

CONCENTRATION DEPENDENCE OF PHOTOCHEMICAL TRANSFORMATIONS OF AMINOCOUMARINES

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Investigations of the luminescence spectra of liquid and frozen aminocoumarin solutions of different concentration before and after irradiation have shown that at low concentration the channels of monomer molecules photochemical transformations dominate. At high concentration photoassociates or photoconformations are formed whose degradation leads to other stable photoproducts. The concentration at which photoassociates are formed is determined by a structure of molecules.

As was noted earlier¹ one and the same additions to active media based on aminocoumarines make different effects on the lifetime of dye lasers with different pumping. This is so because photon–induced transformations in such dyes are very complicated and multichannel, and the ratio of different channel contributions depends on many parameters. In particular, the transformations taking place at different concentration of dyes can be initiated both in monomeric and associated forms of dye and result in different photodissociation products. In this paper an attempt is undertaken to relate stable products of photodissociation to a specific channel of photochemical transformations, i.e., from monomeric or associated forms based on investigation of emission spectra of freshly prepared and irradiated solutions at the temperature of liquid nitrogen 77 K.

As can be seen from spectral characteristics of the fluorescence of freshly prepared solutions (Table I), at sufficiently high concentrations in solutions the aminocoumarines can form associates of the excimer type between the excited molecules and molecules in the ground state via interaction of a carbonyl group of an excited molecule with the electro–negative center of a molecule in the ground state. At room temperature such associates break up without emission¹¹ while at 77 K they emit at longer wavelengths. In the case of frozen solutions of coumarines there appears afterglow with duration τ_a of several seconds and a spectrum λ_a close to the phosphorescence spectrum.⁹ That means that an increase of concentration leads to an increase of the output into a triplet state at aminocoumarin excitation.

These results can also be explained by increasing influence of polar surrounding (with concentration increase) on the capability of aminocoumarin molecule to form TICT or ICT conformations in polar media.² As a result the solution of the same dye at small concentrations ($\leq 10^{-3}$ mole/liter) is subjected to photochemical transformations basically in a plane monomer form, while at high concentrations this occurs through photoassociates or photoconformations stabilized by the surrounding.

TABLE I. Spectro–luminescent characteristics of aminocoumarin in liquid and frozen ethanol solutions.

Dye	Concentration, mM	293 K		77 K	
		λ_{fl}^{max} , nm	λ_{fl}^{max} , nm	λ_{tr} , nm	τ_{tr} , s
K120	0.05	435	415	no	—
K120	10	435	420	no	—
K1	1	460	435	no	—
K1	20	460	450	510	≈ 6
K1CN	1	480	515	620	≈ 3.5
K102	0.01	470	445	no	—
K102	1	470	465	570	≈ 11
K102	25	475	515	570	≈ 11
K102+DABCO	50 + 100	475	520	570	≈ 8
K102CN	0.005	490	480, 550	no	—
K102CN	0.1	490	550	600	≈ 7.5
K153	0.01	540	500	no	—
K153	1	550	520	no	—
K153	10	560	570	no	—
K2	0.05	440	425	no	—
K2	5	440	425	no	—
K2	10	440	425, 480	weak 560	≈ 7

In Ref. 3 irreversible products of photodissociations formed during an aminocoumarin are designated as Φ_1 – Φ_4 and their assumed structure is considered. Listed in Table II are the spectral characteristics of 102 (K102) coumarin photodissociation products at room temperature.

TABLE II. Spectral characteristics of luminescence of K102 photodissociation products.

Product	Φ_1	Φ_2	Φ_3	Φ_4
λ_{max}^{abs} , cm ⁻¹	28000	23000	30000	21000
λ_{max}^{abs} , nm	357	435	333	476
λ_{max}^{fl} , cm ⁻¹	22900	18870	22400	18180
λ_{max}^{fl} , nm	435	530	420	550

It should be noted that the efficiency of fluorescence of Φ_2 and Φ_4 products at room temperature is very low. In the case of frozen solutions (77 K) the fluorescence efficiency increases while being accompanied by small short-wave shifts. The values of shifts are likely to be determined by the structure of a photodissociation product differently interacting with a solvent when being in S_0 or S_1 states.

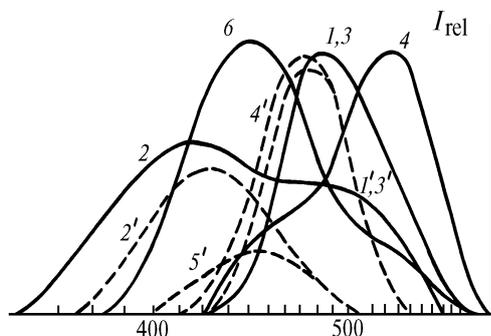


FIG. 1. Fluorescence spectra of K102 solutions at room temperature (1'–5') and 77 K (1–4, 6). $c_{K102} = 5$ (1, 1'; 2, 2'; 3, 3', and; 4, 4'), and 0.1 mmole/liter (5', 6). Addition of DABCO: 50 mmole/liter – 3, 3"; 4, 4'; 1, 1'; and 3, 3' are freshly prepared solutions; 2, 2'; 4, 4'; and 5' are the solutions irradiated by daytime light during 200 days and 6 – $35 \text{ J/cm}^3 = 900 \text{ phot/mole}$ irradiated by XeCl–laser radiation.

Figure 1 shows the fluorescence spectra of nondeoxidized K102 solutions freshly prepared and irradiated with daylight at room temperature and at 77 K. The irradiation of high-concentration solutions ($\geq 5 \cdot 10^{-3}$ mole/liter) mostly yields the Φ_3 product which at room temperature displaces the solution fluorescence spectrum to a short-wave region (curve 2', Fig. 1) as the fluorescence of the initial dye decreases. The absorption bands with the maximum at $30\,000 \text{ cm}^{-1}$ related to Φ_3 (curve 2, Fig. 2) and in the region of dye fluorescence at $23\,000 \text{ cm}^{-1}$ related to Φ_2 (curve 2', Fig. 2) are formed in the absorption spectra of the relevant solutions. In the same solutions at 77 K there are two distinct fluorescence bands: one in the long-wave region from 500 to 510 nm and the other – the fluorescence band of the Φ_3 product at the wavelength 415 nm (curve 2, Fig 1). From this it obviously follows that in these solutions the long-wave radiation at 77 K is related to the Φ_2 product which does not emit at room temperatures. The addition of diazobicyclooctane (DABCO) inhibits the photodissociation of concentrated solutions resulting in Φ_3 formation³ but stimulates the formation of a "long-wave" emitting photodissociation products. However it can be seen from Fig. 1 (curve 4) that in this case the fluorescence at 77 K is observed not at 500–510 nm but at 530–540 nm that means that it is the same as that formed at photochemical transformations of low-concentration solutions (inflection in curve 6, Fig. 1). We think that the DABCO inhibiting the channel of the transformations into Φ_2 and Φ_3 products increases, at the same time, the relative output of the Φ_4 product formed at α -cleavage of the monomer pirone ring.^{3,4}

Irradiation of solutions with 10^{-3} mole/liter concentrations by a XeCl excimer–laser radiation ($\lambda_g = 308 \text{ nm}$, $P_g \approx 70\text{--}100 \text{ MW}$, $\tau_{\text{imp}} = 20 \text{ ns}$, 2.5 Hz) results in the Φ_1 and Φ_4 photodissociation products (curve 6, Fig. 1 and curve 4, Fig. 2) while the increase of concentration to 10^{-2} mole/liter makes the formation of the Φ_3 product most efficient (curve 6, Fig. 2).

As to the mechanism of the photon-induced transformations, it was assumed³ that Φ_3 is the product of photooxidation of aminocoumarines via an aminogroup during the interaction with singlet oxygen which is generated in a solution by aminocoumarine triplets. Thus, the prevalence of Φ_3 outcome must appear due to an increase in the triplet output or concentration and the lifetime of singlet oxygen. It is well known¹¹ that the outcome of triplets in aminocoumarines at concentrations below 10^{-4} mole/liter is low and it increases due to the presence of nonplane conformations (Table I) and photoassociates.

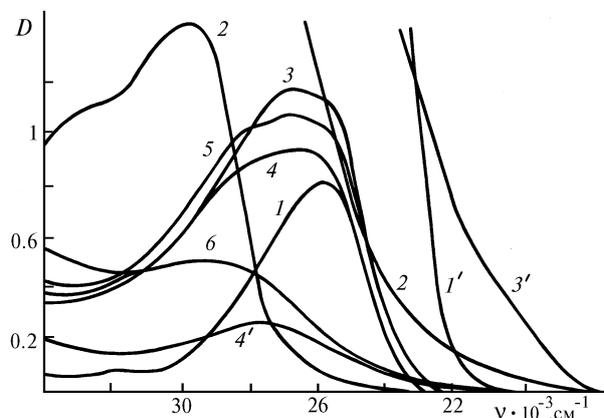


FIG. 2. Absorption spectra of K102 solutions in ethanol: 5 (1, 1'–3, 3'), 0.1 (4'), 0.5 (4, 5), and 10 mmole/liter (6). Addition of DABCO 50 mmole/liter – 3, 3'; 5; 1, 1' are freshly prepared solutions; 2, 2', 3, and 3' are the solutions irradiated by daytime light during 200 days, 4 and 5 are the solutions irradiated by daytime light during 8 days. 4') $20 \text{ J/cm}^3 = 520 \text{ phot/mole}$ irradiated by XeCl–laser radiation, and 6) $2000 \text{ J/cm}^3 = 520 \text{ phot/mole}$ of irradiated by XeCl–laser radiation. $l = 1$ (1–4), $l = 0.025$ (1, 6), and $l = 0.1 \text{ cm}$ (2–5). D is the optical depth, ν is the frequency of incident light.

We assume that the structure of photoassociates is similar to the structure of photocations formed in the S_1 state in solvents having free protons. The formation of K102 photocation as an intermediate product^{1,8} is considered here as the formation of photoassociates similar in structure to a photocation which is a particular case of a photoassociate in a solvent with free protons. The formation of photodissociation products of irreversible decomposition of such photocations which have absorption maxima at $30\,000$ and $23\,000 \text{ cm}^{-1}$ slows down¹ when substituting the oxygen dissolved by argon because oxygen takes part in the formation of these products. Moreover, it is shown in Ref. 5 that photocation fluorescence is quenched in deoxidized media, i.e., the structure of a photocation and, hence, of a photoassociate is stabilized with the dissolved oxygen. The fact that oxygen contributes to stabilization of

photoassociates of aminocoumarines is indirectly confirmed by an increase of the lasing efficiency of concentrated K102 solutions (10^{-2} mole/liter) from 10 % in air to 27 % after solution deoxidation.⁸ Thus it is our belief that the Φ_2 and Φ_3 photochemical dissociation products are formed via photoassociates interaction with the dissolved oxygen. The component DABCO, which is known as a quencher of triplets⁶ and of singlet oxygen,⁷ may inhibit the formation of Φ_2 and Φ_3 in concentrated solutions (Figs. 1 and 2) through reduction of triplet outcome since the DABCO decreases the lifetime of afterglow which we attribute to the dye triplet's glow. When concentration of the initial dye ($5 \cdot 10^{-4}$ mole/s) decreases the DABCO affects only weakly the aminocoumarine photodecomposition¹ and the Φ_1 product with the fluorescence maximum at 435–440 nm (curves 5' and 6, Fig. 1) and absorption at $28\,000\text{ cm}^{-1}$ (curves 4, 4', and 5, Fig. 2) is formed. As to Φ_2 (this is a product of oxidation of coumarine in the 3rd position³), it is formed irrespective of Φ_3 since Φ_3 concentration continues to increase with the increasing the time of irradiation while the concentration of Φ_2 decreases that is observed both from the absorption and fluorescence.

The Φ_1 and Φ_4 products are obviously formed during photodecomposition of monomeric molecules since they dominate in photochemical transformations in low concentration solutions (curve 6, Fig. 1).

The probability of forming photoassociates or photoconformations for dyes with CN-group in the 3rd position is much higher than that for unsubstituted molecules (i.e., they are formed at lower concentrations than in the case of corresponding unsubstituted aminocoumarines). Since the Φ_2 outcome is hampered due to the substitution of the 3rd position,³ the resulting photochemical products emit at temperature of 77 K in a short-wave region (Fig. 3).

Thus the use of fluorescence of frozen solutions of aminocoumarines when increasing the concentration enabled us to detect association or formation of photoconformations of these dyes in the excited states that create photochemical transformation channels which compete with the monomeric ones. This explains the favorable action of the DABCO as an inhibitor of photochemical transformations of associates during laser pumping of active media in which concentrations above $5 \cdot 10^{-3}$ mole/liter are used as well as the absence of such an effect under pumping of the same dyes with a flash lamp when the concentrations below $5 \cdot 10^{-4}$ are usually used.^{1,10} This same fact also explains the absence of the DABCO effect on the photochemical stability of K2 and K120 dyes during laser excitation since

these dyes do not form photoassociates at concentrations below 10^{-2} mole/liter.

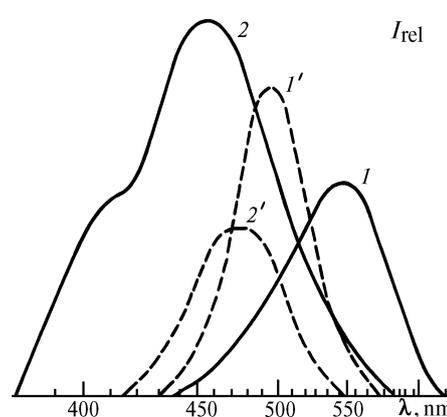


FIG. 3. Fluorescence spectra of K102CN dissolved at room temperature (1' and 2') and 77 K (1 and 2) in ethanol. $c_{\text{K102CN}} = 0.1\text{ mM/l}$; 1, 1' are freshly prepared solutions and 2, 2' are $84\text{ J/cm}^2 = 2184\text{ phot/mol}$ solutions irradiated by XeCl laser.

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