Dyes and Pigments 2 (1981) 31–35

PHOTOFADING OF BASIC TRIPHENYLMETHANE DYES: EVIDENCE FOR ELECTRON TRANSFER

NORMAN S. ALLEN

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

and

BAGHAR MOHAJERANI and JOHN T. RICHARDS

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

SUMMARY

The effects of a radical scavenger, 4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxy, and an electron trap, tetracyanoethylene, on the rates of fading of two basic triphenylmethane dyes in poly(vinyl alcohol) film have been compared with their effects on the primary photochemical behaviour of the dyes on flash photolysis in a model solvent propan-2-ol. The presence of the electron trap markedly inhibits fading of the dyes in the film and also the observation of transient absorption on flash photolysis. The presence of other efficient electron traps, namely acetone and nitrous oxide completely inhibits transient absorption. The importance of an electron transfer step in the photofading of these dyes is discussed.

1. INTRODUCTION

The influence of the substrate on the lightfastness of basic triphenylmethane dyes has been a subject of considerable scientific interest for many years.[1–11] For example, their lightfastness varies from much less than 1 on cotton to 7 on orlon.[1] There have been several studies aimed at understanding this interesting phenomenon and over the years an acceptable picture has been constructed of the general fading mechanism.[4,10,12] The mechanism, shown below, involves the reaction of the dye triplet state with the environment to generate an electron (solvated) which undergoes the reactions shown to yield the dye radical or hydrogen peroxide. The involvement of the solvated electron would clearly be more prevalent in cotton than in an acrylic environment.[12]

$$\text{Dye } D^+ \xrightarrow{h\nu} {}^1D^+ \rightarrow {}^3D^+ \qquad (1)$$

Dyes and Pigments 0143-7208/81/0002-0031/$02·50—
Printed in Northern Ireland

$$^3D^+ + \text{substrate or solvent} \rightarrow D^{\cdot++} + e' \text{ (solvated)} \qquad (2)$$

$$D^+ + e' \text{ (solvated)} \rightarrow D\cdot + \text{solvent} \qquad (3)$$

$$2D\cdot + H_2O \rightarrow DH + D^+ + OH^- \qquad (4)$$

and/or

$$e'\text{(solvated)} + O_2 \rightarrow O_2^{\cdot-} + \text{solvent} \qquad (5)$$

$$O_2^{\cdot-} + H_2O \rightleftharpoons HO_2^{\cdot} + OH^- \qquad (6)$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \qquad (7)$$

$$D^+ + H_2O_2 \rightarrow \text{oxidation products} \qquad (8)$$

In previous studies using flash photolysis evidence was obtained for the involvement of both the dye triplet and the dye radical (D·)[11,13] but evidence for the solvated electron remains elusive.[12] In this short study strong evidence in support of the involvement of the electron transfer step in the photofading of basic triphenylmethane dyes is presented.

2. EXPERIMENTAL

2.1 *Materials*

Malachite Green (CI 42000) and Para rosaniline (CI 42500) were purchased from Hopkin and Williams Ltd, UK. Tetracyanoethylene and 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy were purchased from Eastman Kodak Ltd.

Films of poly(vinyl alcohol) (25 μm thick) were prepared by casting a 5% solution of the polymer in a water/ethanol mixture (100:10 v/v) on to a glass plate and allowing the solvents to evaporate overnight in an air-oven at 30°C. The final concentration of the dyes and additives were about 10^{-5} and 10^{-4}M respectively.

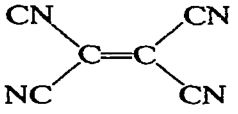
2.2. *Apparatus and equipment*

The dyed films were exposed in a Microscal apparatus containing a 500 W high pressure mercury/tungsten lamp (55°C and ambient humidity). This light source has a spectral distribution reasonably close to that of natural sunlight (wavelengths > 300 nm). Spectral changes in the dyed films were recorded using a Pye–Unicam SP1800 absorption spectrometer.

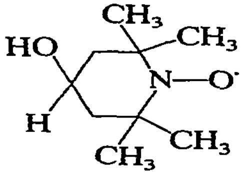
Flash photolysis experiments were carried out using a micro-second apparatus with a photoflash of 300J and a half-life of 10 μs. A 10 cm pyrex cell was used in these experiments to simulate as closely as possible the exposure conditions in the Microscal unit (i.e. wavelengths > 300 nm). The concentrations of the dyes and stabilisers used were 10^{-6} and 10^{-4}M respectively. Solutions of the dyes were also saturated with nitrous oxide gas.

3. RESULTS AND DISCUSSION

In a previous study we found that the presence of a hydrogen atom donor, benzhydrol, and a triplet sensitiser, benzophenone, markedly accelerate the fading of malachite in an acrylic environment.[13] In agreement with these findings both compounds enhanced transient absorption due to the triphenylmethyl radical in acetonitrile. In this study we have examined the effects of two potential stabilisers, a well known electron trap, namely tetracyanoethylene (structure I) and a well known radical trap, namely 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy (structure II).[14–16]



(I)



(II)

According to reactions (2) and (3) the electron transfer process is an important precursor to the generation of the triphenylmethyl radical (D·). If these reactions indeed occur, then the presence of the electron trap should effectively inhibit radical formation and hence fading of the dyes. That this would appear to be so is shown by the following data.

Table 1 shows the effects of the electron and radical traps on the intensity of the transient absorptions, due to the triphenylmethyl radical, produced on flash photolysis of the dyes in anaerobic (nitrogen saturated) propan-2-ol. It is seen that the electron trap significantly reduced the transient absorptions compared with the radical trap and control solutions. Interestingly, the presence of

TABLE 1

EFFECT OF ADDITIVES ON THE TRANSIENT ABSORPTION PRODUCED ON FLASH PHOTOLYSIS OF MALACHITE GREEN AND PARA ROSANILINE IN NITROGEN SATURATED PROPAN-2-OL (PYREX CELL).

Additive	*Transient absorption* ($\log_{10} I_0/I_t$) *Malachite Green*[a]	*Para rosaniline*[b]
Control	$4{\cdot}2\times10^{-2}$	8×10^{-2}
N-oxy radical	$2{\cdot}2\times10^{-2}$	$4{\cdot}1\times10^{-2}$
Tetracyanoethylene	$2{\cdot}9\times10^{-3}$	$4{\cdot}8\times10^{-3}$
Acetone	None	None
Nitrous oxide	None	None

[a] $\lambda_{max} = 450$ nm.
[b] $\lambda_{max} = 440$ nm.

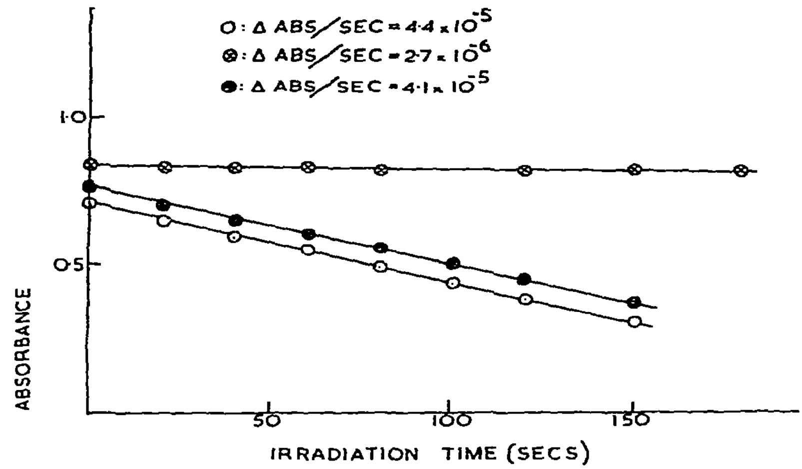


Fig. 1. Change in the absorbance of the longest wavelength absorption band of Malachite Green in poly(vinyl alcohol) film (25 μm thick) containing O— no additives, ⊗— 10^{-4}M tetracyanoethylene and ●— 10^{-4}M 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy. (λ max = 620 nm).

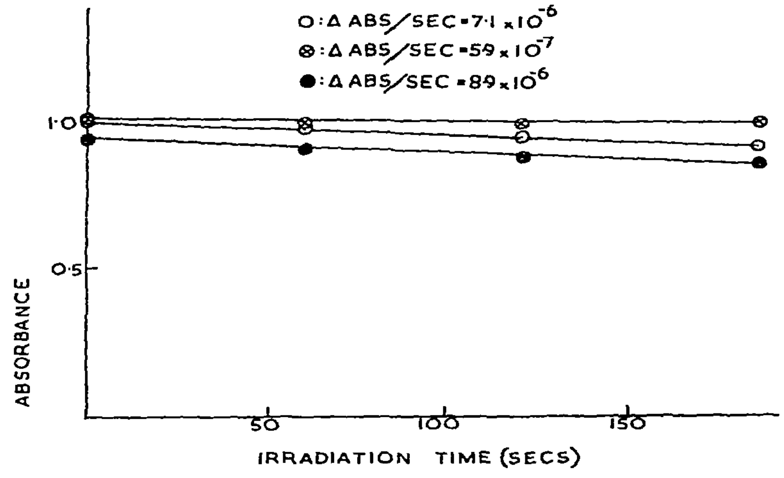


Fig. 2. Change in the absorbance of the longest wavelength absorption band of Para rosaniline in poly(vinyl alcohol) film (25 μm thick) containing O— no additives, ⊗—10^{-4}M tetracyanoethylene and ●— 10^{-4}M 4-hydroxy-2,2,6,6-tetramethylpiperidine-*N*-oxy. (λ max = 585 nm).

acetone, a very powerful electron trap,[14] completely inhibited transient absorption. Saturation of the dye solutions with another well known electron trap, nitrous oxide,[14] also completely inhibited transient absorption. Further, following one flash the visible absorptions of the dyes showed virtually no change in the presence of the electron traps whereas they were significantly reduced in the presence of the radical trap and control solutions.

Figures 1 and 2 demonstrate the effects of the electron (I) and radical (II) traps on the rates of photofading of the two dyes, Malachite Green and Para rosaniline, in poly(vinyl alcohol) film. In agreement with the above flash photolysis data it is seen that in both cases the presence of the electron trap (I) inhibits fading of the dyes by one order of magnitude less than the control films. The radical trap (II) had virtually no effect on the fading rates of the dyes. Evidently, once the radical is formed the presence of the radical trap has no effect on the subsequent reaction steps. As a matter of interest another radical trap of the hindered phenol type (Topanol OC-2,6-ditert-butyl-*p*-cresol)[15,16] also had little effect on transient absorption and dye fading.

It would appear from the above results that the electron transfer process in reaction (2) is an extremely important step in the photofading mechanism of basic triphenylmethane dyes. Conclusive evidence for this is shown by the effects of nitrous oxide on radical formation (Table 1). It is also reasonable to conclude that the high light stability of these dyes in an acrylic environment could be due to the electron trapping ability of the cyano-groups.

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