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Photolysis of Aminoanthraquinones in Matrices

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Abstract—The efficiency of photolysis of aminoanthraquinones in cellulose and cellulose-like matrices depends not only on the chemical nature of the substrate but also on the energy of the excitation radiation and reaction conditions; the latter factors govern the mechanism of photochemical degradation of aminoanthraquinones: reductive (under the action of a labile hydrogen atom of the medium at a carbinol carbon atom) or oxidative (under the action of generated singlet oxygen).

As found in [1–5], the efficiency of photochemical degradation of some dyes in solutions, on fabrics, or in polymers is governed not only by the nature (chemical structure) of the dye but also by the energy of the quanta absorbed by the dye and the properties of the medium (physicochemical and chemical characteristics of the matrix, atmosphere, humidity, etc.). The mechanism of photochemical degradation largely depends on all these factors.

In this work we studied photolysis of a series of amine-containing anthraquinones, which are ready forms of dyes or their precursors, in oxygen or in an inert atmosphere with the aim to reveal the mechanism and determine the efficiency of their photochemical degradation.

As photochemically active substrates we chose 1-amino- (**I**), 2-amino- (**II**), 1,8-diamino- (**III**), 1-amino-4-hydroxy- (**IV**), 1,4-diamino- (**V**), 1,5-diamino- (**VI**), 1,2-diamino- (**VII**), 2,6-diamino- (**VIII**), 1,4,5,8-tetraamino- (**IX**), and 1,4-diamino-2-methoxyanthraquinones (**X**).

The matrices were a cotton fabric (43% cotton and 57% linen) preliminarily bleached chemically and subjected to no other actions (optical bleaching etc.) (system A) and a polyvinyl alcohol film (system B); polyvinyl alcohol is a fairly adequate chemical model of cellulose, as it is a macromolecular compound with hydroxy groups at secondary and tertiary carbon atoms. To compare the luminescence-spectral properties of aminoanthraquinones **I**–**X** in solutions and in matrices A and B, we chose as solvent 2-propanol (system C), which also simulates cellulose in the same parameters (except high molecular weight and the presence of primary hydroxy groups).

Aminoanthraquinones **I**–**X** exhibit in the visible range not only absorption but also fluorescence (Table 1). Previous study [6] of photolysis of **I**, **III**, and **V** in the liquid phase (2-propanol–water, 1 : 1) chemically simulating cellulose matrices revealed formation of no intermediate and final products absorbing at wavelengths above 400 nm and interfering with evaluation of the absorption, excitation, and emission of the substrate.

In view of the above facts, the photochemical degradation of dyes **I**–**X** in matrices could be monitored by electronic absorption or reflection spectroscopy, or by luminescence spectroscopy using approximate correlations of the aminoanthraquinone concentration in a matrix or solution c with the fluorescence intensity, $I_{\mathrm{fl}} \approx a \log c$ (see, e.g., [7]), or with the characteristic fading time t_F, $t_F \approx Bc$ [6], where a and B are coefficients.

Data on the efficiency of photochemical degradation in matrices could be compared to the corresponding data for solutions, since variations of the spectra in the systems A–C suggest a weak effect of environment on the microlevel on the absorption, reflection, and fluorescence spectra of aminoanthraquinones **I**–**X** (Table 1). We revealed no regular trends in variation of the spectral characteristics of the compounds in hand in going from one system to another.

To minimize the effect of photolysis products of aminoanthraquinones **I**–**X**, solvent, and matrices on the efficiency and mechanism of photochemical degradation of aminoanthraquinones **I**–**X**, we studied the kinetics of photochemical degradation at substrate conversions not exceeding 20%, as in [6, 7]. Preliminary experiments showed that luminescence spectros-

Table 1. Fluorescence spectra and long-wave absorption and reflection maxima of aminoanthraquinones **I**–**X**[a]

Comp. no.	λ^{fl}_{max}, nm			λ^{abs}_{max}, nm		λ^{refl}_{max}, nm	
	A	B	C	A	B	A	B
I	640	634	628	483	480	480	484
II	635	629	640	460	452	463	454
III	642	641	638	508	606	498	502
IV	632	629	635	562	568	570	565
V	643	651	658	588	592	595	596
VI	612	608	610	484	487	483	491
VII	644	638	640	530	527	532	530
VIII	659	668	668	424	422	425	428
IX	682	690	688	608	608	610	606
X	621	618	621	545	541	547	543

[a] For designation of the systems, see text.

copy gives insufficiently reliable results, since the combination of extremely low fluorescence intensity (Φ_{fl} 10^{-3}–10^{-2}) of compounds **I**–**X** [8] with a low degree of their conversion results in significant errors in monitoring the variation of the intensity of the substrate emission in the course of photolysis. Therefore, the reaction progress was monitored by the electronic absorption or reflection spectroscopy.

The most adequate criterion of the reactivity and performance of substrates in the electronically excited state is the quantum efficiency of the process φ (in the case of the monochromatic radiation); however, its measurement in the matrix, as compared to solution, involves a number of difficult problems [9]; therefore, in this study we restricted our consideration to determination of t_F. Often the quantity t_F, varying in inverse proportion with the rate constant of photochemical degradation, is used with indication of the admissible level of the dye fading [1]; in this work we used $t_{F,0.2}$. The variation of the absorption was measured in the reflection minimum of colored samples, corresponding to the maximum of the longest-wave absorption band of the substrate in the visible range. Irradiation was performed in the following ranges: UV + visible ($\lambda_{exc} \geq 240$ nm), UV ($240 \leq \lambda_{exc} \leq 400$ nm), near-UV ($300 \leq \lambda_{exc} \leq 440$ nm), and visible ($\lambda_{exc} \geq 400$ nm).

However, it is incorrect to make any conclusions about the real efficiency of photochemical degradation and spectral sensitivity of the photochemical process on the basis of the $t_{F,0.2}$ values. The reason is that at monochromatic and polychromatic irradiation of colored samples t_F is always a latent function of *f* and of the number of absorbed quanta of the photochemically active light (*I*); if the substrate absorption in a matrix is significant, t_F is also a function of its concentration. In the general form, this dependence can be expressed as $1/t_{F,0.2} = (\varphi I)/C$ (*C* is the proportionality coefficient necessarily including in the latent form the substrate concentration) [6]. Determination of φ directly from this relation is difficult because of indefinite value of *C*.

Therefore, taking into account that *c* is constant (i.e., equal to the initial concentration c_0 insofar as at low conversions its variation is negilible) and hence for each of the studied aminoanthraquinones **I**–**X** in matrices *C* is also practically constant, in further consideration we used the quantity β proportional to φ; $\beta = 1/(t_{F,0.2}\gamma)$, where γ is the fraction of light absorbed by the substrate in the definite spectral range.

In determination of γ, we initially used the relative intensity of the light fluxes calculated from the emission spectra of xenon lamps [1, 4] and transmission spectra of the color filters used; we found that the calculated relative intensity of the light fluxes practically coincided with the experimentally determined value (in this work, we used the averaged results). Then, for each of the matrices dyed with aminoanthraquinones **I**–**X** we calculated the quantity γ taking into account the spectral distribution of the radiation transmitted by the given color filter and the absorption of the substrate in the range of color filter transmission, assuming that the spectral characteristics of the substrate in the matrices and solution are similar.

As seen from Table 2, the quantities β are similar for photolysis of the same substrate in systems A and B, which shows once again that photochemical processes in cellulose matrices can be modeled by those in polyvinyl alcohol.

The determined values of β show that the efficiency of photochemical degradation of aminoanthraquinones **I**–**X** is determined by their structure, although no definite conclusions can be made on the influence of the position and number of amino and other functional groups in the anthraquinone core. At the same time, we found that the process efficiency largely depends on the conditions (excitation range and surrounding atmosphere). For example, in an inert atmosphere singlet oxygen $^1O_2$ cannot be generated by the substrate in the T^1_{CT} state [10]. In this case, only photochemical degradation of the substrate occurs, based on the initial photoreduction to the T^1_{n,π^*} state by hydrogen abstraction from the tertiary carbinol group of the matrix or solvent molecule (λ_{max} corresponding to the n,π^* transition lies in the range 400–

Table 2. Quantities β in photolysis of aminoanthraquinones **I**–**X** in matrices in air[a]

Comp. no.	$\lambda_{exc} \geq 240$ nm		$240 \leq \lambda_{exc} \leq 400$ nm		$300 \leq \lambda_{exc} \leq 440$ nm		$\lambda_{exc} \geq 400$ nm	
	A	B	A	B	A	B	A	B
I	0.56 (0.61, 0.54)	0.57 (0.62, 0.53)	0.56 (0.63, 0.57)	0.61 (0.60, 0.56)	0.60 (0.62, 0.54)	0.63 (0.68, 0.56)	0.16 (0.61, 0.09)	0.14 (0.59, 0.08)
II	0.32 (0.34, 0.27)	0.33 (0.35, 0.26)	0.34 (0.36, 0.28)	0.35 (0.37, 0.27)	0.33 (0.37, 0.29)	0.32 (0.38, 0.30)	0.08 (0.42, 0.05)	0.08 (0.41, 0.05)
III	0.29 (0.27, 0.23)	0.26 (0.28, 0.23)	0.27 (0.26, 0.23)	0.27 (0.28, 0.25)	0.26 (0.28, 0.24)	0.28 (0.25, 0.21)	0.05 (0.32, 0.04)	0.05 (0.30, 0.03)
IV	0.28 (0.30, 0.23)	0.27 (0.29, 0.25)	0.26 (0.27, 0.23)	0.28 (0.26, 0.23)	0.28 (0.28, 0.25)	0.29 (0.27, 0.25)	0.06 (0.34, 0.03)	0.07 (0.37, 0.02)
V	0.36 (0.45, 0.39)	0.37 (0.47, 0.37)	0.35 (0.45, 0.38)	0.35 (0.45, 0.37)	0.36 (0.41, 0.35)	0.37 (0.42, 0.34)	0.09 (0.49, 0.06)	0.10 (0.48, 0.06)
VI	0.41 (0.51, 0.41)	0.42 (0.52, 0.42)	0.44 (0.58, 0.40)	0.42 (0.58, 0.43)	0.49 (0.53, 0.41)	0.47 (0.58, 0.38)	0.12 (0.58, 0.07)	0.13 (0.56, 0.05)
VII	0.42 (0.49, 0.37)	0.40 (0.50, 0.37)	0.38 (0.49, 0.38)	0.40 (0.51, 0.36)	0.42 (0.50, 0.34)	0.44 (0.49, 0.36)	0.10 (0.51, 0.05)	0.12 (0.52, 0.05)
VIII	0.43 (0.58, 0.51)	0.44 (0.54, 0.48)	0.41 (0.61, 0.49)	0.40 (0.60, 0.45)	0.43 (0.59, 0.45)	0.41 (0.62, 0.40)	0.15 (0.60, 0.08)	0.15 (0.62, 0.07)
IX	0.41 (0.50, 0.36)	0.40 (0.51, 0.38)	0.39 (0.51, 0.34)	0.39 (0.50, 0.33)	0.41 (0.49, 0.35)	0.38 (0.50, 0.34)	0.11 (0.53, 0.05)	0.12 (0.52, 0.04)
X	0.53 (0.62, 0.51)	0.52 (0.60, 0.52)	0.54 (0.59, 0.50)	0.55 (0.60, 0.55)	0.52 (0.61, 0.53)	0.53 (0.59, 0.51)	0.15 (0.58, 0.09)	0.14 (0.59, 0.08)

[a] For designations of matrices, see text. In parentheses, the first figure refers to photolysis in oxygen, and the second figure, to photolysis in an inert atmosphere (argon).

410 nm [11]). Then the arising radicals (anthrasemiquinones) or anthrahydroquinones undergo subsequent dark or photochemical processes (deamination, transformation or elimination of other functional groups, degradation of the anthraquinone or anthracene core). This is the reductive pathway of photochemical degradation of aminoanthraquinones. On the contrary, in oxygen the photochemical degradation of aminoanthraquinones follows the oxidative pathway: The dye in the T^1_{CT} state generates active $^1O_2$, which induces oxidative deamination and oxidative cleavage of the anthraquinone core (for the charge-transfer band, $\lambda_{max} > 420$ nm [11]). In air, both pathways of photochemical degradation of aminoanthraquinones can be realized, depending on the intensity and spectrum of the radiation.

This reasoning is confirmed by data in Table 2. Indeed, in both systems A and B, when photolysis is performed in an inert atmosphere, for all the examined excitation ranges except $\lambda_{exc} > 400$ nm the values of β are approximately equal for each substrate, because the efficiency of the interconversion $S^n_{\pi,\pi^*} \rightsquigarrow T^1_{n,\pi^*}$ is close to unity (the latter state is responsible for reduction of the anthraquinone core), and drastically decrease in going to the range $\lambda_{exc} > 400$ nm in which the T^1_{n,π^*} state practically is not occupied. At the same time, in oxygen the values of β for each aminoanthraquinone **I**–**X** are also practically equal in all the examined excitation ranges, because the interconversion S^n_{π,π^*} $(S^1_{n,\pi^*}) \rightsquigarrow T^1_{CT}$ (the latter state is responsible for generation of $^1O_2$) occurs with the probability very close to unity [10]. The order of activities of aminoanthraquinones in oxidative photochemical degradation (**III**, **IV** < **II** < **V** < **VII**, **IX** < **VI** < **VIII** < **X** < **I**) does not coincide with the order of the relative rates of their reactions with chemically generated $^1O_2$ (**I** < **V** < **X** < **III** < **IX** < **II**, **VI** < **VIII** < **IV** < **VII**) [10]. However, here we should take into account a complex relationship between the quantum efficiency of photochemical generation of $^1O_2$ (increase in the $^1O_2$ yield: **II**, **IV** < **V** < **VII** < **VIII**, **X** < **IX** < **I** < **II** < **VI** [10]) and decomposition of aminoanthraquinones **I**–**X** under the action of the forming $^1O_2$ (increase in the activity in degradation: **I** < **V** < **X** < **III** < **IX** < **II**, **VI** < **VIII** < **IV** < **VII** [10]).

Apparently, the quantum efficiency of oxidative photochemical degradation of aminoanthraquinones **I**–**X** is higher than that of their reductive degradation (cf. the values of β for each of aminoanthraquinones **I**–**X** in oxygen and in an inert atmosphere, Table 2).

Under ambient conditions (air, prevalence of the visible light in the spectral composition of the natural and especially artificial light), the oxidative pathway can become prevalent.

EXPERIMENTAL

The electronic absorption spectra of solutions were taken on an SF-46 spectrophotometer, and the reflection spectra of dyed samples of fabric and polyvinyl alcohol films (in the latter case, on an alumina support with the degree of reflection no less than 97%), on an SF-18 spectrophotometer. The fluorescence spectra were taken at 25°C with a Neva-3 spectrofluorimeter (λ_{exc} 436 or 544 nm).

As substrates (aminoanthraquinones **I**–**X**) we used samples submitted by the Central Laboratory of the Rubezhnoe Chemical Plant (Ukraine); all these samples were additionally purified by recrystallization from appropriate solvents and by column chromatography using as support silica gel KSK or alumina (activity grade II) and appropriate eluents. The purity of the samples was proved by TLC on alumina or Silicagel-UV plates using several eluents. Polyvinyl alcohol, ethanol, and 2-propanol were of chemically pure grade.

The fabric was dyed with aminoanthraquinones **I**–**X** by applying them in solutions. Films of polyvinyl alcohol with aminoanthraquinones **I**–**X** were prepared by casting at a molar ratio water : polyvinyl alcohol : aminoanthraquinone 1 : 1 : 1 (ethanol was added to increase the solubility of aminoanthraquinone).

The dyed matrices were irradiated under similar conditions in a UIS-1 unit equipped with two DPKs-1500 xenon lamps. The polychromatic ranges of the excitation light were cut with color filters UFS-1 ($240 \leq l_{exc} \leq 400$ nm), FS-7 ($300 \leq \lambda_{exc} \leq 440$ nm), ZhS-3 ($\lambda_{exc} \geq 400$ nm), and BS-1 ($\lambda_{exc} \geq 240$ nm). Prior to irradiation, the matrices were placed in screwed metallic cells with quartz windows 40 mm in diameter. Hollow metallic shells of the cells were equipped with four sleeves: two for temperature control with running water (25 ± 5°C) and two for bubbling of air, oxygen, or argon.

The intensities of light fluxes were measured with an LK-2 quantometer. The relative intensity of the light fluxes measured by this procedure was 0.11, 0.16, 0.87, and 1.00 for the UFS-1, FS-7, ZhS-3, and BS-1 color filters, respectively (published data [4]: 0.13, 0.14, 0.80, and 1.00, respectively). In this work we used the mean values: 0.12, 0.15, 0.83, and 1.00, respectively.

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