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Photofading of Diethylaminoazobenzene Dyes on Polyester Film and in Ethyl Acetate Solvent. Part I: Luminescence, Derivative Spectroscopy and Flash Photolysis Studies

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SUMMARY

The photofading of 4′-methoxy-2′-nitro-N,N-diethylaminoazobenzene is examined on polyester film and in ethyl acetate solvent. On the basis of the products, it is shown that the fading occurs via N-dealkylation and photoreduction pathways. Luminescence, flash-photolysis and derivative spectroscopy studies of some disperse azo dyes derived from 4-N,N-diethylaminoazobenzene support the hypothesis of the formation of a complex between the diethylamino group and the ester function in the ground state.

1. INTRODUCTION

The photofading of azobenzene derivatives in solution occurs through reduction at the azo-group.[1] In only one case,[2] in which the fading of

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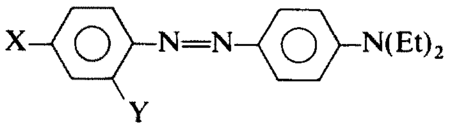
2′,4′-dinitro-4-*N,N*-dimethylaminoazobenzene in oxygenated propan-2-ol was studied, was an oxidative pathway with the formation of an azoxy compound found.

For fading on substrates such as poly(ethylene terephthalate) (PET), nylon-6 (N6), etc., due to the difficulty of isolation and characterization of the fading products, the nature of the fading process is analyzed using the correlation between substituent effects and light fastness values of the dyes. In general, it is observed that electron-withdrawing substituents increase the photostability of dyes on polyester, suggesting an oxidative process, and decrease their photostability on polyamide.[3,4]

The photo-oxidative process may occur at two positions on the dye molecule: at the azo group to give an azoxy compound,[5] and at the amino group to give dealkylation products. This latter conclusion is based on indirect evidence and has been proposed by Griffiths,[6] by analogy with the dealkylation reaction of a tertiary amine. However, this reaction requires experimental evidence to establish fully its occurrence.

Although the light fastness values of azobenzene dyes depend on the substrate, there has been little attempt to examine the role of the latter on dye fading. For example, Irick *et al.*[7] have observed an anomalously high fading for one *N,N*-diethylamino substituted azo dye on polyester relative to nylon-6,6 polymer when using 350 nm irradiation conditions. In this context, we have examined in this work the photolysis of various dyes of general structure **I**. In particular we have studied the photofading of dye **4** on polyester film in ehyl acetate solvent, using light with a maximum output at 300 nm. We have also examined the role of the polymer in the process.

(I)



1 X=H, Y=H; **2** X=OCH$_3$, Y=H; **3** X=NO$_2$, Y=H;
4 X=OCH$_3$, Y=NO$_2$; **5** X=NHCOCH$_3$, Y=H.

The results provide some information with regard to the interaction which occurs between *N,N*-diethylamino substituted azo dyes and polyester and which would appear to account for the anomalous photofading phenomena observed previously.[7]

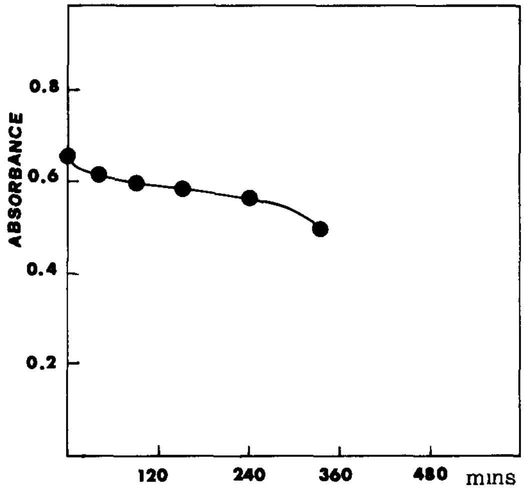


Fig. 1. Photofading curve of azo dye 4 on polyester film obtained by exposure of dyed film, fixed to the front of a pyrex cell, in a rayonet photoreactor equipped with a series of eight lamps emitting at 300 nm.

2. RESULTS AND DISCUSSION

2.1. Photofading

The photofading of the azo dye **4** on polyester (Fig. 1) exhibits a behaviour similar to that observed by Giles *et al.*[8] for some azo-naphthol dyes.

In ethyl acetate solvent, the fading of dye **4**, measured at 500 nm† over the first 10–15% of conversion, follows first-order kinetics, as indicated by a linear correlation between $\log A_0/A_t$ vs time and by identical slopes observed at different dye concentrations (Fig. 2). This result indicates that the dye is involved in the rate-determining step.

By HPLC preparative analysis, three principal products were isolated from an extractable product of the photolyzed dyed film. One unidentified product was colourless and was not observed when the dye

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† At this wavelength, within the initial 10–15% of dye fading and assuming only formation of the dealkylation product, its contribution to the dye absorbance can be neglected.

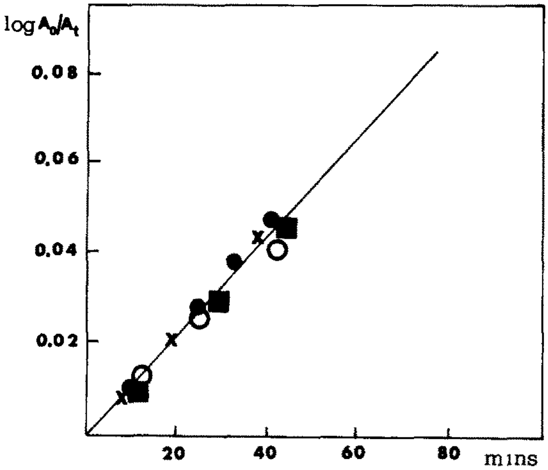
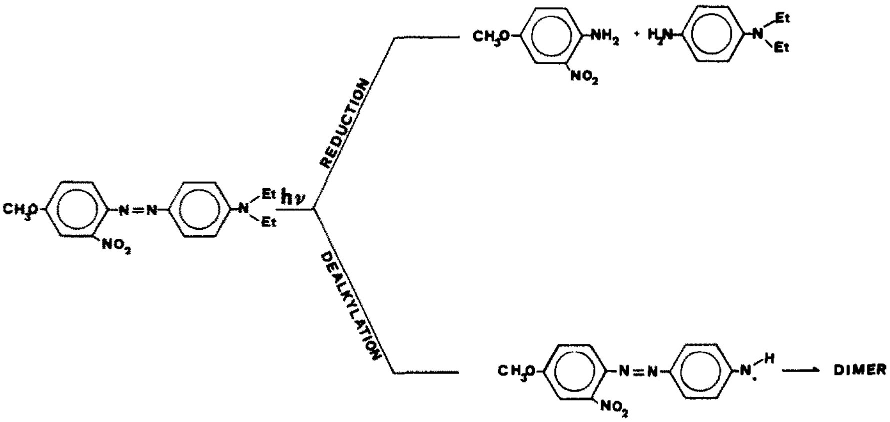


Fig. 2. First-order rate plot obtained by exposure in nitrogen-saturated ethyl acetate solutions of dye **4** in PTFE-stoppered pyrex cells at 300 nm. The concentrations of the solutions were: ●, $2{\cdot}12 \times 10^{-5}$ M; ○, $4{\cdot}24 \times 10^{-5}$ M; ■, $6{\cdot}8 \times 10^{-5}$ M; ✖, 10^{-4} M.

was present in the film at higher concentration; the other fading products were coloured and have been attributed to the following compounds:

(1) 2-nitro,4-methoxyaniline, identified spectrophotometrically by comparison with a standard compound and by its mass spectrum;
(2) 4,4′-(bis-2-nitro-4-methoxyphenylazo)hydrazobenzene, as the mass spectrum suggests (Fig. 3).

The latter two products were also obtained from dye solutions in ethyl



Scheme 1.

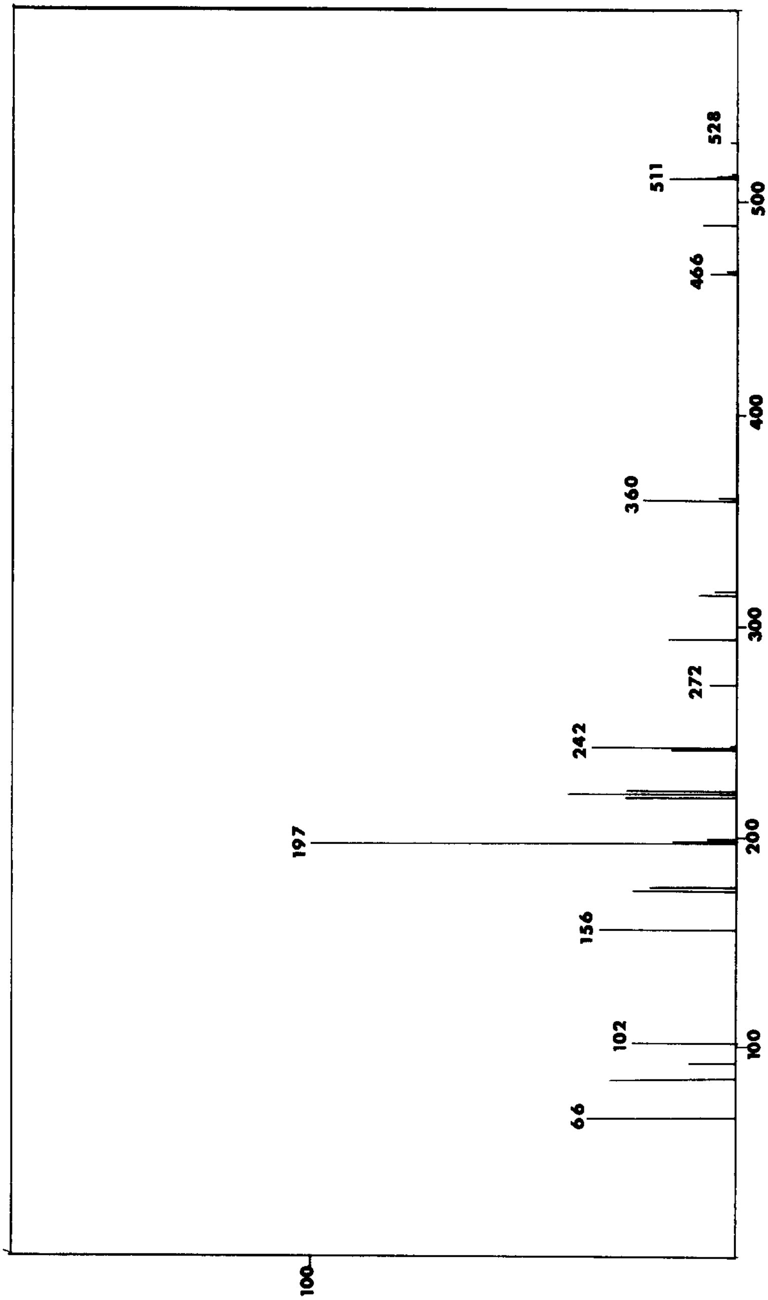


Fig. 3. Mass spectrum ascribed to 4,4′-(bis-2-nitro-4-methoxyphenylazo)hydrazobenzene.

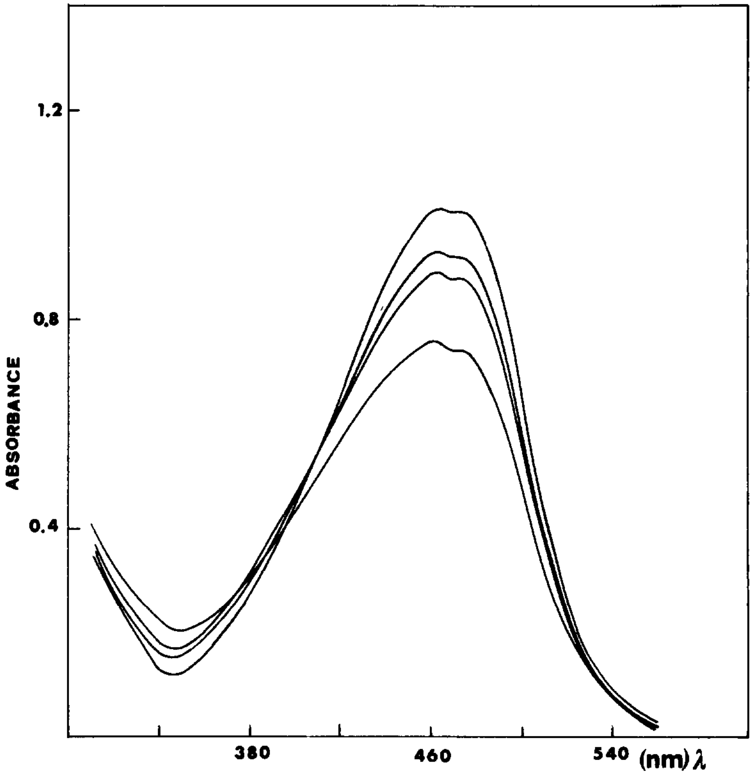


Fig. 4. Changes in the absorption spectrum of dye 4 in PET film, during irradiation in the rayonet reactor at 300 nm. Irradiation times: 0, 90, 150 and 330 min.

after exposure. Moreover, from spectral changes of the dye on polyester film and in ethyl acetate, within the initial 10–15 % of fading an isosbestic point is observed (Figs 4, 5). On continuing the exposure, this point disappears.

On the basis of the reaction products, together with the latter observation, it is suggested that the primary photochemical process is probably dealkylation (see Scheme 1).

2.2. Luminescence and second-derivative ultraviolet spectra

Figures 6 and 7 show the fluorescence and phosphorescence excitation and emission spectra of PET film and dyed PET films. At 300K, PET film exhibits an emission band at 392 nm and an excitation band with

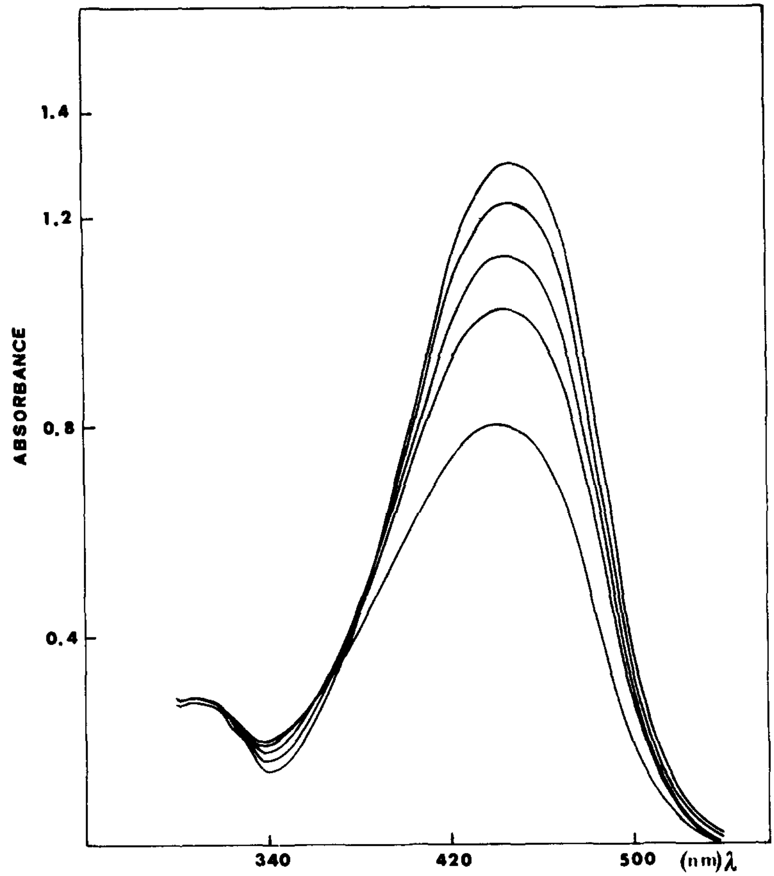


Fig. 5. Changes in the absorption spectrum of dye 4 in ethyl acetate, during irradiation in the rayonet reactor at 300 nm. Irradiation times: 0, 40, 70, 130 and 310 min.

wavelength maxima at 340 and 358 nm, whereas at 77 K, the phosphorescence emission exhibits a maximum at 460 nm with excitation maxima at 330 and 340 nm. In the presence of the azo dyes both fluorescence and phosphorescence emissions are suppressed compared with those of the basic film and a shoulder appears in the range 500–570 nm. This shoulder is slightly shifted to longer wavelengths in the emission phosphorescence spectra with respect to the fluorescence spectra.

The reduction in the emissions (fluorescence and phosphorescence) relative to basic PET is evidently due to reabsorption effects since the dyes

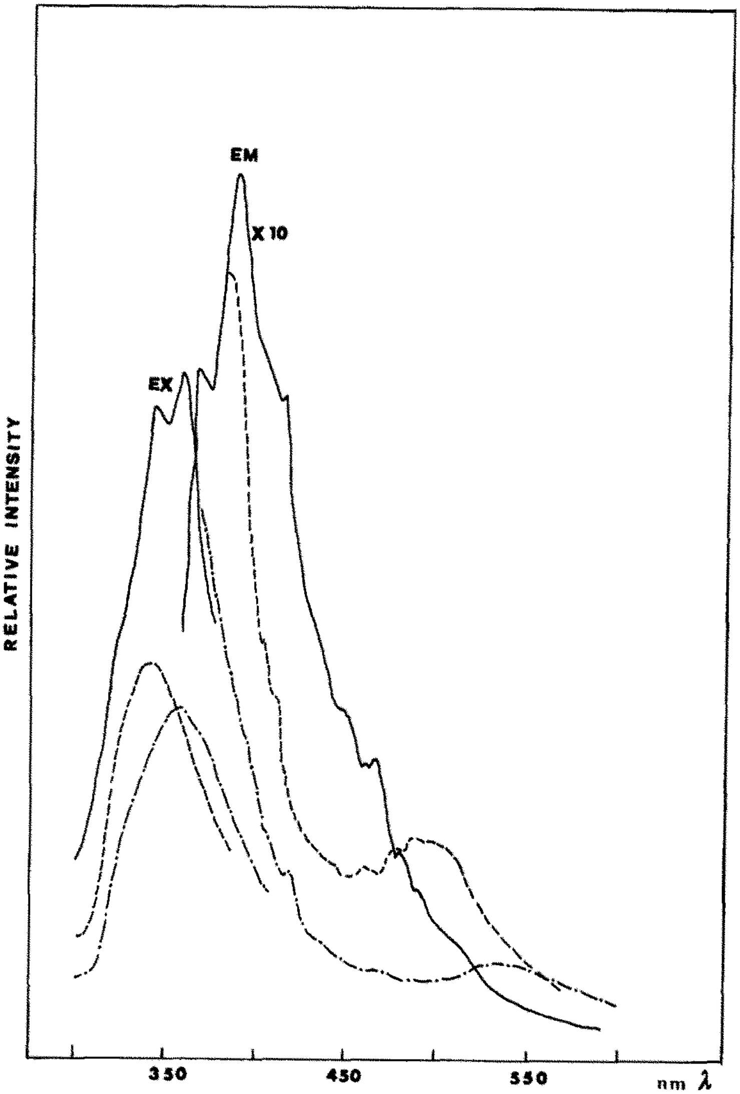


Fig. 6. Fluorescence emission spectrum of Poly(ethyleneterephthalate) (PET) film (36 μm) containing (——) no dyes, (—·—) dye **4** ($A = 1{\cdot}2$), (– – –) dye **1** ($A = 1{\cdot}3$), sensitivity = 30 at 300 K. Excitation wavelength, 340 nm.

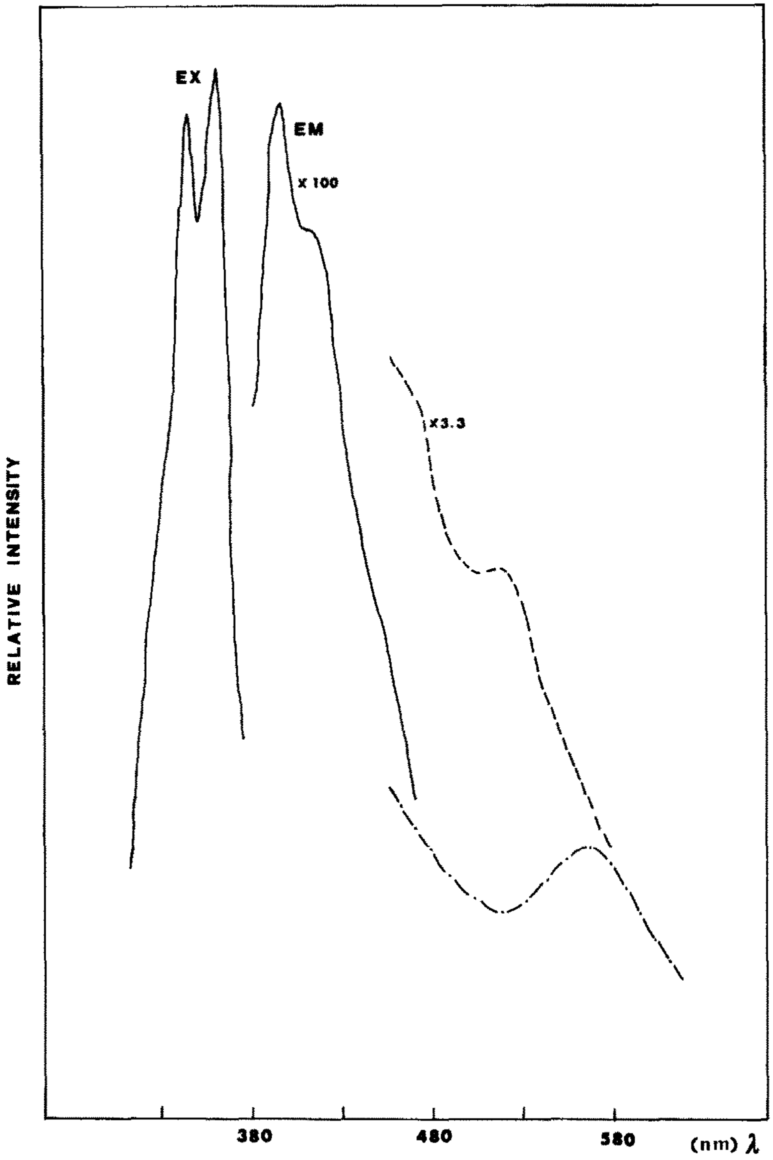


Fig. 7. Phosphorescence emission spectrum of Poly(ethyleneterephthalate) (PET) film (36 μm) containing (——) no dye, (- - -) dye **1** ($A = 1{\cdot}3$), (—·—) dye **4** ($A = 1{\cdot}2$), sensitivity = 100 at 77 K. Excitation wavelength, 350 nm.

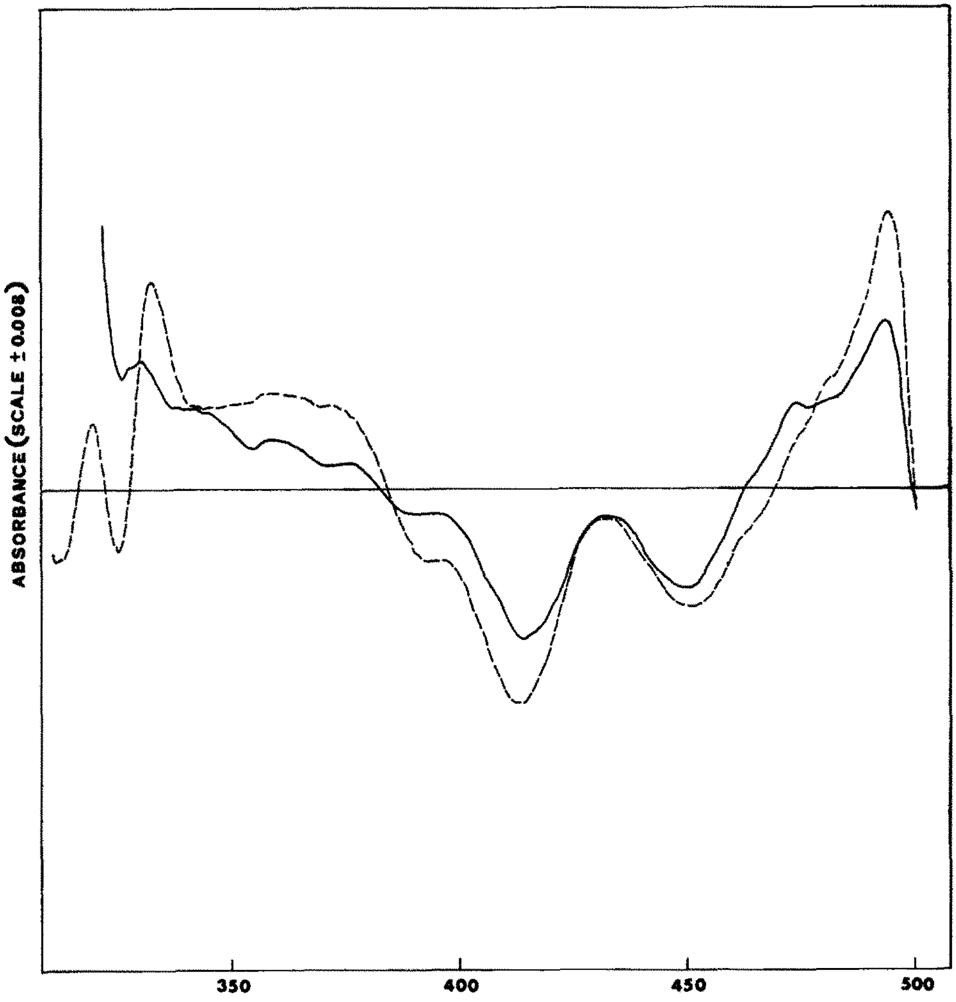


Fig. 8. Second-order derivative spectra of 4-*N*,*N*-diethylaminoazobenzene on polyester (——) and nylon-6 (- - -) films. Dye absorbance at its maximum is, respectively, 0·8 on nylon-6 and 0·63 on polyester.

overlay the emission spectra, i.e. the charge-transfer band of the dye (visible region). Moreover, considering that the dyes also absorb below 350 nm, they will screen absorption by the PET film.

Triplet-to-singlet resonance energy transfer does not seem to be involved, on the basis that other dyes with no dialkyl groups do not exhibit this phenomenon.

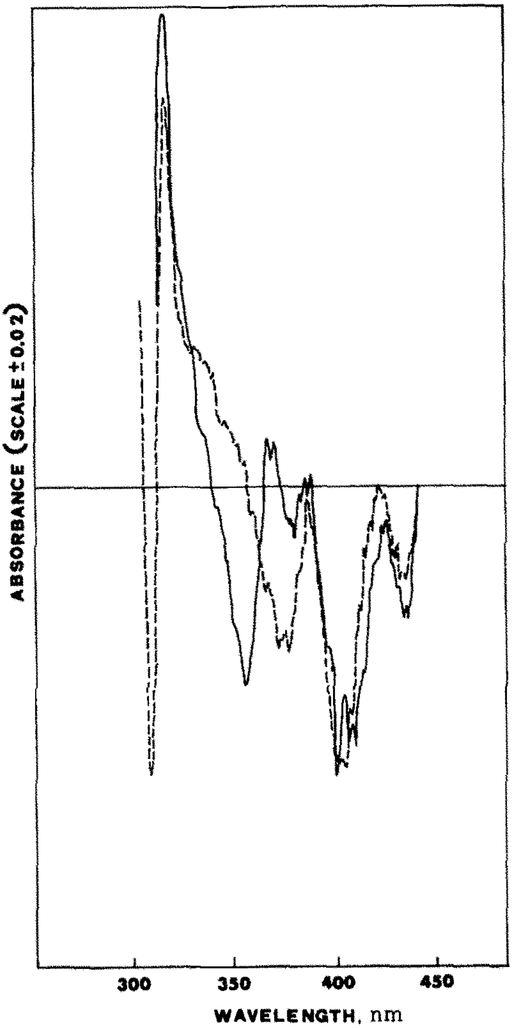


Fig. 9. Second-order derivative spectra of 4-*N*,*N*-diethylaminoazobenzene (10^{-4} M) in propan-2-ol (– – –) and in ethyl acetate (——).

Exciplex formation may also be excluded because one can observe an excitation band at 360 nm for the emission shoulder at 540 nm (Fig. 6). Exciplexes (or excimers) have no separate ground-state bands. Thus, the excitation band at 360 nm and the corresponding emission at 540 nm may be due to some type of ground-state molecular association complex between the *N*,*N*-dialkylamino group and the ester function. This

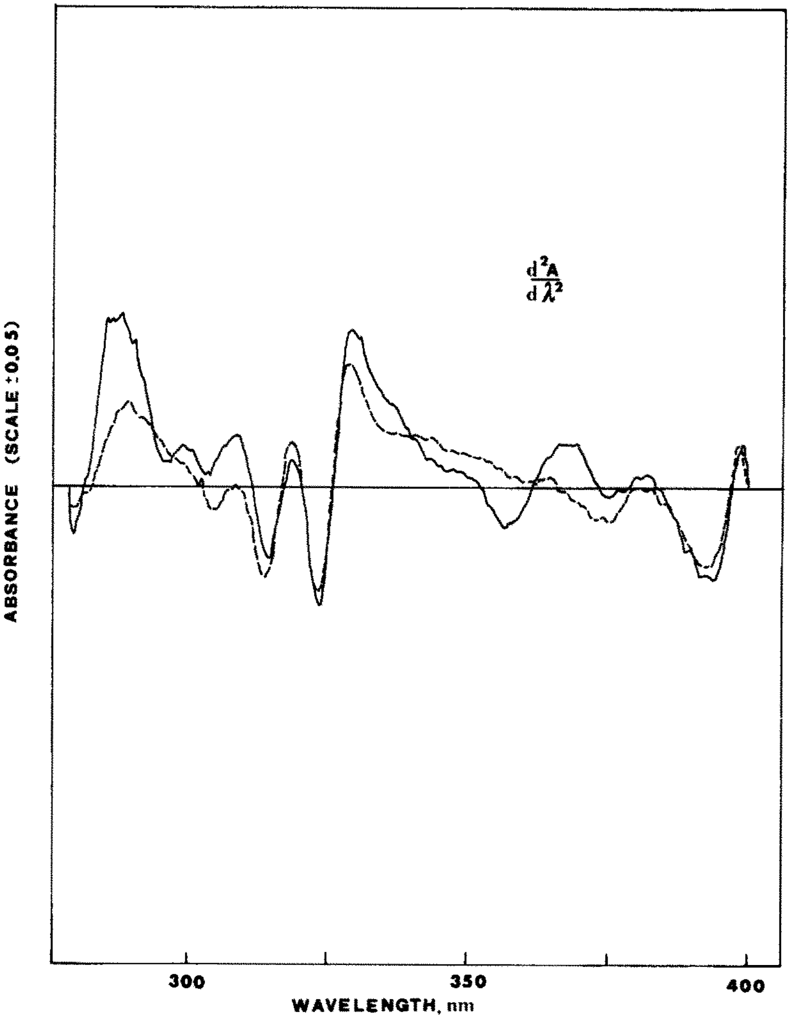


Fig. 10. Second-order derivative ultraviolet–visible absorption spectra of dye **5** (10^{-4} M) in ethyl acetate (——) and 2-propanol (– – –).

hypothesis is supported by the following factors: (i) dyes without an *N*,*N*-dialkylamino group do not exhibit this phenomenon; (ii) the excitation bands at 350 and 360 nm, respectively, for dyes **1** and **4** (Fig. 6) are not present in undyed film. There is probably excitation in undyed film at this wavelength but this is due to the strong monomeric and dimeric components of the polyester chain.[9] Finally, the second-derivative UV absorption spectra of dye **1** on polyester and on nylon-6 film (Fig. 8) show that in the former polymer there is an absorption band centred at 355 nm which does not appear in the second substrate, thus supporting the hypothesis of the formation of a molecular complex between the *N*,*N*-dialkylamino group of the dye and the ester group of the PET in the ground state. Studies on polymer films give the best examples of this effect, because in the polymer the complex appears to be very stable. Solution studies indicated the formation of a similar complex in an ester solvent such as ethyl acetate. However, in this solvent, for a number of dyes the *cis*-isomer band at 360 nm appeared to interfere and shifted to 380 nm (Fig. 9). This presented us with difficulties in its assignment and identification. For dye **5** however, there was little interference from any *cis*-isomer and the absorption band at 335 nm is clearly observed (Fig. 10).

2.3. Flash photolysis behaviour in solution

End-of-pulse transient absorption spectra obtained by flash phtolysis of the dyes **I** in *n*-hexane and in ethyl acetate are shown in Figs 11–14. These

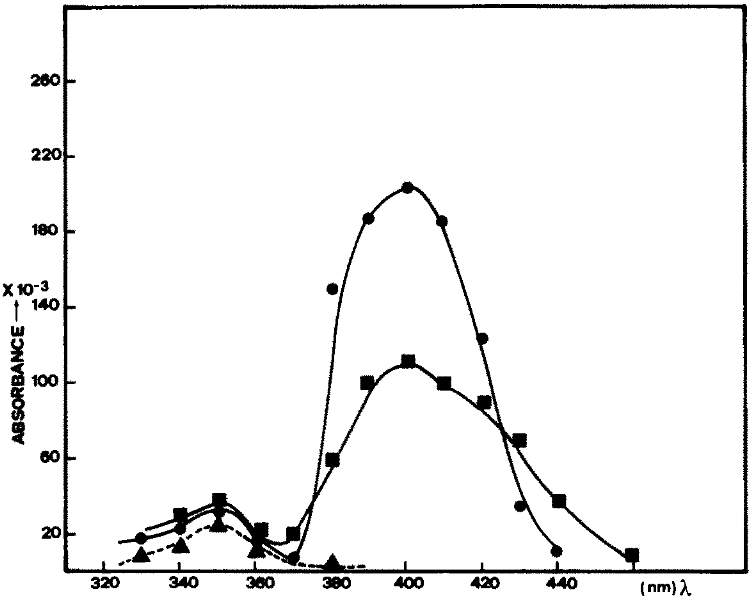


Fig. 11. End-of-pulse transient absorption spectra produced by flash photolysis of dye **1** (~10^{-5} M) in: ●, nitrogen-saturated *n*-hexane; ■, nitrogen-saturated ethyl acetate; ▲, oxygen-saturated ethyl acetate.

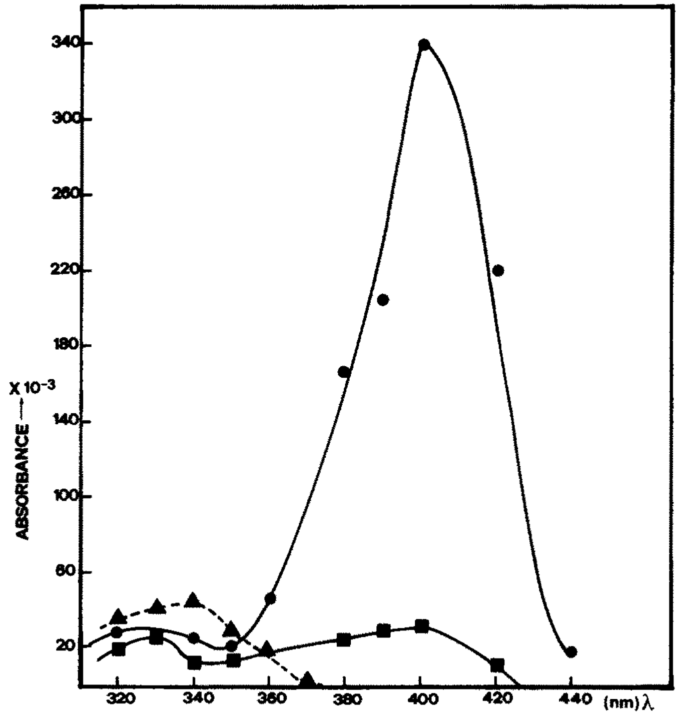


Fig. 12. End-of-pulse transient absorption spectra produced by flash photolysis of dye **2** (~10^{-5} M) in: ●, nitrogen-saturated *n*-hexane; ■, nitrogen-saturated ethyl acetate; ▲, oxygen-saturated ethyl acetate.

absorption spectra show two characteristic bands. One of these, situated in the 330–350 nm range may be associated with a hydrazyl radical;[10] the assignment for the other is uncertain, but a possibility is that this transient originates from the dealkylation process, according to the reaction scheme shown.

Enhanced transient formation below 400 nm in ethyl acetate for the dyes **3** and **4** (Figs 13, 14) suggests that the dye and the solvent are interacting (via the ground state) to give greater radical production, i.e. hydrazyl radical formation. The formation of the complex between the *N*,*N*,-dialkylamino group and the ester function would also explain the reduction in direct bond scission at this position in preference to hydrogen atom abstraction from the solvent.

In the case of dyes **1** and **2** (Figs 11 and 12) hydrazyl radical formation below 400 nm is slightly enhanced or slightly reduced. The effect of oxygen on the two transient absorptions is variable. It does not

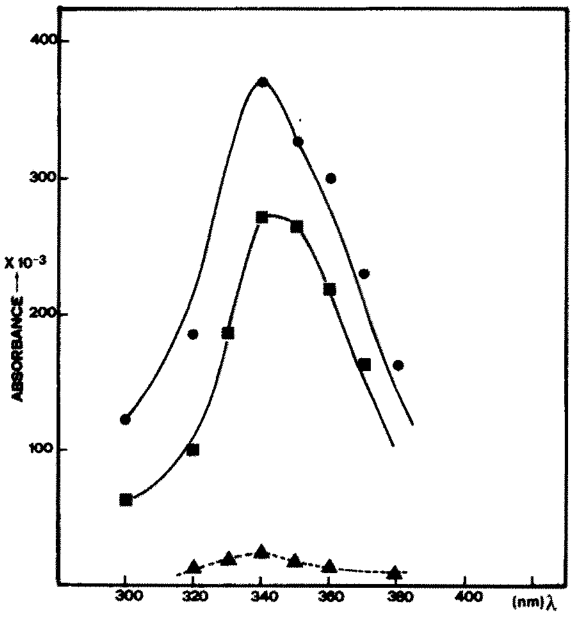


Fig. 13. End-of-pulse transient spectra produced by flash photolysis of dye 3 (~ 10^{-5} M) in: ▲, nitrogen-saturated *n*-hexane; ●, nitrogen-saturated ethyl acetate; ■, oxygen-saturated ethyl acetate.

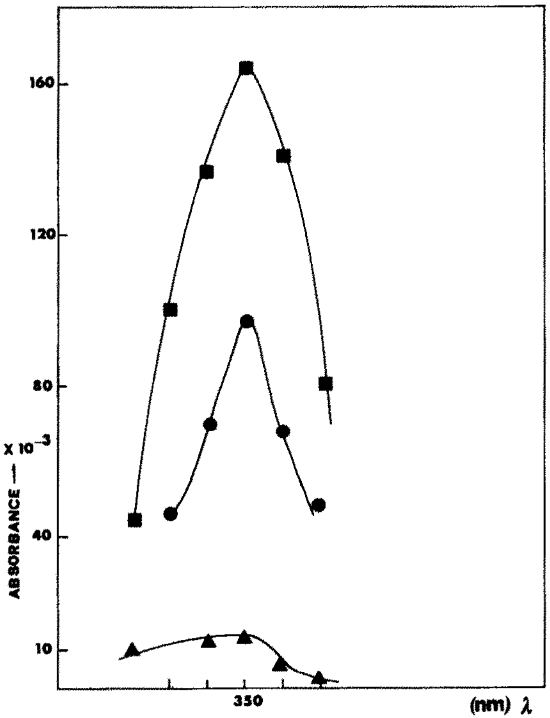


Fig. 14. End-of-pulse transient spectra produced by flash photolysis of dye 4 (~ 10^{-5} M) in: ▲, nitrogen-saturated *n*-hexane; ●, nitrogen-saturated ethyl acetate; ■, oxygen-saturated ethyl acetate.

significantly influence the transient absorption at 340–350 nm, but it quenches that centred at 400 nm, suggesting that the lowest excited triplet state of the dye is involved in free-radical formation.

3. EXPERIMENTAL

3.1. Materials

The dyes and dyed polyester films (thickness 36 μm) were supplied by ACNA. Dyed PET films were also prepared using the method described by Giles.[8]

The dyes were purified by recrystallization from ethanol.

Spectroscopic-grade solvents were used without further purification.

3.2. Kinetics of photofading

Ethyl acetate solutions of dye **4** (2×10^{-5}–10^{-4} M) and dyed films were photolyzed in PTFE stoppered pyrex cells (1 cm) at 25 °C using a rayonet photoreactor equipped with a series of eight lamps with maximum emission at 300 nm. De-aerated conditions of the solutions were obtained by bubbling dry nitrogen into the solution for 30 min. The kinetics were followed by removing the cell at suitable intervals and monitoring spectrophotometrically the residual absorbance at 500 nm. Fading products of exposed dyed films were extracted using chlorobenzene under reflux for half an hour and were isolated, initially, by column chromatography on silica using CCl_4–MeOH (98:2) as eluent, and then by HPLC preparative analysis using the same eluent.

3.3. Spectroscopic measurements

Ultraviolet–visible absorption spectra were recorded using Perkin–Elmer model 554 and 330 spectrophotometers equipped with a microprocessor for recording second-order ($d^2A/d\lambda^2$) spectra.

Fluorescence and phosphorescence spectra were recorded, respectively, at room temperature (300 K) and at 77 K (liquid nitrogen) using an uncorrected Perkin–Elmer MPF-3L fluorescence spectrophotometer.

3.4. Flash photolysis

Conventional μs flash photolysis equipment was employed utilizing two high-energy xenon-filled flash lamps at an operating voltage of 10 kV. All solutions were deoxygenated with oxygen-free nitrogen (< 5 ppm).

4. CONCLUSION

It is concluded from the results that there is a reasonable correlation between the photofading of azo dyes on polyester and in ethyl acetate. In both environments the photolysis occurs via dealkylation and photoreduction pathways. The ester function and the *N*,*N*-dialkylamino group of the dyes interact to give a molecular complex in the ground state.

ACKNOWLEDGEMENT

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