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The photostability of some fluorescent disperse dyes derivatives of coumarin

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Abstract

The photochemical behaviour (in UV and visible light) of C.I. Disperse Yellow 232 and related heterocyclic compounds in ethanol, DMF and ethyl benzoate in the presence or absence of air was investigated. The lightfastness of the dyes on synthetic fibres was studied in relation to their photostability in the solvents. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fluorescent dyes suitable for application to synthetic fibres are used especially when aesthetic or functional reasons are required. Since the end of 1960s coumarins represent one of the most investigated and commercially important groups of such dyes [1]. Widely used examples of such dyes are disperse dyes which contain in the 7-position of the coumarin ring an electron releasing group such as *N*,*N*-diethylamino group and in the 3-position, a heterocyclic electron-acceptor residue. The present study concerns disperse dyes of structure shown in Fig. 1 which yield greenish-yellow shades of excellent brilliance. Commercial dyes of this group whose structures have been disclosed in the Colour Index are dye **V** (C.I. Disperse Yellow 82: X = NH, R = H) and dye **II** (C.I. Disperse Yellow 232: X = O, R = Cl). The latter is reported to have much good fastness to light, sublimation and washing on polyester [2]. Derivatives of coumarin generally show good photostability which is rather unusual among fluorescent dyes.

The photofading behaviour of some simple coumarins and related compounds in solution and on nylon and polyester films has been previously studied [3–5]. However, the photostability of dyes of the above general structure has not been investigated so far with the exception of some brief information connected with dye **II** [5].

A key objective of the present study was to compare the lightstability of compounds **I–V**. In the first step of this investigation, the photodegradation quantum yield ϕ of the dyes in ethanol, *N*,*N*-dimethylformamide (DMF) and ethyl benzoate solutions was determined. Dyeings on polyamide and polyether fibres were also produced

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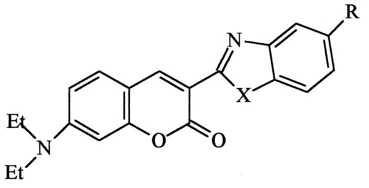
and the photofading of the dyeings assessed. Irradiation was conducted under both aerobic and anaerobic conditions, limiting the extent of photolysis to 15–25% so as to minimise the secondary degradation process.

2. Experimental

Dyes **I–V** used in this investigation were synthesised according to the methods described in the patent literature [6–8] and were purified by recrystallisation. The purity of the final dyes was checked by TLC. Dye solutions ($2.4 \cdot 10^{-5}$ mol/l) in ethanol, DMF and ethyl benzoate housed in a quartz vessel were faded in a Rayonett photolytic reactor RPR-200 equipped with eight 300 nm lamps. Anaerobic and aerobic conditions were achieved by bubbling dry nitrogen or air respectively into the solution for 30 min before irradiation. The extent of fading was determined according to the decrease in absorption at $\lambda_{\max}$ of the dye. Since the dye solutions obeyed the Lambert–Beer law, the concentration of the remaining dye was determined spectrophotometrically. Visible spectra were recorded on Perkin Elmer Lambda 40 spectrophotometer. The intensity of the photolysis lamps was determined using uranyl oxalate actinometry [9] the actinometer having been prepared by treating a solution of uranyl sulphate with excess oxalic acid and, when placed in the quartz vessel, irradiating with UV light. The decrease in oxalate concentration during photolysis was measured on the basis of the difference in the amount of potassium permanganate (in the presence of sulfuric acid) used in the titration of equivalent amounts used in the illuminated and unilluminated actinometer. The number of quanta per s absorbed by the system was calculated from the amount of oxalate molecules decomposed from the established quantum yields of the decomposition of oxalate molecules per quantum absorbed ($\Phi_{300} = 0.57$). The quantum yield of dye fading was calculated from the number of dye molecules decomposed and the number of quanta absorbed over the same time. The ϕ values were estimated on the base at least three determinations (Table 1).

Dyeings (0.25% omf) of dyes **I–V** on polyamide and polyester fabrics were carried out to determine light fastness. Light fastness was measured on a Hanau Xenotest apparatus according to Polish Standards which correspond to British Standards [10]. FAB spectra were recorded on a Finingan



I X=O, R=H **II** X=O, R=Cl **III** X=O, R=CH_3

IV X=S, R=H

V X=NH, R=H

Fig. 1.

Table 1
Photodegradation quantum yields Φ and light fastness of dyes **I–V**

Dye	Light fastness		Photodegradation quantum yield ϕ		
	Polyamide	Polyester	Ethanol	DMF[c]	Ethyl benzoate[c]
I	4	4	5.10×10^{-5}[a]	7.35×10^{-5}	29.40×10^{-5}
II	4	5–6	6.10×10^{-5}[b]	7.00×10^{-5}	16.40×10^{-5}
III	4	4–5	4.40×10^{-5}[b]	7.00×10^{-5}	17.28×10^{-5}
IV	4	4–5	4.90×10^{-5}[a]	14.00×10^{-5}	10.00×10^{-5}
V	3–4	3–4	42.50×10^{-5}[a]	10.20×10^{-5}	12.30×10^{-5}

[a] Photolysis extent: 25%.

[b] Photolysis extent: 15%.

[c] Photolysis extent: 20%.

Table 2
E_{LUMO} and heat of radical anion formation for dyes **I**, **IV** and **V**

Dye	E_{LUMO}	Heat of radical anion formation (kcal/mol)
I	−1.2493[a] −1.3060[b]	−64.4648[a] −56.4871[b]
IV	−1.1299[a] −1.2545[b]	−63.8535[a] −56.7553[b]
V	−1.2393[a] −1.2075[b]	−61.6219[a] −53.5740[b]

[a] MNDO.
[b] AM1.

Table 3
Effect of coumarins **I**–**V** and TPC degradation after 6 h irradiation with Xenotest light

Dye	Fading of dye (%)		TPC fading
	No additive	DABCO	
I	0	0	Strong
II	0	0	Complete
III	4.0	4.0	Strong
IV	10.20	1.86	Complete
V	17.30	5.50	Moderate

Mat MAT 94 spectrometer in 3-nitrobenzyl alcohol in positive mode.

2.1. Photo-oxidation of dyes I–V

Ten millilitres of ethanolic solutions of dyes **I**–**V** (concentration: 2.4×10^{-5} mol/l) were sealed in quartz tubes under air. After 6 h irradiation in the Xenotest, the concentration of the remaining dyes was analysed spectrophotometrically. The irradiation of solutions (10 ml) was repeated in the presence of 1,4-diazobicyclo[2.2.2]-octane (DABCO, 1 mg) under the same conditions (Table 3).

2.2. Photo-oxidation of tetraphenylcyclopentadienone (TPC) sensitised by dyes I–V

Ten millilitres of ethanolic solutions of dyes **I**–**V** (concentration: 2.4×10^{-5} mol/l) containing TPC (2 mg) were sealed in quartz tubes under the air. After 6 h irradiation with the Xenotest, the disappearance of TPC was observed (Table 3). When a control solution containing only TPC was irradiated simultaneously the concentration of TPC was not reduced.

3. Results and discussion

The results for the photodegradation of dyes **I**–**V** in DMF, ethanol and ethyl benzoate solutions at 300 nm under anaerobic conditions are given in Table 1.

It is clear that in EtOH and DMF comparable dyes photodegradation quantum yields were achieved for the five dyes used; only dye **V** shoved exceptionally low photostability ($\Phi=42.50\times10^{-5}$) in EtOH. With this exception, the degradation of the coumarins was somewhat enhanced in DMF but retarded in alcohol. Additional investigations under aerobic conditions showed that the photostability of examined dyes strongly depends on the presence of air. For dyes **I**–**III** after 2 h irradiation in EtOH only 6–8% degradation was achieved, whereas in the presence of nitrogen, 18–25% destruction occurred within 60–90 min. The highest photostability under aerobic conditions in EtOH was given by **IV** and **V** (contrary to the results obtained under nitrogen), showing after 2 h photolysis nil and 2% degradation, respectively. Similar results were obtained for photolysis experiments conducted in DMF. All dyes showed only 2–7% degradation after 1 h irradiation in the presence of air, whereas 35–70 min irradiation in the presence of nitrogen caused some 20% destruction.

The results of photolysis in ethyl benzoate are less consistent with the results obtained in DMF or ethanol. In this particular medium, the photodegradation quantum yield was slightly higher in comparison with the other two solvents and the order of photostability was also different. However, the presence of air strongly limited the extent of degradation of the dyes. All dyes when irradiated in ethyl benzoate under a nitrogen atmosphere incurred some 15–27% degradation, whereas the presence of air minimised this to 6–8% after 30–60 min irradiation. The data are not sufficient to present the precise mechanism of the destruction of dyes **I–V** but the inhibiting effect of air for each of solvents used suggests a reductive process, possibly of the lactone moiety. Similar results have previously been reported in the literature [11]. An attempt was made to isolate and define the structure of the major photolysis products of **I–V** conducted in ethanol. It is noteworthy to mention that the composition of the photodegradation products in other solvents was the same. We focused on three dyes namely **I**, **IV** and **V**. After photolysis under nitrogen, independently of the starting dye structure, among the many degradation products, two major identical materials were found (TLC, R_F). For dyes **I** and **IV** these degradation products were analysed by FAB spectrometry which revealed that the dyes degraded in a similar way, probably via abstraction of the heterocyclic residue possibly via a reductive process; it is possible that dealkylation also occurred. These conclusions were drawn from the following observations:

- the presence of peaks characterised by m/z 550.9 and 577.8 in FAB spectra of the two major degradation products of both dyes **I** (M.W. = 334) and **IV** (M.W. = 350.4) which contained different heterocyclic rings;
- the absence of these two degradation products in EtOH in the case of dye **IV** in the presence of air (they existed however in a lesser amounts in the other solvents used);
- a decrease in the amount of photodegradation products (m/z 550.9 and 577.8) of dye **I** in each used solvent during photolysis conducted in the presence of air;
- a difference of the molecular mass of the two major degradation products corresponds to the loss of an ethyl group.

According to the estimated light fastness and the degradation quantum yields of the examined dyes in both EtOH and DMF (Table 1) we can conclude that alcohol is slightly better than DMF as a model solvent for the prediction of the photostability of these dyes on polyamide. The moderate light fastness on polyamide fibre is more consistent with the order of their degradation in ethanol than in DMF. Although the photodegradation of the dyes in both alcohol and DMF generated the same products, the two solvents may possibly differ in the mechanism of their reduction; two possible photoreduction ways might be considered. The excited dye molecule may participate in hydrogen abstraction or in electron transfer from the environment, followed by protonation of the radical anion formed. During photolysis, while both ethanol and DMF could undergo hydrogen abstraction, according to the literature, this process dominates, especially under 300 nm irradiation [12]. Alternatively, using the AM1 and MNDO calculation we found that the investigated dyes have relatively high electron affinity (Table 2), so the chance of electron transfer is possible.

It seems that the first step of the photodestruction in alcohol is electron transfer from the solvent to the excited molecule of the dye, followed by protonation. The influence of DMF can be more complex and two possible processes should be considered. DMF may participate in electron transfer to the photoexcited dye molecule and/or be a donor of hydrogen. The observed light fastness of dyes **I–V** on polyamide is then more consistent with the photostability in alcohol, since polyamide is predominantly an electron donating environment [13].

The next step of this study was to examine the photolytic behaviour of dyes **I–V** in alcohol under the influence of visible light in the presence of air. It is well known that coumarins produce singlet oxygen and that their photodegradation is accelerated by singlet oxygen sensitizers (Methylene Blue) and is hindered by singlet oxygen quenchers (β-carotene). The ethanolic solutions of dyes **I–V** were illuminated without light filtering in Xenotest for 6 h. Three sets of experiments were run using solutions that comprised:

- the dye alone;
- the dye with DABCO (${}^1O^*_2$ quencher);
- the dye with TPC (${}^1O^*_2$ scavenger).

The results of these experiments are presented in Table 3.

It is evident that each of the coumarins produce singlet oxygen under the influence of visible light. A compound that is particularly suitable for the detection of singlet oxygen is tetraphenylcyclopentadienone (TPC) because, purple TPC oxidizes in singlet oxygen presence to the colourless α,α′-cis dibenzoylstilbene. An alternative method of proving the intermediacy of singlet oxygen in the photodegradation of coumarins was to use the singlet oxygen quencher DABCO. Table 3 shows that the addition of DABCO strongly retarded the oxidation of coumarins, especially **IV** and **V**.

The results obtained show that the lowest photostability in the presence of air was displayed by dye **V**, which is consistent with its low photostability on polyester fibre.

Acknowledgements

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