liat-ions, I-the ionic strength, e_0-electron charge, K-Boltzman constant, and T-temperature; 298 K.

D_+ and D_- are the diffusion coefficients of cations and liat-ions calculated according to the Stokes-Einstein $E_q(2)$ of the diffusion of a spherical particle of radius r in a viscous medium.

$$D_a = \frac{kT}{6\pi r \eta} \tag{2}$$

where η is the viscosity of the medium.

According to some approximations the closest distance, a between ions within a complex is 0.7 nm [6]. The value, a is equal in all solvents due to the similarity of the luminophore structures. Also $a \approx 2r$;

the significance of D-for the liat-ions of H_2O, ethanol, and DMFA was also calculated from the specific electrical conductivity, while N is Avogadro's number; I the ionic strength and e^- the electron charge, k the Boltzmann constant, $T = 298K$ and the solvents (ε and η): ethanol (25.0; 1.20), DMFA (36.1; 0.796), water (81, 1), acetone (20.7 0;32) and DMSO (45.0,-).

The approximation of K_{diff} was performed according to E_q (3).[7].

$$K_{diff} = \frac{8RT}{2000\eta} \cdot A_1 \tag{3}$$

were η is the dynamic viscosity, R the universal gas constant, A_1 the coefficient taking into account the influence of interionic forces in the case of ionic interaction, $\delta/e^\delta - 1$.
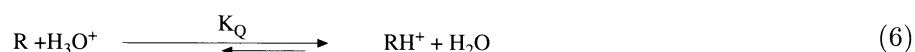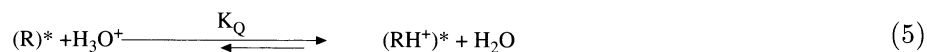
The validity of applying diffusion constants was established according to refs [7,10]. The reaction rate of the deactivation of the excited state of various forms was calculated according to E_q (4)[10].

$$\frac{1}{\tau} = K_f + K_d \tag{4}$$

where K_f and K_d are the rate constants of the radiative and radiationless deactivation of the excited states of the molecular or ionic forms; τ the fluorescence lifetime of certain forms of luminophores.

Results and Discussion

One of the main problems in the study of photoprotolytic equilibria is establishment of the mechanism of deprotonation, i.e. determining whether there is sufficient time for the protolytic equilibrium to be established before the excited state is deactivated (reaction 5) or the reaction proceeds according to a static mechanism (reaction 6).

$$(R)^* + H_3O^+ \xrightarrow{\text{K}_Q} (RH^+)^* + H_2O \tag{5}$$

$$hv_{exit}K_f \,\Updownarrow\, K_d \qquad Hv_{exit}K_f' \,\Updownarrow\, K_d'$$

$$R + H_3O^+ \xrightarrow{\text{K}_Q} RH^+ + H_2O \tag{6}$$

where E_q 5 represents a reaction involving the singlet excited molecule, while E_q 6 represents a reaction which involves the ground state.

The kintic curves of the quenching of the luminescence of various organic luminophores (OL) are presented in Fig.1 for the case of B_1 in DMSO, 60-80 vol % in H_2O and B_2 in DMFA, 60-80 vol %

On the basis of the obtained experimental data, the fluorescence lifetimes of the excited molecules were calculated at various H_3O^+ concentrations (Table 2). The decrease of the radiation lifetime with changing H_3O^+ concentration confirms the participation of the excited states of the organic luminophore molecules in the reaction.

In Figs.2 and 3 the typical Stern-Volmer curves, as well as the functions $1/\tau_Q - 1/\tau_R$ vs $[H_3O^+]$ are shown for the examples of OL B_1 and B_2. Stern-Volmer dependence (Fig.2) of the relative decrease of the radiation lifetime of the organic compounds (τ_0/τ), radiation intensity (I_0/I) and increase of $[H_3O^+]$ were experimentally tasted. The dynamic quenching mechanism was confirmed, i.e. of the participation in the reaction of acid-base mutual action of singlet excited molecules.

N	1	2	3	4	5
$[H_3O]10^{-3}$	2.11	2.60	3.34	3.99	4.90
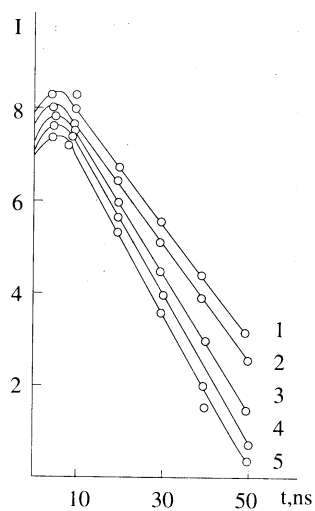
N	1	2	3	4	5
$[H_3O]10^{-3}$	2.06	2.69	3.41	4.21	5.13

(a)
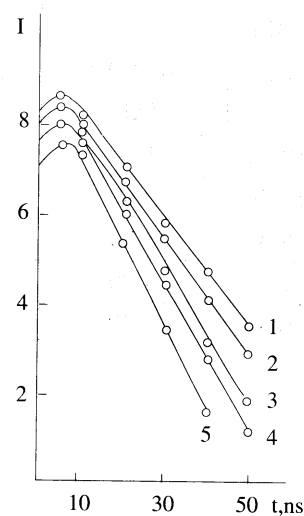
(b)

N	1	2	3	4	5
$[H_3O]10^{-3}$	2.95	4.00	5.26	6.61	8.42
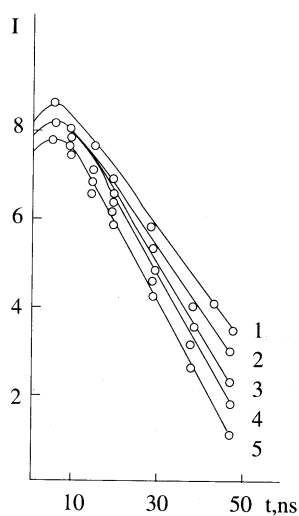
(c)

Figure 1. Quenching of luminophore luminescence, samples B_2 (a) and B_1 (b, c) in various solvents: $C_R = 5.10^{-4}$ mol/dm^3. Solvents: a) 80 vol % DMFA; b) 80 vol % DMSO; c) 20 vol % DMFA

The rate constants of bimolecular reactions of fluorescence quenching by H_3O^+ ions in various solvents are shown in Table 3. They are high and are in the range of $1.0 \times 10^{10} - 4.5 \times 10^{10}$ dm^3/mol, s for the solvents DMFA, DMSO; ethanol, acetone and H_2O.

Table 2. The dependance of the fluorescence lifetimes of the luminophores on H_3O^+ concentration, n=5, P=0,95

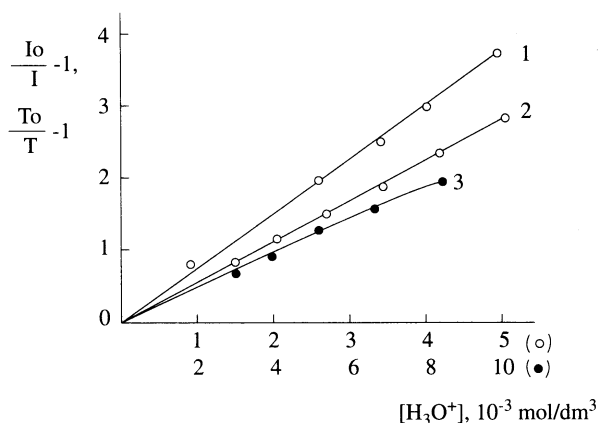| OL B_2 (DMFA)[1]		OL B_1 (DMSO)		OL B_1 (H_2O)	
Lifetime, τ (ns)	$[H_3O^+]10^{-3}$ (M)	Lifetime, τ (ns)	$[H_3O^+]10^{-3}$ (M)	Lifetime, τ (ns)	$[H_3O^+]10^{-3}$ (M)
12,11	1,91	11,93	2,06	13,55	2,95
10,50	2,60	10,49	2,69	12,29	4,00
8,48	3,34	8,52	3,41	10,41	5,26
7,59	3,99	7,76	4,21	9,36	6,61
6,40	4,99	6,66	5,13	8,24	8,42

Figure 2. The kinetic curves of the quenching of luminophore B_2 (1) and B_1 (2, 3) radiation in Stern-Volmer coordinates. $C_R = 5.10^{-4}$ M; Solvents: 1) 80 vol % DMFA; 2) 80 vol % DMSO; c) 20 vol% DMFA
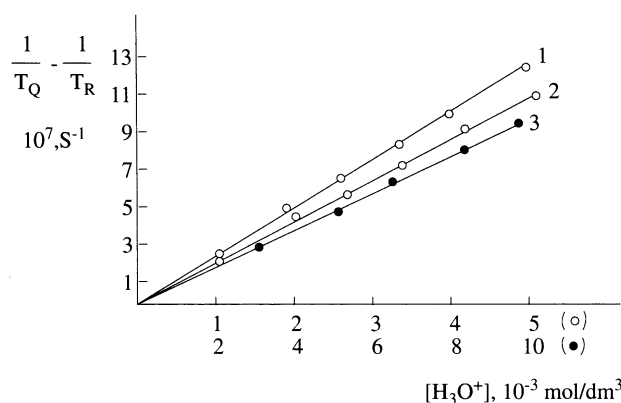
Figure 3. Determination of the rate of B_2 (1) and B_1 (2, 3) radiation quenching by $[H_3O^+]^+$ ions; $C_R = 5.10^{-4}$ M; Solvents: 1) 80 vol % DMFA; 2) 80 vol % DMSO; c) 20 vol% DMFA

These approximations are in good agreement with the values of the rate constants of the diffusion constant of the ions (K_{diff}) at 298 K calculated according to the procedure presented $(E_q 3, 5)$. This confirms a diffusion controlled type of process, the rate of which as is known changes depending on the viscosity and dielectric constant of the solvent. The low value for the Arrhenius activation energy of the quenching reaction (7-12 KJ/mol) confirms the diffusion mechanism of the process.
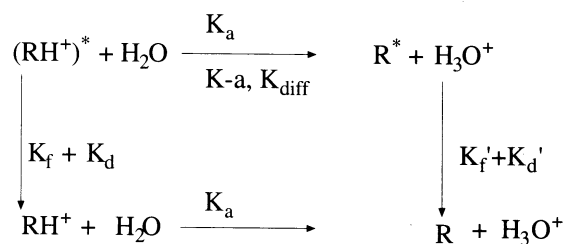
The kinetic characteristics of the deprotonation of luminophores chromophore groups ($CH =, N-, OH, CO$) determined by the Weller method, are presented in Table 4. The calculated values of the deactivation rate constants $(K_f + K_d)$ of the molecular, protonated and ionic form of various luminophores are also given.

As the results of experiments, it was concluded that;

Photoprotolytic reactions are faster than reactions of excited state deactivation

$$K_a > K_f + K_d \quad \text{and} \quad K_Q \cdot C_R > K_f + K_d$$

-The kinetic scheme of photoprotolytic reactions of electronically excited molecules of oxyazomethine luminophores can be presented in the following way:

$$(RH^+)^* + H_2O \xrightarrow[\text{K-a, K}_\text{diff}]{\text{K}_a} R^* + H_3O^+$$

$$\downarrow K_f + K_d \qquad\qquad \downarrow K_f{}' + K_d{}'$$

$$RH^+ + H_2O \xrightarrow{\text{K}_a} R + H_3O^+$$

The values for K_a and $K_f + K_d$ are $10^7 - 10^8$ and 10^7 respectively[1].

-In strongly basic solvents (DMFA, DMSO), that rate of photoprotolytic reactions are considerably increased (by 2-3 orders of magnitude) and are determined by the proton-acceptor properties of the solvent.

-Photoprotolytic equilibrium is established in an interval shorter than the fluoroscence lifetime of the molecular and inonic forms of the luminophores.

Table 3. Kinetic characteristics of diffusion controlled reactions of proton phototransfer for some luniophores in various solvents, $C_R = 0.5.10^{-3}$ mol/dm^3

Compound Solvent	Quenching rate constant $K_Q 10^{-10}$		Diffusion constant $K_{diff}.10^{-10}$ (dm^3/mol s)	Rate constant of radiation deactivation $(K_f + K_d).10^7 \pm 0.15 s^{-1}$	Arrheius reaction activation energy (kJ/mol)
(50-80 vol.%)	Stern-volmer	According to time dependence*			
	n=5,P=0.95				
B_1	2.18±0.15	2.17±0.20	2.05	3.28	8.79
B_2	2.50±0.20	2.55±0.20	2.85	3.88	10.46
B_2	1.00±0.10	0.99±0.15	1.10	4.13	12.97

* dependence $1/\tau_Q - 1/\tau_R - [H_3O]^+$

Table 4. Kinetic characteristics of photoprotolityci reactions of luminophore deprotonation in aqueus and non-aqueous solvents

Luminophore	Solvent (50-80%)	Fluorescence τ, (ns)	Lifetime, τ (ms)	Deprotonation, K_a, 10^7, m^3/mol	Rate constant, K_a, 10^{-7}, m^3/mol	Deactivation, $(K_f + K_d)_R 10^7$,	Rate constant $(K_f + K_d)_R 10^7$ (s^{-1})
B_2^*	H_2O	24.20	17.50	7.41±0.15	1.05	4.13	5.71
	DMFA	25.74	15.80	2.06 10^{-7}±0.18	2.60	3.88	6.33
	DMSO	28.95	10.50	4.70 10^{-2}±0.12	2.10	3.45	9.52
	Acetone	24.20	17.00	2.68±0.15	4.35	4.08	5.88
B_1^{**}	H_2O	29.80	35.60	3.55±0.10	1.00	3.26	3.91
	DMSO	30.45	23.70	2.70$10^2$±0.12	2.15	3.38	4.22

* deprotonation reaction $RH^+(K_a/K - a)R - H^+$

** deprotonation reaction $RCH^+(K_a/K - b)RO^- + H^+$

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