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THE EFFECTS OF FLUORESCENT SUBSTANCES ON THE PHOTOFADING OF COLOURS. PART 4—PHOTOCHEMICAL INTERACTION BETWEEN FLUORESCENT BRIGHTENING AGENT OF A PYRAZOLINE TYPE AND 1,4-DIAMINOANTHRAQUINONE†

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SUMMARY

The catalytic fading of 1,4-diaminoanthraquinone by a fluorescent agent of a pyrazoline type was demonstrated on irradiation with 366 nm light in aerobic acetonitrile solution. The quenching study with a singlet oxygen quencher and the chromatographic analysis of the photoproducts revealed a singlet oxygen intermediate. The fluorescent agent generated singlet oxygen in cellulose acetate films as well, causing a small amount of enhanced fading of the dye. No acceleration of the fading was observed either in ethanol or in nylon films. On 253 nm light irradiation the dye and the fluorescent agent suppressed each other's fading.

1. INTRODUCTION

Recently there has been a great deal of interest in the increased photofading (catalytic fading) in dye mixtures. Asquith and Ingham have isolated an active impurity which caused catalytic fading of an azo dye mixture in nylon, wool and aqueous solution.[1] We have reported the acceleration of the photofading of triphenylmethane dyes[2] and azo dyes[3,4] by fluorescent brighteners in methanol and in aqueous solutions, in which triplet energy transfer from the brighteners to the dye was involved. Rembold and Kramer have described the role of a singlet oxygen intermediate in the catalytic fading of azo dyes by anthraquinonoid dyes in ethylcellulose films.[5]

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† Parts 1, 2 and 3 of this paper appear in references 3, 2 and 4 respectively.

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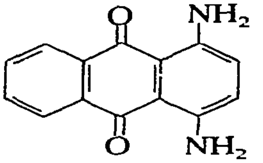
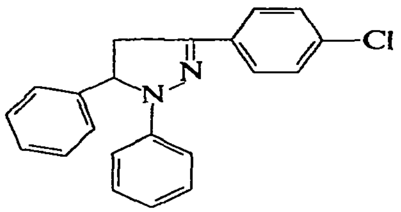
In this study we have investigated the photofading of a typical anthraquinonoid dye: 1,4-diaminoanthraquinone (DAAQ) in the presence of a fluorescent brightener: 1,5-diphenyl-3-(*p*-chlorophenyl)-Δ^2-pyrazoline (F_w).



DAAQ



F_w

DAAQ was expected to show a different photochemical behaviour from those of azo or triphenylmethane dyes, because the ability of the triplet state of the former compound to cause degradation is much higher than that of the latter.

2. EXPERIMENTAL

2.1. *Materials*

DAAQ (CI Disperse Violet 1) was supplied by the Nihon Kayaku Co. Ltd, and purified by column chromatography. The preparation of F_w has been described elsewhere.[2] The other compounds used were all commercially available and recrystallised before use. Methanol, ethanol, acetonitrile and *N,N*-dimethylformamide were purified by standard procedures.

2.2. *Polymer films*

(a) *Nylon:* Nylon was supplied by the Kojin Co. Ltd as an undrawn 6-nylon film (100 μm thick) which was washed by immersing in boiling methanol for 3 h and dyed with ethanol solutions of DAAQ and F_w. The absorbances at the absorption maxima were 0·29 and 0·25 for DAAQ and F_w, respectively.

(b) *Cellulose acetate:* The *N,N*-dimethylformamide solution containing 8×10^{-4} mol litre^{-1} of DAAQ and 100 g litre^{-1} of cellulose acetate, which was purchased from Wako Pure Chemical Ind. Ltd, was spread on a glass plate to dry *in vacuo* at 40°C for 5 h. The polymer film was removed from the plate and dried *in vacuo* at 40°C for another 20 h. The thickness was 30 μm. The films containing an equimolar amount of F_w as well as 20 molar amount of 1,4-diazabicyclo[2.2.2]octane (DABCO) were prepared in a similar manner.

2.3. *Photofading reaction*

Air saturated acetonitrile or ethanol solutions of DAAQ (2×10^{-5} mol litre)$^{-1}$ contained in 1 cm quartz cells were mounted on a revolving stand and irradiated at 22–24°C with a 6 W low pressure mercury lamp (lamp A), or with a 100 W high pressure mercury lamp with a combined filter of Pyrex and Cation X solution[6] (lamp B). Lamps A and B emitted mainly 253 and 366 nm light, respectively. The spectral changes were recorded at regular intervals using a Shimadzu UV 200 spectrometer and a Hitachi 101 spectrophotometer. The DAAQ was also irradiated in the presence of an equimolar amount of F_w. In order to see the effect of the dissolved oxygen, some of the sample solutions were degassed by the technique of freeze–pump–thaw cycles with liquid nitrogen, and irradiated in a similar manner. The polymer films were irradiated by fixing them on the front side of quartz cells.

2.4. *Determination of the triplet energy of F_w*

(a) *Sensitisation of* F_w *by triplet sensitisers:* F_w in an aerobic acetonitrile or ethanol solution (2×10^{-5} mol litre^{-1}) was irradiated in the presence of an equimolar amount of biacetyl or fluorenone with lamp B. The fading rate was measured as described above.

(b) *Sensitisation of trans-α-methylstilbene by* F_w*:* According to the method of Lamola and Hammond,[7] a solution of F_w (5×10^{-3} mol litre^{-1}) and *trans*-α-methylstilbene (2×10^{-2} mol litre^{-1}) in degassed benzene was exposed to 334 nm light emitted by a 100 W high pressure mercury lamp through a combined filter of naphthalene–benzene, aqueous nickel(II) sulphate and aqueous cobalt (II) sulphate–potassium chromium(III) sulphate. The isomerisation of the *trans*-olefine to the *cis*-one was investigated by ultraviolet spectroscopy as well as by gas chromatography.

2.5. *Identification of the photoproducts*

An acetonitrile solution of DAAQ (10^{-4} mol litre^{-1}) and F_w (3×10^{-4} mol litre^{-1}) was irradiated with internal lamp B for 2 h. After removing the solvent the reaction mixture was analysed by silica gel thin layer chromatography (t.l.c.) with benzene : ethyl acetate (in a 3 : 1 ratio) as eluent. The spots, other than visible and fluorescent ones, were detected by exposing the t.l.c. plate to iodine vapour. T.l.c. analysis was also undertaken with the DAAQ solution exposed to lamp A. Furthermore a mixture of DAAQ and methylene blue (both in 10^{-4} mol litre^{-1}) in acetonitrile was irradiated with a set of tungsten lamps to analyse the products by t.l.c.

3. RESULTS AND DISCUSSION

3.1. *Acetonitrile solution*

Figure 1 shows the ultraviolet and visible spectrum of DAAQ together with the absorption and fluorescence spectra of F_w. The dye–fluorescent agent mixture gave a spectrum whose absorbance corresponded to the sum of the components, implying that there is a minimal amount of ground state interaction between them.

Irradiation with lamp B for 1 h caused little fading of DAAQ either in the aerobic or anaerobic solution. F_w did not decay in the anaerobic solution but in the aerobic solution it decayed to an extent of 90%, yielding 1,5-diphenyl-3-(*p*-chlorophenyl)pyrazole as in the case of the photoreaction in methanol.[2] When irradiated together with the fluorescent agent, the dye faded dramatically in aerobic solution. It is noteworthy that this catalytic fading did not take place in the degassed solution.

At the initial stage of the reaction, decreases in the absorbances at the longest wavelength maxima of both DAAQ and F_w obeyed good first order kinetics. The rate constants k of the photoreactions are summarised in Table 1 together with the ultraviolet screening factors I/I_0, where I and I_0 denote the light absorbed by the components in the presence and absence of their counterparts, respectively.[2] The rate constant of the photofading of F_w was reduced by a factor of 0·29 when mixed with DAAQ. This factor (k/k_0) is far below the value of 0·996 estimated assuming that the reduction of the rate was

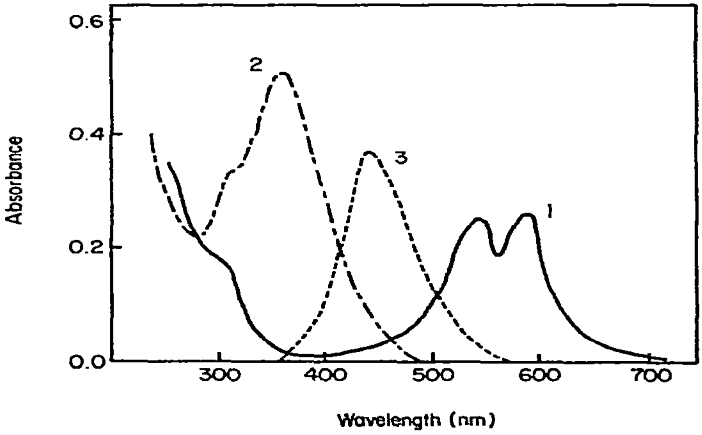


Fig. 1. Absorption spectra of DAAQ (1) and F_w (2), and the fluorescence spectrum of F_w (3) in acetonitrile. Concentration, 2×10^{-5} mol litre^{-1}; the fluorescence spectrum gives relative intensity.

TABLE 1
RATE CONSTANT AND LIGHT ABSORPTION IN ACETONITRILE

Compound	*Lamp*	k_0 (min^{-1})	k (min^{-1})	k/k_0	I/I_0
DAAQ	B	0·0000	0·0043	∞	0·261
DAAQ	A	0·0078	0·0058	0·74	0·740
F_w	B	0·037	0·010	0·29	0·996
F_w	A	0·022	0·087	0·40	0·563

k and I denote, respectively, the rate constant and quanta of light absorbed by DAAQ in the presence of F_w and those by F_w in the presence of DAAQ. k_0 and I_0 are the values of k and I of DAAQ alone or F_w alone, respectively.

Concentration: 2×10^{-5} mol litre^{-1}; aerobic solution.

derived only from the ultraviolet screening by DAAQ. Evidently DAAQ quenched the photofading of F_w.

Irradiation with the shorter wavelength light using lamp A induced the fading of both DAAQ and F_w. As shown in Table 1, the dye and the fluorescent agent suppressed each other's fading. The factor k/k_0 of DAAQ matches closely the light screening factor of F_w, whereas the effect of DAAQ on the fading of F_w is composed of light screening (73%) and quenching (27%).

The catalytic fading induced by fluorescent agents on azo and triphenylmethane dyes has been ascribed to triplet energy transfer from the fluorescent agents to the dyes.[2–4] The quenching effect of DAAQ on the photofading of F_w indicates that the triplet of F_w derived from 365 nm excitation can transfer its energy to DAAQ to raise it to the first triplet which is in turn related to the visible region absorption band. This energy transfer does not appear to be responsible for the catalytic fading of DAAQ by F_w, since the dye did not fade on the irradiation at wavelengths in the visible spectrum range but at those shorter than 300 nm. In fact, the photoreaction of DAAQ in anaerobic alcohols occurs on irradiation at the 280 nm band, involving a triplet process with a triplet energy E_T of 62–68 kcal mol^{-1}.[8] A comparison of the absorption spectrum of F_w with that of DAAQ suggests that the lowest triplet of the former compound is lower in energy than the second triplet of the latter one. The triplet energy E_T of F_w was determined with sensitisers; that is, an equimolar amount of biacetyl (E_T 55 kcal mol^{-1},[9]) sensitized the fading of F_w increasing the rate by a factor of more than 30, whereas fluorenone (E_T 53 kcal mol^{-1},[9]) left the photoreaction unchanged. F_w itself sensitised the *cis–trans* isomerisation of *trans*-α-methylstilbene (E_T 50 kcal mol^{-1},[7]). Hence E_T of F_w was estimated to be 53–55 kcal mol^{-1}, evidently too low to sensitise the degradation of DAAQ.

Recently many researchers have suggested the involvement of singlet oxygen in the photofading of dyes.[5,10] We examined here the effect of a singlet oxygen quencher DABCO on the interaction between DAAQ and F_w. Figure 2

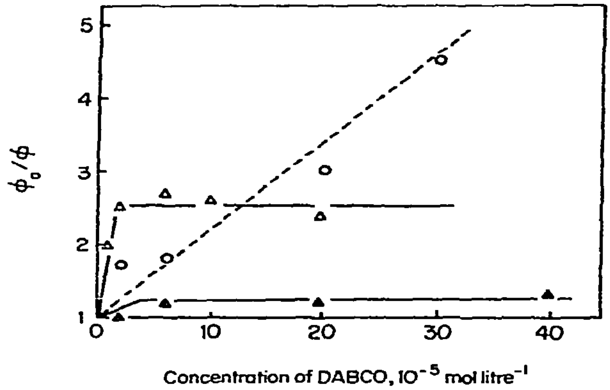


Fig. 2. Stern–Volmer plots for DABCO quenching of photofading reaction of DAAQ and F_w on 366 nm irradiation in aerobic acetonitrile. Concentrations of DAAQ and F_w, 2×10^{-5} mol litre^{-1}. ○ DAAQ, in the presence of F_w; △ F_w; ▲ F_w, in the presence of DAAQ.

exhibits a plot of ϕ_0/ϕ against the concentration of the quencher, where ϕ_0 and ϕ denote, respectively, the quantum yield for the fading reaction in the absence and presence of the quencher; ϕ_0/ϕ was deduced from the rate ratio. This Stern–Volmer plot indicates that there is effective quenching of the photoreaction of the dye, revealing that the reaction is due to oxidation by singlet oxygen. The fading of F_w was also quenched by DABCO with ϕ_0/ϕ reaching a maximum of 2·5, implying that the reaction is composed of a singlet oxygen process of 60% and simple singlet and triplet energy transfer processes of 40%. Similarly a singlet oxygen process was suggested to be responsible for 18% of the fading of F_w in the presence of an equimolar amount of DAAQ.

These observations lead to the following mechanistic scheme for the interaction between the dye (D) and the fluorescent agent (F):

$$F \xrightarrow{h\nu} {}^1F^*$$

$${}^1F^* \rightarrow {}^3F^*$$

$${}^3F^* + {}^3O_2 \rightarrow F + {}^1O_2$$

$${}^1F^* \text{ or } {}^3F^* \xrightarrow{{}^3O_2} F_{prod}$$

$$F + {}^1O_2 \rightarrow F_{prod}$$

$$D + {}^1O_2 \rightarrow D_{prod}$$

That is, F in the triplet state (${}^3F^*$) sensitises ground sate oxygen (${}^3O_2$) to yield singlet oxygen (${}^1O_2$) which in turn oxidises D to give the product (D_{prod}); the photoproduct of F (F_{prod}) is formed by the oxidation of F by $^1O_2$ as well as by the oxidation of F in the excited states ($^1F^*$ and $^3F^*$) by ground state oxygen.

The photofading interaction was further investigated by analysing the photoproducts by t.l.c. When irradiated with lamp B in the presence of F_w, DAAQ yielded photoproducts with a reddish spot at R_f of 0·54 (product I) and a colourless one at R_f of 0·83 (product II). The same compounds were produced from DAAQ on irradiation in acetonitrile with a set of tungsten lamps in the presence of methylene blue, a well-known singlet oxygen sensitiser, thus confirming the above mentioned mechanism for the interaction between DAAQ and F_w. Product I showed an absorption spectrum with a maximum at 525 nm in acetonitrile, which resembled that of one of the photoproducts of 1,4-bis(methylamino)anthraquinone (CI Disperse Blue 14) on cellulose acetate[11] and poly(ethylene terephthalate).[12] Couper has identified this compound as 1,4-diiminoanthraquinone.[11] Irradiation of the aerobic solution of DAAQ with lamp A also afforded I and II together with a yellow compound (R_f 0·40) and a red one (R_f 0·02). In this case the reaction to give I and II may involve a singlet oxygen intermediate which was formed through sensitisation by the dye in the triplet state. Otherwise they may be derived from the direct oxidation of the dye in the excited state by ground state oxygen.

3.2. *Ethanol solution*

Table 2 shows the result of the fading reaction in aerobic ethanol. The photodegradation of F_w caused by 366 nm light in aerobic ethanol was in part quenched by DABCO, indicating the involvement of singlet oxygen in the reaction. However irradiation with the same light resulted in little fading of DAAQ either in the presence or in the absence of the fluorescent agent. Even

TABLE 2
RELATIVE FADING (%) OF DAAQ AND F_w

Compound	*Additive*	EtOH		*Nylon*		*Cellulose acetate*	
		A	B	A	B	A	B
DAAQ	none	2·0	0	53	0	12	0·0
DAAQ	F_w	2·6	0	38	0	6·7	2·0
DAAQ	F_w+DABCO	—	—	—	—	—	0·0
F_w	none	15	66	46	62	54	27
F_w	DAAQ	7·5	54	15	38	30	16
F_w	DABCO	—	61	—	—	—	18

A and B denote lamps A and B, respectively.
Irradiation time: 1 h (EtOH), 6 h (nylon) and 5 h (cellulose acetate).
Concentration in EtOH: 2×10^{-5} mol litre^{-1} (DAAQ and F_w) and 4×10^{-4} mol litre^{-1} (DABCO); for concentration in polymers see Section 2.3.

if singlet oxygen is formed in this solvent, it seems not to attack the dye, perhaps because of its shorter life-time (12 μs) than that in acetonitrile (30 μs).[13] On 253 nm irradiation in aerobic solution DAAQ faded very slowly in marked contrast to the rapid decay in degassed solution, in which solvent addition reaction takes place.[8] Anthraquinone compounds are often photochemically reduced to yield semiquinone radicals which are in aerobic condition quickly reoxidised to recover the starting compounds. This redox cycle retards their apparent decay.[14] The photofading of F_w on exposure to both 366 and 253 nm light was suppressed by DAAQ in a similar manner as in acetonitrile solution.

3.3. *Polymer films*

From a practical point of view the interaction between the fluorescent agent and the dye was investigated in nylon and cellulose acetate films. On irradiation with lamp B, slightly accelerated fading of DAAQ by F_w was observed in the cellulose acetate film as shown in Table 2. Rembold and Kramer have reported the fading of azo dyes induced by singlet oxygen in ethylcellulose films.[5] Likewise, singlet oxygen appears to be produced in the present cellulose acetate film as evidenced by the quenching of the fading of F_w by DABCO. It is open to question why DAAQ acquires such a marked resistance in the film toward singlet oxygen in contrast to the azo dyes.

In the nylon film no catalytic fading of the dye was observed at all. In the film the detection of singlet oxygen was unsuccessful because of the difficulty in applying DABCO to the film treated with the dye or the fluorescent agent. Even if the fluorescent agent produced singlet oxygen, the polymer matrix would consume it to protect the dye from degradation.

Irradiation with lamp A gave rise to fading of both DAAQ and F_w in nylon as well as in cellulose acetate. The dye and the fluorescent agent suppressed each other's fading as was found in acetonitrile solution.

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