Russian Journal of General Chemistry, Vol. 72, No. 7, 2002, pp. 1104–1106. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 7, 2002, pp. 1180–1183.

Photodegradation of Aminoanthraquinones and Dyes Derived from Them in the Presence of Complexones

R. P. Ponomareva, O. P. Studzinskii, and L. M. Borisova

Mechnikov State Medical Academy, St. Petersburg, Russia

St. Petersburg State Trade and Economic Institute, St. Petersburg, Russia

Received December 27, 2001

Abstract—Photodegradation of model aminoanthraquinones and dyes derived from them was studied. Addition of organic complexones having carboxy or phosphinoyl groups to substrate solutions which simulate cellulose or to colored cellulose-containing fabrics accelerates photobleaching of the dyes.

An essential disadvantage of all synthetic dyes is their bleaching on the surface of colored samples due to photoinduced degradation. Various attempts were made to stabilize dyes to the action of light. Most frequently, some photostabilizing substances are added to the dyeing mixture or to samples that are to be dyed [1]. Such additives suppress the photodegradation process usually following two mechanisms: they act as either UV absorbers (it is quite probable that this process involves reabsorption in the near UV and visible regions) or quenchers of reactive electronically excited states of dyes (which are thus converted into inactive singlet ground state) [2, 3]. The photostabilizing effect depends on a number of factors, and its magnitude is not always so large as desired. Therefore, the problem of searching for new potential light stabilizers remains significant and important for finishing processes of textile and light industries.

We previously obtained encouraging results in photostabilization of luminescent dyes (optical bleaching agents) by organic complexones having carboxy and phosphinoyl groups [4]. Assuming that the mechanism of photodegradation of optical bleaching agents [5] is more or less analogous to photoinitiated bleaching of anthraquinone dyes [6], we made an attempt to elucidate the effect of such complexones on the photoinduced decomposition of widely used anthraquinone dyes in liquid systems (solutions) and matrices.

As model compounds we selected the simplest aminoanthraquinones: 1-aminoanthraquinone (**I**), 2-aminoanthraquinone (**II**), 1,4-diaminoanthraquinone (**III**), 1,4-diamino-2-methoxyanthraquinone (**IV**), and 1,5-diaminoanthraquinone (**V**) (Table 1). The dyes to be examined were Red 2B (**VI**), Rose Y (**VII**), Violet 2B (**VIII**), Orange p/e (**IX**), and Yellow 6G (**X**) (Table 2). Nitrilotris(methylphosphonic acid) (**XI**), hydroxyethylidenediphosphonic acid (**XII**), iminodiacetic acid (**XIII**), and diethylenetriaminepentaacetic acid (**XIV**) were used as complexones.

The model reaction medium was a 1:1 water–2-propanol mixture (by volume) whose components simulate structural units of cellulose materials (2-propanol) and atmospheric moisture (water) in photo-

Table 1. Photodegradation of aminoanthraquinones **I**–**V** in model solutions (2-propanol–water) in the presence of complexones **X**–**XIV**

Dye (λ_{max}^{abs}, nm, $\varepsilon \times 10^{-3}$)	Complexone	λ_{max}^{abs}, nm	$\Delta D/\Delta D_0$
I	**XI**	480	1.16
(483, 6.2)	**XII**	480	1.23
	XIII	483	1.44
II	**XI**	453	1.30
(456, 6.4)	**XII**	455	1.00
	XIII	453	1.12
	IX	456	0.93
III	**XI**	594	6.43
(598, 25.4)	**XII**	593	1.72
	XIII	597	1.66
	XIV	596	3.48
IV	**XI**	571	1.86
(573, 22.0)	**XII**	570	0.61
	XIII	574	1.20
	XIV	576	2.04
V	**XI**	486	1.08
(492, 10.2)	**XII**	488	0.17
	XIII	489	0.40
	XIV	487	1.41

chemical processes (Table 1). In all cases, the concentration of complexones in solutions of aminoanthraquinones **I**–**V** was 1 g l^{-1}. The solutions were irradiated with UV light (254 nm ≤ λ_{excit} ≤ 400 nm). The photodegradation kinetics was monitored spectrophotometrically: relative change of the optical density $\Delta D/\Delta D_0$ at the long-wave absorption maximum of the substrate was measured at equal time intervals for each aminoanthraquinone **I**–**V**; here, ΔD and ΔD_0 are the changes in the optical density in the absence and in the presence of complexone, respectively.

The long-wave absorption band of aminoanthraquinones **I**–**V** corresponds to the charge-transfer state, and its position remains almost unchanged on addition of complexones to a concentration given above (Table 1). By special experiments we showed that photodegradation products do not absorb in the region above 400 nm. In our experiments, the conversion of aminoanthraquinones **I**–**V** did not exceed 15%, so that the photodegradation products could not affect in one or another way the efficiency of bleaching of the substrate.

The results of model experiments are collected in Table 1. As follows from the $\Delta D/\Delta D_0$ values, in all cases complexones **XI**–**XIV** accelerate photobleaching of aminoanthraquinones **I**–**V**. Probably, a catalytic effect of acid group (phosphonic or carboxylic) is observed [7–9], which is lacking in photostabilization of optical bleaching agents by the same complexones due to a different photodegradation mechanism. The stabilizing effect was found only for acid **XII** toward aminoanthraquinones **IV** and **V**.

Taking into account that solid matrices often give rise to effects differing from those observed in solutions, we examined photodegradation of aminoanthraquinone dyes applied to fabrics, i.e., under conditions close to usage. Samples of a semiflax fabric consisting of 57% flax, 40% cotton, and 3% Dacron were dyed with compounds **VI**–**X** with addition of complexones **XI**–**XIV** (which were added to solutions of dyes **VI**–**X** to a concentration of 0.5 g l^{-1}).

The dyed samples were treated in a setup simulating exposure to sunlight. In this case, the photodegradation kinetics was monitored by electronic spectroscopy on the basis of electronic reflection spectra at the minimum of the long-wave absorption band in the visible region. We determined the relative changes in the optical density at the most long-wave reflection minimum during irradiation for equal time intervals: $\alpha = \Delta D/D$ and $\alpha_0 = \Delta D_0/D_0$ (ΔD and ΔD_0 are the changes in the optical density during irradiation, and D and D_0 are the optical densities of nonirradiated samples; ΔD and D values refer to samples treated with complexones, and ΔD_0 and D_0, to those which were not treated with complexones); this parameter varies in the opposite direction to the lightfastness. Below are given dye no. and $\lambda_{\text{min}}^{\text{refl}}$, nm: **VI**, 540; **VII**, 520; **VIII**, 580; **IX**, 470; **X**, 460. Within the experimental error ($\lambda \pm 5$ nm, $D \pm 0.05$), addition of complexones to the dyeing solution caused no detectable changes in the position of the absorption minima and optical density of the dyed sample at a given wavelength.

Table 2. Photolysis of dyes **VI**–**X** applied to cellulose-containing fabrics in the presence of complexones **XI**–**XIV**

Dye	Complexone	α_0	α	$(\alpha - \alpha_0)/\alpha$, %
VI	**XI**	0.06	0.06	0
	XII	0.06	0.08	+33
	XIII	0.06	0.08	+33
	XIV	0.06	0.07	+17
VII	**XI**	0.03	0.12	+300
	XII	0.03	0.03	0
	XIII	0.03	0.04	+33
	XIV	0.03	0.05	+67
VIII	**XI**	0.09	0.11	+22
	XII	0.09	0.08	–11
	XIII	0.09	0.09	0
	XIV	0.09	0.08	–11
IX	**XI**	0.03	0.06	+100
	XII	0.03	0.07	+133
	XIII	0.03	0.01	–67
	XIV	0.03	0.06	+100
X	**XI**	0.03	0.07	+133
	XII	0.03	0.03	0
	XIII	0.03	0.03	0
	XIV	0.03	0.09	+200

Provided that the degree of photobleaching of dyes **VI**–**X** was no more than 15%, products of photodegradation of the fabric, dye, and complexone **XI**–**XIV** should not affect the results of kinetic monitoring (we showed in [10] that photodegradation products of dyes **VI**–**X** do not absorb in the visible region). Therefore, the quantity $[(\alpha - \alpha_0)/\alpha_0] \times 100$, %, may be regarded as a parameter characterizing the effect of added complexone **XI**–**XIV** on the rate of photodegradation of dyes **VI**–**X**; its positive values indicate acceleration of photodegradation, and negative values correspond to its inhibition.

The results are summarized in Table 2. It is clearly seen that the sign and magnitude of the complexone effect on photodegradation of dyes strongly depend on the nature of both the dye and the complexone. Nevertheless, a general tendency toward photodegradation acceleration in the presence of complexones is observed (dyes **VII**, **IX**, and **X**); only in a few cases, a weak inhibition of photodegradation was revealed (**VIII** and **IX**).

The data obtained for solutions and fiber matrices are consistent. We can thus conclude that organic complexones having carboxy and phosphono groups act as photostabilizers for various optical bleaching agents; however, neither in solution nor on fiber they exert photostabilizing effect on aminoanthraquinones and dyes derived from them. The different effects of the examined complexones on optical bleaching agents and anthraquinone dyes may be interpreted in terms of different photodegradation mechanisms of these compounds.

EXPERIMENTAL

The electronic absorption and reflection spectra were measured, respectively, on SF-46 (1-cm glass cell) and SF-18 instruments (aluminum oxide support with a reflection coefficient of no less than 97% was used).

The solvents were double-distilled water and 2-propanol of chemically pure grade which was not subjected to additional purification. Aminoanthraquinones **I**–**V** and dyes **VI**–**X** were supplied by the central laboratory at the Rubezhnoe Chemical Industrial Complex (Ukraine); the substrates were additionally purified by recrystallization from appropriate solvents, followed by column chromatography on KSK silica gel or alumina of Brockmann activity grade II. Their purity was checked by TLC on UV-sensitized Silufol plates or on plates with a fixed layer of alumina (Brockmann activity grade II).

Aminoanthraquinones **I**–**V** were dissolved in 2-propanol–water (1 : 1, by volume) to a concentration at which the optical density at the long-wave absorption maximum (visible region) was no larger than 1.2; the concentration of complexones **XI**–**XIV** was 1 g l^{-1}. Fabric samples dyed with compounds **VI**–**X** (57% flax, 40% cotton, and 3% Dacron) were prepared by keeping the dyed sample in an aqueous solution of complexone **XI**–**XIV** at 45°C for 20 min.

Model solutions of aminoanthraquinones **I**–**V** were subjected to photolysis in a 12-ml rectangular quartz cell (layer thickness 1 cm) which was maintained at 20 ± 1°C under continuous stirring. The solutions were irradiated with the aid of an Ul’trakhemiskop instrument equipped with two BUV-15 low-pressure mercury lamps and a UFS-1 glass light filter. For each aminoanthraquinone **I**–**V**, the distance to the light source in a series of experiments was maintained constant, and in all cases the conversion did not exceed 15%.

Samples of dyed fabrics were irradiated under similar conditions using a UIS-1 setup for speed testing for lightfastness, which was equipped with two DPKs-1500 high-pressure xenon lamps simulating sunlight; samples were maintained at 22 ± 2°C. In all cases, the change in the optical density at analytical wavelength did not exceed 15%.

REFERENCES

1. Krichevskii, G. and Gombkete, Ya., *Svetostoikost’ okrashennykh tekstil’nykh izdelii* (Lightfastness of Colored Textiles), Moscow: Legkaya Industriya, 1975.
2. *The Chemistry of Synthetic Dyes,* Venkataraman, K., Ed., New York: Academic, 1971, vol. 4. Translated under the title *Khimiya sinteticheskikh krasitelei*, Leningrad: Khimiya, 1975, vol. 4, p. 363.
3. Barltrop, J.A. and Coyle, J.D., *Excited States in Organic Chemistry,* London: Wiley, 1975.
4. Studzinskii, O.P., Dyatlova, N.M., and Makashev, Yu.A., *Zh. Prikl. Khim.*, 1981, vol. 54, no. 8, p. 1823.
5. Turro, N.J., *Molecular Photochemistry,* New York: W.A. Benjamin, 1965.
6. Calvert, J.G. and Pitts, J.N., Jr., *Photochemistry*, New York: Wiley, 1966.
7. Studzinskii, O.P., Grebenkina, V.M., and Ponomareva, R.P., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 1984, vol. 27, no. 7, p. 799.
8. Ponomareva, R.P. and Studzinskii, O.P., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 5, p. 809.
9. Ponomareva, R.P. and Studzinskii, O.P., *Zh. Obshch. Khim.*, 2001, vol. 71, no. 10, p. 1704.
10. Studzinskii, O.P., Grebenkina, V.M., and Proskuryakova, T.V., *Zh. Org. Khim.*, 1987, vol. 23, no. 4, p. 845.