Dyes and Pigments 2 (1981) 219–229

FACTORS INFLUENCING THE PHOTOFADING OF COMMERCIAL ANTHRAQUINONE DYES IN SOLUTION

NORMAN S ALLEN and KENNETH O FATINIKUN

Department of Chemistry, John Dalton Faculty of Technology, Manchester Polytechnic,
Chester Street, Manchester M1 5GD, Great Britain

A KEITH DAVIES

Department of Biochemistry, University of Salford,
Salford M5 4WT, Lancs , Great Britain

BARRY J PARSONS and GLYN O PHILLIPS

School of Natural Sciences, Kelsterton College,
N E Wales Institute, Connahs Quay Clwydd, N Wales, Great Britain

SUMMARY

The photofading of two anthraquinone dyes has been studied in aqueous solution using ultraviolet–visible absorption spectroscopy and flash photolysis. The influence of alcohol concentration, pH, atmosphere, photosensitisers and stabilisers have been examined and these lead to some important conclusions on the mechanism of dye fading Essentially, the results indicate the photoexcited triplet state of the dye undergoes a process of either electron or hydrogen-atom abstraction depending on the nature of the environment. Other factors such as aggregation and singlet oxygen also appear to play an important role in solution photofading. The relevance of these results to photofading in a polymeric phase is discussed

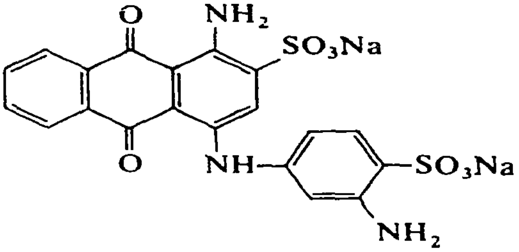
1 INTRODUCTION

Anthraquinone derivatives are a commercially important class of compounds used as dyes for synthetic fibres [1,2] One of the most important criteria used in assessing the commercial use of a dye is its stability to light.[3 4] The photofading of anthraquinone dyes has been widely studied and through the use of modern photochemical techniques their behaviour is reasonably well understood.[4] However, the relative importance of various mechanisms that have been put forward over the years is still a topic of wide interest. For example, various workers have

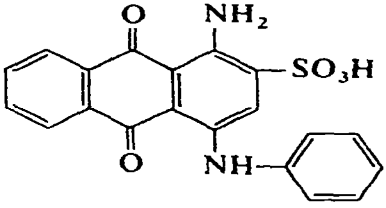
Dyes and Pigments 0143-7208/81/0002-0219/$02 50

argued the contribution of aggregation,[5–7] singlet oxygen[8–10] and electron or hydrogen-atom abstraction.[3,4,9,11] The nature of the polymer and the structure of the dye are probably the two most important factors in controlling the relative contribution of these processes in photofading.[4]

To examine the contribution of the above processes we have studied the influence of alcohol concentration, atmosphere, pH, sensitisers and stabilisers on the photofading of two commercial anthraquinone dyes, namely 1-amino-4-(3′-amino-4-sulphonyl)anilino-9,10-anthraquinone-2-sulphonic acid disodium salt and 1-amino-4-anilino-9,10-anthraquinone-2-sulphonic acid of the structures **I** and **II**, respectively.



(I)



(II)

In this case photofading was carried out in aqueous solution since many of the above conditions cannot be conveniently studied in a polymeric phase. Irradiation of the dye solutions was carried out using repetitive flash photolysis on a conventional apparatus.

2 EXPERIMENTAL

2.1 *Materials*

The dyes used in this study of structures **I** and **II** were supplied by the Fine Chemicals Service of ICI Ltd. Both dyes were purified by dissolution in dimethylformamide, filtration, and finally precipitation by addition of chloroform.

All the reagents used were of ANALAR grade, and water distilled from alkaline permanganate was used throughout.

2.2 *Irradiation*

The dye solutions were irradiated using repetitive flash photolysis. The lamps were xenon filled, each flash having an energy of 450 J. The reaction vessel used was a modified 1 cm path-length rectangular fluorimeter cuvette. The top of the cell was fitted with a T-shaped neck having a 'Rotaflow' PTFE tap. The cell was suspended in the flash chamber by trapping its neck in the chamber lid.

Dye solutions were in the range 10^{-4}–10^{-5}M. Deoxygenation was performed by bubbling the solution with nitrogen (<5 ppm oxygen).

Ultraviolet–visible absorption spectra were recorded using a Perkin–Elmer Model 554 spectrophotometer. Relative percentage fading was determined by monitoring the changes in absorbance of the longest wavelength absorption band of the dye after exposure to a suitable number of photoflashes.

$$\text{Relative \% fading} = \frac{A_0 - A_t}{A_0}$$

where A_0 = absorbance at λ_{max} before flashing and A_t = absorbance at λ_{max} after flashing.

3. RESULTS AND DISCUSSION

3.1. *Effect of Alcohol Concentration*

In this study we carried out an examination on the effect of propan-2-ol concentration on the photofading of the dyes **I** and **II** in the presence of oxygen. The results are summarised in Table 1 where it is seen that with increasing alcohol concentration there is an increase in the percentage fading of the dyes after five photoflashes. On the basis of earlier work this effect would be expected since in alcohols anthraquinone dyes are highly susceptible to photoreduction.[4,11] However, one of the most interesting features of the results obtained here was the observation of an increase in the initial absorbance of the dyes with increasing alcohol concentration. This effect is shown in Fig. 1 and could be associated with disaggregation of the dyes.[5,7] The unusual behaviour with dye **I** is probably due to the formation and breaking of aggregates. Thus, apart from an increase in photoreduction, disaggregation of the dyes may also contribute to their increased rate of photofading. This effect would be consistent with the earlier findings of Giles and coworkers.[5-7]

TABLE 1
EFFECT OF PROPAN-2-OL CONCENTRATION ON PHOTOFADING

Concentration of propan-2-ol (M)	*% Fading after 5 photoflashes* Dye **I**	Dye **II**
0	10.5	3.6
0.654	36.5	11.2
3.27	52.7	24.2

3.2. *Effect of pH*

Figure 2 shows the effect of ten photoflashes on the absorption spectra of air-saturated and nitrogen-saturated solutions of dye **I** in aqueous 1.5M-sodium

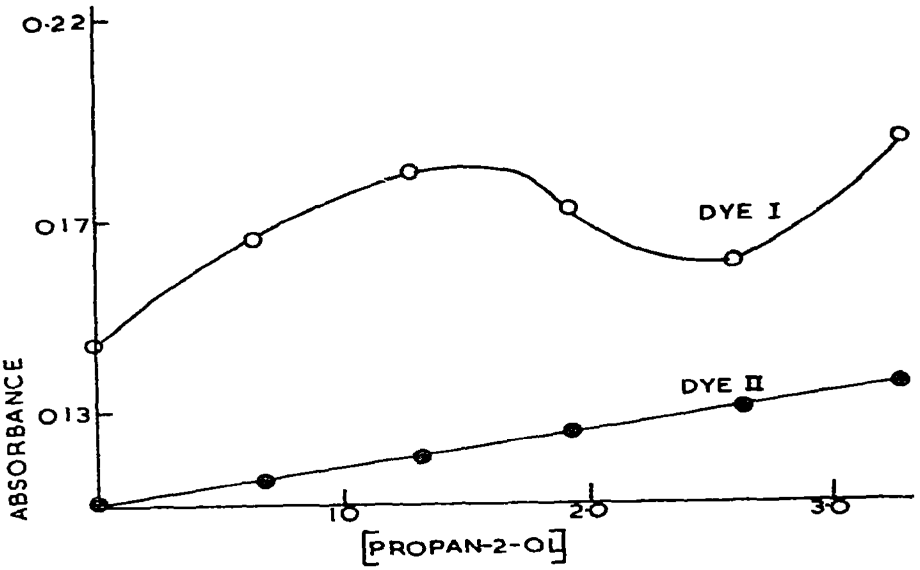


Fig 1 Effect of propan-2-ol concentration (mole dm^{-3}) on the absorbance of ○ dye I and ● dye II in water

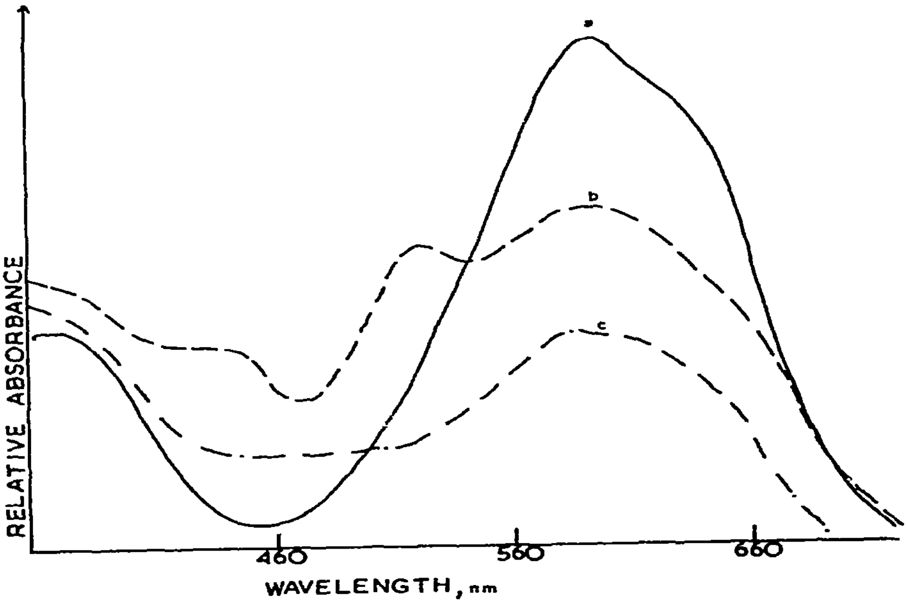


Fig 2 Absorption spectra of dye I in 1 5M-NaOH (a) (——) nitrogen-saturated before flashing, (b) (– – –) nitrogen-saturated after 10 photoflashes, (c) (—·—) in a corresponding air-saturated solution after 10 photoflashes

hydroxide. It is seen that in de-oxygenated solution the dye is much more stable to light than in a corresponding air-saturated solution. Also, in the absence of oxygen a new absorption peak appears at *ca* 505 nm which is associated with the hydroquinone form of the dye formed by hydrogen-atom abstraction On shaking with oxygen this absorption, as expected, disappears and the dye is regenerated This is a well-known phenomenon with anthraquinone dyes.[4,11] The same results were obtained with dye **II**.

In a further set of experiments, the effect of increasing alkali concentration on dye fading was examined Air-saturated solutions containing between 0·0M- and 4·0M-sodium hydroxide were exposed to a series of photoflashes and the absorbance was recorded after two photoflashes. All the solutions had an initial absorbance of 0·281. Figure 3 shows a plot of the fraction of dye remaining after each double flash against the total number of flashes. It is seen that the fraction of dye remaining after ten photoflashes decreases as the alkali concentration is increased. The initial rates of fading also followed this pattern.

It is apparent from these results that the light stability of the dye is markedly influenced by the alkalinity of its environment Under these conditions photoreduction through electron abstraction would be increased.[4,11] However, the

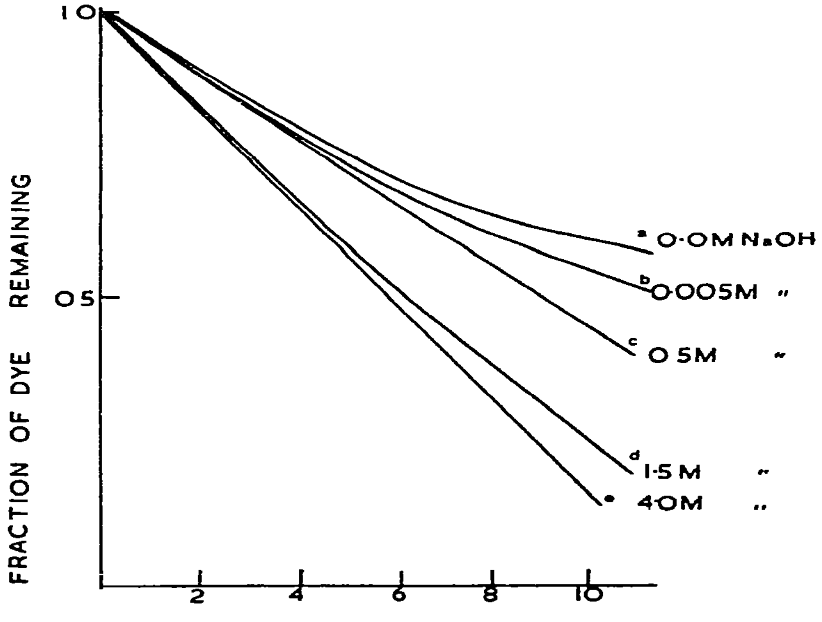


Fig 3 Photofading of dye I in air-saturated aqueous solution containing (a) 0·0M, (b) 0·005M; (c) 0·5M, (d) 1·5M, and (e) 4·0M-NaOH.

above results also indicate that singlet oxygen plays an important role in dye fading in solution. In a polymeric phase, oxygen diffusion is minimal and under these conditions the photostability of the dye would be enhanced. This is exactly what is observed in solution (Fig. 2).

Figure 4 shows the effect of ten photoflashes on the absorption spectrum of dye **I** in aqueous solutions of 0.005M- and 4.0M-hydrochloric acid. It is seen that for each

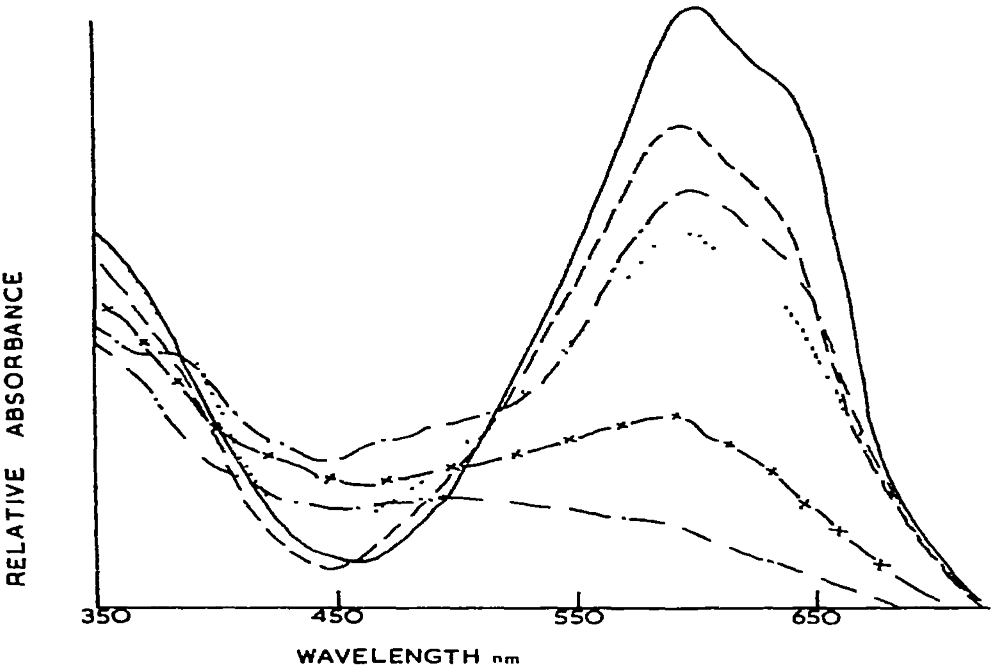


Fig. 4. Absorption spectra of dye **I** in 4M-HCl (——) nitrogen-saturated before photoflashing, (—— –) nitrogen-saturated after 10 photoflashes (–×–×) air-saturated after 10 photoflashes and in 0.005M-HCl (- - -) nitrogen-saturated before photoflashing, (   ) nitrogen-saturated after 10 photoflashes, and (— –) air-saturated after 10 photoflashes.

acid concentration the dye fades faster in air-saturated solution than in a deoxygenated one. Dye fading also increases with increasing protonation although the effect is not so marked as with sodium hydroxide.

The effect of pH was also examined on dye **II** and the results are summarised in Fig. 5. Here the relative percentage fading is plotted against pH. It is seen that in strongly acid or alkali solutions the rate of fading of the dye is significantly greater than in neutral or weakly acid solutions. From these results it would also appear that protonation of the dye is important in photofading.

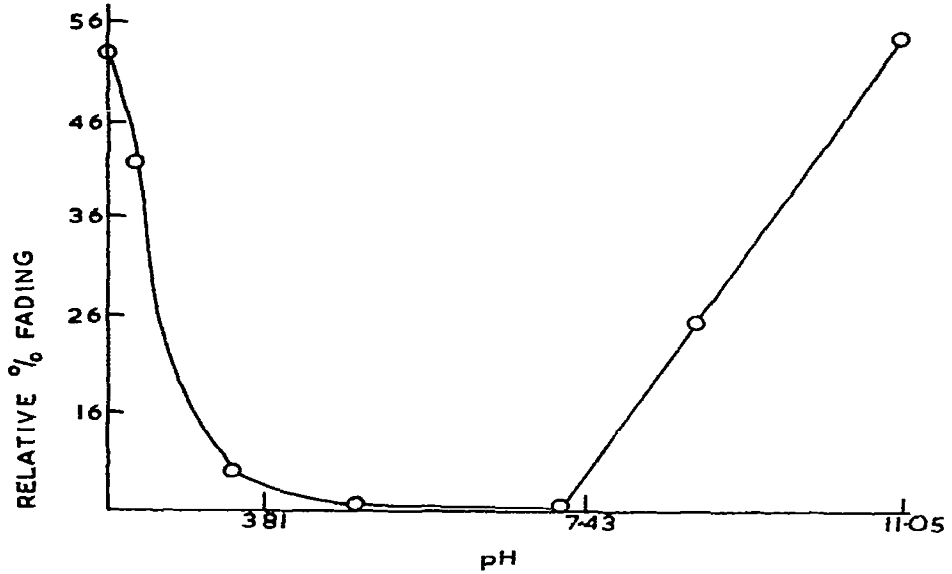


Fig 5 Effect of pH on the photofading of dye II in air-saturated aqueous solution

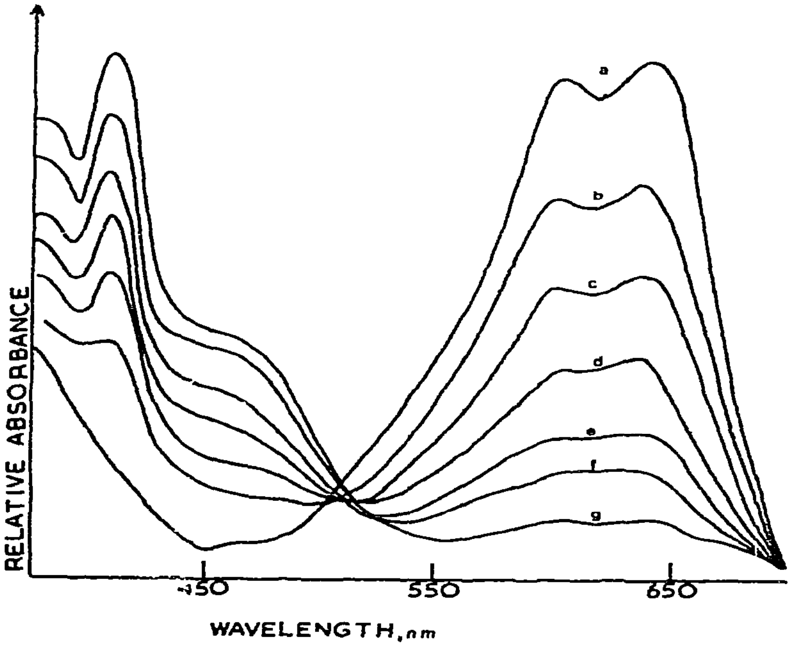


Fig 6 Absorption spectra of dye II in the presence of benzophenone (10^{-3}M) in nitrogen-saturated 3·2 v/v propan-2-ol-water (a) before photoflashing, (b), (c), (d), (e), (f) and (g) after each successive flash

3.3. *Effect of sensitisers and stabilisers*

The effect of a well-known triplet sensitiser, benzophenone, on the photofading of dye **II** is shown in Fig. 6. The dye was dissolved in a 3.2 v/v propan-2-ol:water mixture to give an initial absorbance of 0.12. Aliquots of 0.1M-benzophenone in propan-2-ol were added to give an effective benzophenone concentration of 10^{-3}M. The Figure shows that in nitrogen-saturated solution fading of the dye occurs rapidly after each successive photoflash compared with the dye alone (see Fig. 7). The fading is also accompanied by the appearance of a new absorption peak at 410 nm which is associated with the hydroquinone form of the dye. This was confirmed for the control fading experiment shown in Fig. 7 where it is seen that anthra-hydroquinone, chemically produced using sodium dithionate as a reducing agent,[9] showed an identical peak at *ca* 410 nm. Thus, it is apparent from these results that the triplet state of the dye is important in photofading. A chemical interaction between the benzophenone ketyl radical and the dye would appear under these conditions to be unimportant.[12] This conclusion is supported by the effects of another triplet sensitiser (see Table 2).

Table 2 summarises the results of a series of experiments carried out to observe the

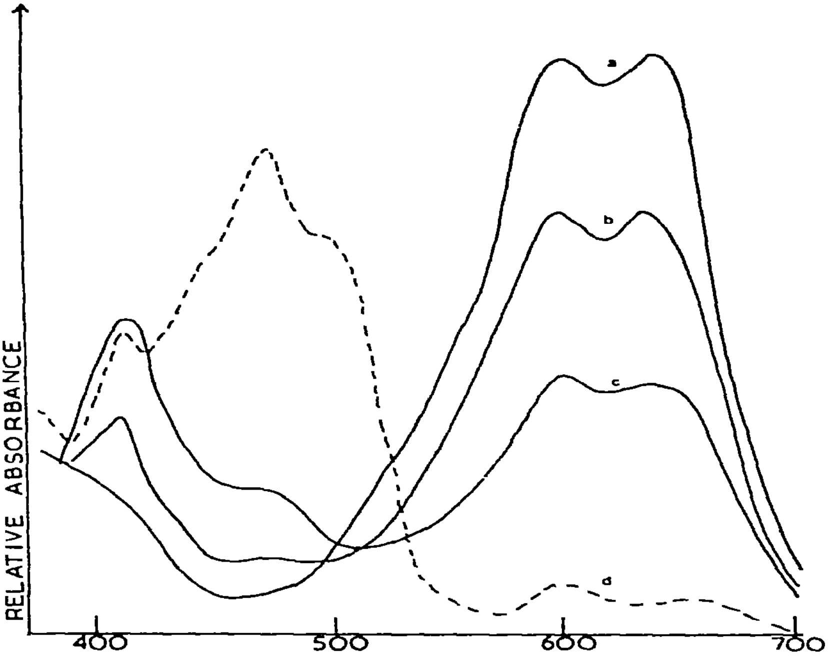


Fig. 7. Absorption spectra of dye **II** in nitrogen-saturated aqueous solution (a) before photoflashing, (b) after 2 photoflashes (c) after 5 photoflashes and (d) (- - - -) after reduction with sodium dithionate

TABLE 2

EFFECT OF SENSITISERS AND STABILISERS ON THE PHOTOFADING OF DYE **II** IN N_2-SATURATED 3:2 v/v PROPAN-2-OL:WATER MIXTURES

Additive[a]	*% Fading after 10 photoflashes*
Control	40
DABCO	29.3
Ethylenediamine	22.4
Potassium thiocyanate	23.6
Benzophenone	99.2
o-phenylphenol	19.5
p-phenylphenol	23.0
Diphenyl	78.3
Tetracyanoethylene	4.6
4-hydroxy-2,2,6,6-tetramethyl *N*-oxypiperidine	2.9

[a] 1×10^{-3}M concentration.

effect of various sensitisers and stabilisers on the extent of fading of dye **II** in nitrogen-saturated solution after ten photoflashes. The dye solutions had an initial absorbance of 0.85 and all the reagents were 10^{-3}M.

It is seen from the results that another triplet sensitiser apart from benzophenone is diphenyl. The sensitising effect of this compound may also be due to triplet energy transfer from the diphenyl to the dye. For this process to occur the triplet energy of diphenyl must lie above that of the dye. Diphenyl has a triplet energy of 270 kJ mole^{-1}.[13] Although the triplet energy level of the dye is not known, it can safely be assumed to lie below that of its first excited singlet state. The energy of the first excited singlet state of the dye for a wavelength of maximum absorption of 632 nm was calculated to be 189.52 kJ mole^{-1}. The corresponding triplet energy would be lower than this. Since this lies below the triplet energy level of diphenyl, energy transfer from the latter to the former is very likely.

All the other chemical compounds listed in Table 2 acted as stabilisers to varying extents. The influence of DABCO, a well-known singlet oxygen quencher,[10] was at first very surprising since the fading experiments were carried out in de-oxygenated solutions. DABCO, however, is an amine and the inhibiting effect in this case is most likely to be due to its ability to quench the excited states of the dye either through electron transfer[14] or collisional quenching. This would appear to be confirmed by the stabilising effect of ethylene diamine also shown in the Table.

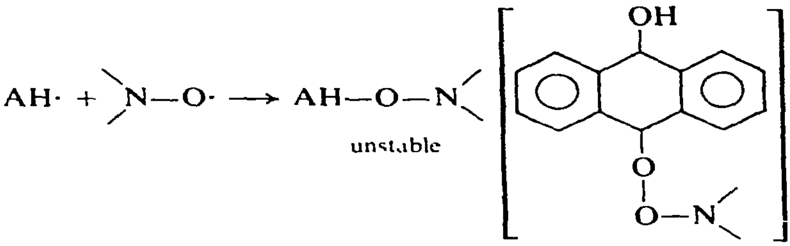
The effects of *o*- and *p*-phenylphenol are interesting since these compounds are used as carriers in the dyeing of polyester fibres.[2] Some disperse dyes have their lightfastness impaired by carriers,[3,4,7] but in this case they are protective. These carriers have high absorbances in the ultraviolet region of the spectrum and their action here may be due to a screening effect. Their ability to act as radical traps would be expected to be low since they are not hindered phenols.

The stabilising effect of potassium thiocyanate is interesting since this seems to suggest that the photofading of the dye in alcohol/water mixture involves hydroxyl radicals. Potassium thiocyanate is a well-known hydroxyl radical trap[15] and in this experiment the degree of photofading was reduced by *ca* 50%.

Finally, the powerful stabilising effects of tetracyanoethylene and the *N*-oxy radical compounds are worthy of some detailed discussion The former is a well-known electron trap[16] and the latter is an efficient radical trap.[17] Both stabilising mechanisms are consistent with the photofading mechanisms of anthraquinone dyes.[4] The powerful electron-trapping ability of the tetracyanoethylene clearly suggests that electron transfer, to give the radical anion (A^-), is important in the photofading of anthraquinone dyes The powerful stabilising effect of the *N*-oxy radical is clearly due to its efficient radical trapping ability Previous work by one of the authors with anthraquinone[18] has shown that the *N*-oxy radical inhibits transient formation on flash photolysis due to the semiquinone radical (AH) Inhibition was attributed to two possible mechanisms The first involves direct trapping of the semiquinone radical (AH) by the *N*-oxy radical to give an unstable molecule The semiquinone radical is formed by hydrogen-atom abstraction by the photoexcited triplet state of the anthraquinone

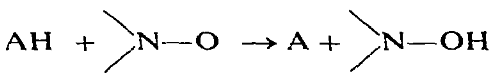
$$A \xrightarrow{h\nu} {}^1A \xrightarrow{ISC\dagger} {}^3A \xrightarrow{R-H} AH\cdot + R \qquad (1)$$

where R—H is solvent



(2)

The second mechanism involves a hydrogen atom transfer from the semiquinone radical to the *N*-oxy radical regenerating the anthraquinone and producing a hydroxylamine



$$AH + {>}N{-}O \rightarrow A + {>}N{-}OH \qquad (3)$$

Of the two mechanisms it would appear that the second is more important for the dye since it involves a regeneration process and would therefore act in a protective manner In the case of anthraquinone the first mechanism is important since the presence of the *N*-oxy radical did not inhibit the photolysis of the anthraquinone [19]

---

† Intersystem crossing

4. CONCLUSIONS

It may be concluded from the above that a number of factors are important in the photofading of anthraquinone dyes. The presence of dye aggregates would almost certainly result in some enhancement of light stability. The nature of the environment however, would appear to play a major role in controlling light stability and from the above results pH has a powerful influence on photofading Thus, the washing of fibres to remove residual acid or alkali could be important Regarding the photofading mechanism it would appear that electron and/or hydrogen-atom abstraction are important processes On a more technological note, the powerful stabilising effects of tetracyanoethylene and the *N*-oxy radical would seem to suggest that they could be useful as postdyeing treatments to enhance the lightfastness of dyed fabrics

REFERENCES

1 *Colour index*, 3rd edn Bradford, UK, Society of Dyers and Colourists (1971)
2 E R TROTMAN, *Dyeing and chemical technology of textile fibres*, 4th edn London, Griffin (1970)
3 N S ALLEN and J F MCKELLAR, *Photochemistry of dyed and pigmented polymers* London, Applied Science Publishers (1980)
4 N S ALLEN and J F MCKELLAR, *Developments in polymer photochemistry—1*, ed N S Allen Chapter 7, pp 191–217 London, Applied Science Publishers (1980)
5 C H GILES and R B MCKAY, *Text Res J*, **33**, 528 (1963)
6 C H GILES and J DE BERNAT, *Text Res J* **46**, 673 (1976)
7 C H GILES and S D FORRESTER, in *Photochemistry of dyed and pigmented polymers* ed N S Allen and J F McKellar, Chapter 2, pp 51–91 London, Applied Science Publishers (1980)
8 G S EGERTON, *Text Res J*, **18**, 659 (1948)
9 G S EGERTON N E N ASSAAD and N D UFFINDELL *Chemy Ind* (*London*), 1172 (1967)
10 J GRIFFITHS and C HAWKINS, *Polymer*, **17** 1113 (1976)
11 J F MCKELLAR, *Rad Res Revs* **3** 141 (1971)
12 N S ALLEN, J F MCKELLAR and B MOHAJERANI, *Dyes & Pigments*, **1** 49 (1980)
13 A K DAVIES, R FORD, J F MCKELLAR and G O PHILLIPS, *J Chem Soc, Perkin II*, 923 (1972)
14 N S ALLEN S A PROTOPAPPAS and J F MCKELLAR, *J Appl Chem & Biotechnol*, **27**, 269 (1977)
15 A DATYNER, C H NICHOLLS and M T PAILTHORPE, *J Soc Dyers & Colourists*, **93**, 213 (1977)
16 N S ALLEN, B MOHAJERANI and J T RICHARDS, *Dyes & Pigments*, **2**, 31 (1981)
17 N S ALLEN, J F MCKELLAR and D WILSON, *Polym Deg & Stab*, **1**, 205 (1979)
18 N S ALLEN *Polym Deg & Stab*, **2**, 269 (1980)
19 N S ALLEN, K O FATINIKUN, J LUC-GARDETTE and J LEMAIRE, *Polym Deg & Stab*, in press