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LIGHTFASTNESS AND SPECTROSCOPIC PROPERTIES OF BASIC TRIPHENYLMETHANE DYES: EFFECT OF THE SUBSTRATE

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SUMMARY

The lightfastness of five basic triphenylmethane dyes in cotton and acrylic fibres is compared with their primary photochemical behaviour on flash photolysis in appropriate model solvents. The low lightfastness of the dyes in cotton is paralleled by the observation of strong transient absorption in propan-2-ol whereas their higher lightfastness in acrylic fibre is paralleled by a lack of transient absorption in acetonitrile. The transient species is attributed to the triphenylmethane radical formed by electron transfer. Further, the relative importance of photoreduction and triplet sensitisation in dye fading is also examined using benzhydrol as a hydrogen-atom donor and benzophenone as a triplet sensitiser.

1. INTRODUCTION

Basic dyes based on triphenylmethane are historically interesting, as they were amongst the earliest synthetic dyes to be discovered. However, because of their poor lightfastness in cotton and wool, their use was gradually discontinued until it was found that they would dye acrylic fibres to give bright shades with good lightfastness.[1] Although a number of research papers have appeared dealing with the photofading of triphenylmethane dyes in both solution and polymer films, no definite conclusions have been reached to account for the effect of the substrate.[2–6]

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One tentative suggestion is that differences in the moisture content of the fibres could account for the difference in lightfastness.[1–2] Here we have used conventional flash photolysis to examine the effect of environment on the lightfastness of basic triphenylmethane dyes. Recently, we found that these techniques provide valuable information on the effect of environment on the lightfastness of anthraquinone disperse dyes.[7–10] Five commercial basic triphenylmethane dyes were selected for study, the structures of which may be obtained from the colour index through their chemical constitution numbers given in Table 1 later.

Finally, we have also examined the photochemical behaviour of one dye, Malachite Green, in polymer films and solution in the absence and presence of a hydrogen-atom donor, benzhydrol, and a triplet sensitiser, benzophenone.

2. EXPERIMENTAL

2.1. *Materials*

The dyes, Crystal Violet and Astrazone Blue G (Bayer, West Germany) and Brilliant Green YN (I.C.I. Ltd) were obtained from their respective manufacturers while Malachite Green and Pararosaniline were purchased from Hopkin & Williams Ltd, UK.

The dyes were applied to the fabrics (cotton poplin and Orlon) from an aqueous dyebath containing 1% acetic acid. The cotton was mordanted beforehand with tannic acid and antimony potassium tartrate. See Giles[11] for further experimental details.

Films of poly(acrylonitrile) (from Orlon fibre) and poly(vinylalcohol) (25 μm thick) were prepared by casting 5% solutions of the polymers in dimethylformamide and water/ethanol mixture (100 : 10 v/v) respectively on to glass plates and allowing the solvents to evaporate overnight in an air-oven at 30°C. The poly(acrylonitrile) solution was filtered beforehand to remove the delustrant (titanium dioxide). Requisite amounts of Malachite Green dye with and without benzhydrol and benzophenone were added to the solutions beforehand. The final concentrations of dye and benzhydrol or benzophenone in the polymer films were about 5×10^{-4} and 10^{-3} M respectively.

All the solvents used were of Analar or spectroscopic quality.

2.2. *Lightfastness*

The dyed fabrics and films were irradiated in a Xenotest-150 fadeometer (Original Hanau, Quarzlampen, G.m.b.H.) set-up for simulated sunlight exposure conditions out-of-doors. Lightfastness was assessed in accordance with the standard I.S.O. test method.[12]

2.3. *Spectroscopic experiments*

Ultraviolet-visible absorption spectra were recorded using a Perkin–Elmer Model 554 spectrometer.

The flash photolysis experiments were carried out using a microsecond apparatus with a photoflash of 300J and a half-life of 10 μs.

2.4. *Continuous photolysis*

Continuous photolysis experiments on dye solutions were carried out using a Microscal apparatus containing a 500W mercury/tungsten lamp.[13] The light source was filtered with a 0·5% w/v aqueous solution of potassium dichromate (wavelengths > 500 nm).

3. RESULTS AND DISCUSSION

From the lightfastness data shown in Table 1 it is seen that all the dyes have higher lightfastness values in an acrylic substrate than in cotton. In agreement with this data, it is also seen from Table 1 that for all the dyes, whereas no transient absorption is observed in nitrogen saturated acetonitrile, a good model for acrylic fibres, strong transient absorption is observed in propan-2-ol, a good model for cotton. The addition of up to 50% v/v of water to the propan-2-ol had no effect on the intensity of the transient absorption, possibly indicating that moisture content has no effect on the photochemical behaviour of the dyes as suggested previously.[1,2] Further, following one flash, the visible absorptions of all the dyes in anaerobic propan-2-ol decrease substantially whereas those in acetonitrile show very little change. This is demonstrated in Fig. 1 for Malachite Green. The addition of dilute hydrochloric acid to the

TABLE 1
LIGHTFASTNESS AND FLASH PHOTOLYSIS OF TRIPHENYLMETHANE DYES

Dye	*Colour index Constitution No.*	*Transient absorption*		*Lightfastness 1/1 Depth*	
		Acetonitrile	*Propan-2-ol*	*Acrylic*	*Cotton*
Malachite Green (Basic Green 4)	4200	None	Strong	3	1
Brilliant Green YN (Basic Green 1)	42040	None	Strong	3	1
Crystal Violet (Basic Violet 3)	42555	None	Very strong	3	1
Astrazone Blue G (Basic Blue 1)	42025	None	Strong	3	1
Pararosaniline (Basic Red 9)	42500	None	Strong	4–5	1

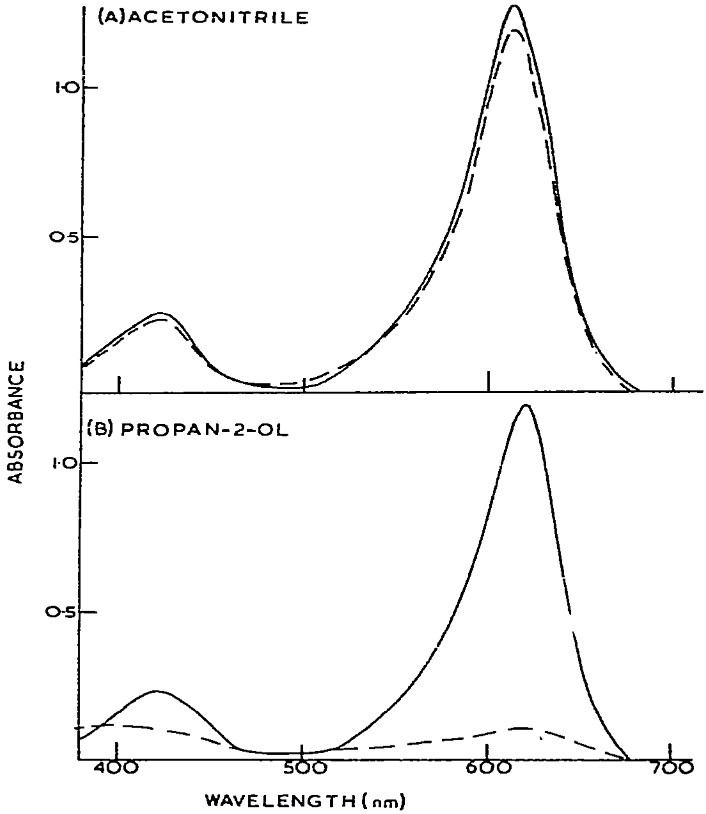

Fig. 1. Absorption spectra of 10^{-6} M solutions (10 cm path length) of Malachite Green in (A) acetonitrile and (B) propan-2-ol before (——) and after (– – –) one photoflash.

photolysed solutions did not regenerate the dyes indicating that under our conditions fading of the dyes to their leuco-form is not an important mechanism. No transient absorption or dye fading occurred on flashing air-saturated solutions, indicating that oxygen is effectively quenching the excited triplet state of the dyes. This observation also supports earlier conclusions[4,5] that dye fading proceeds via the excited triplet state (none of the dyes studied here exhibited any phosphorescence emission). Thus, it is evident that there is a correlation between the lightfastness of the dyes in fabric and their photochemical behaviour on flash photolysis in solution despite (a) a change in the nature of the substrate from solid polymer to solution and (b) the presence of delustrant in the fabric.

The transient absorption spectra of all the dyes in anaerobic propan-2-ol are shown in Fig. 2. It is seen that the transient species are similar with wavelength maxima at about 390 nm. The transients for all the dyes have a mean lifetime ($\tau_{1/e}$) of 50 ms. It is also seen from Fig. 2 that apart from a small 'red'-shift, the absorption spectra of all the transients are similar to that of the tri-(4-dimethylaminophenyl)methane radical produced during the electrolytic reduction of Crystal Violet in dimethylformamide.[4] The red-shift of the absorption spectrum of the radical in dimethylformamide is due to the greater polarity of this solvent compared with that of propan-2-ol.

The triphenylmethane radical is a stable species but is photolysed rapidly on exposure to ultraviolet light.[4] Thus, the decay of the radical observed on flash photolysis is due to its subsequent rapid photochemical decomposition by the intense continuous monitoring light source. However, continuous photolysis of the dyes with a filtered light source (wavelengths > 500 nm) in anaerobic propan-2-ol results in a gradual decrease in the intensity of the longest wavelength absorption band of the dye and the appearance of a weak absorption at about 400 nm. The new band at 400 nm is due to the formation of the triphenylmethane radical which is stable in the presence of visible light wavelengths > 500 nm. This effect is shown in Fig. 3 for Malachite Green. The

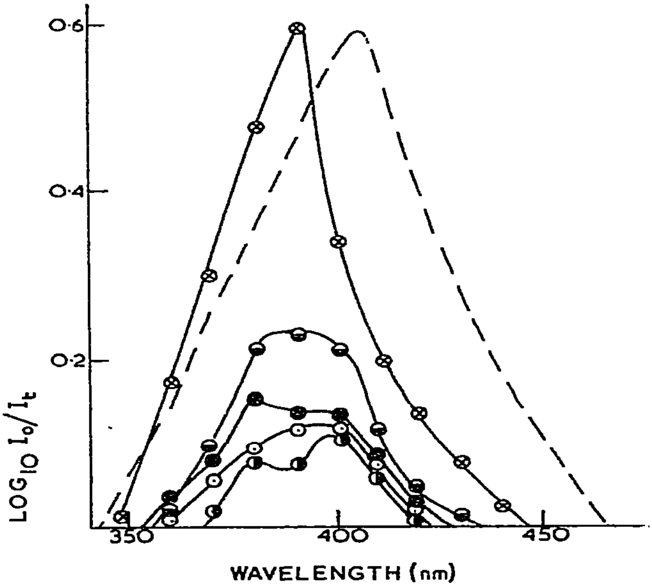

Fig. 2. Transient absorption spectra produced in the flash photolysis of nitrogen saturated (<5 ppm oxygen) 10^{-6} M solutions of ○-Brilliant Green YN, ◑-Malachite Green, ●-Astrazone Blue G, ⊖-pararosaniline and ⊗-Crystal Violet in propan-2-ol compared with the absorption spectrum of tri-(4-dimethylaminophenyl)methyl radical in dimethylformamide (– – –).

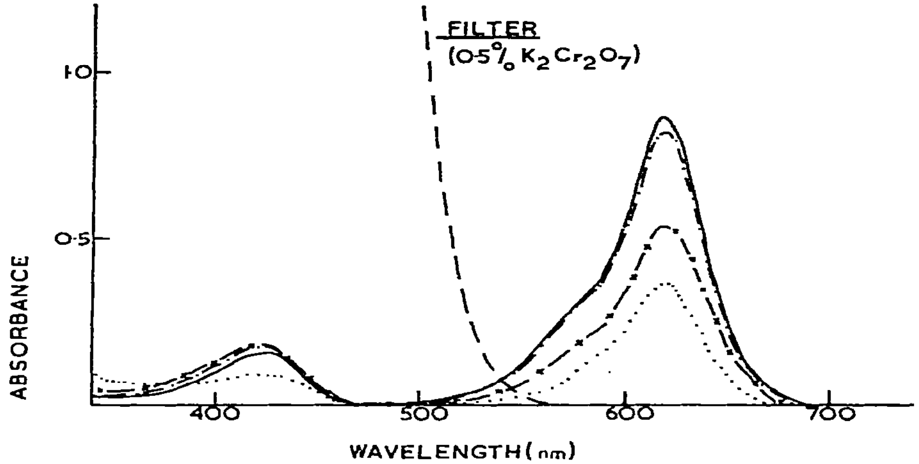

Fig. 3. Absorption spectrum of Malachite Green in anaerobic propan-2-ol after 0 h (——) 6 h (–·–) 15 h (–×–) of irradiation in the Microscal apparatus using filtered light (wavelengths >500 nm), and (. . . .) subsequent exposure of photolysed solution to unfiltered light (wavelengths >300 nm) for 0·5 h. Absorption spectrum of 0·5% w/v potassium dichromate in water as the filter solution (1 cm path length) (- - -).

fact that the radical is unstable on exposure to ultraviolet and visible light of wavelength < 500 nm is shown by the result that the absorbance at 400 nm decreases rapidly on subsequent exposure of the dye solution to unfiltered light (Fig. 3).

One of the dyes, Malachite Green, was selected for fading studies in poly(acrylonitrile) and poly(vinyl alcohol) films. Figure 4 compares the rates of fading of the dye in both films in the absence and presence of a well-known hydrogen-atom donor, benzhydrol, and a triplet sensitiser, benzophenone. It is seen that, in the absence of these compounds, the dye fades by half an order of magnitude faster in poly(vinyl alcohol) than in poly(acrylonitrile). The presence of benzhydrol and benzophenone however, markedly accelerates the fading of the dye in both polymer films; the benzophenone being much more effective than the benzhydrol. At a concentration of 10^{-3} M, whereas benzhydrol increased the rate of fading by one order of magnitude in both polymer films, benzophenone increased the rate by two orders of magnitude in poly(acrylonitrile) and three orders of magnitude in poly(vinyl alcohol).

In agreement with the above fading rates on poly(acrylonitrile) film the presence of both benzhydrol and benzophenone initiated transient formation on flash photolysis of the dye in acetonitrile (Figs. 5 and 6 respectively). Again benzophenone was much more efficient than benzhydrol. For example, whereas

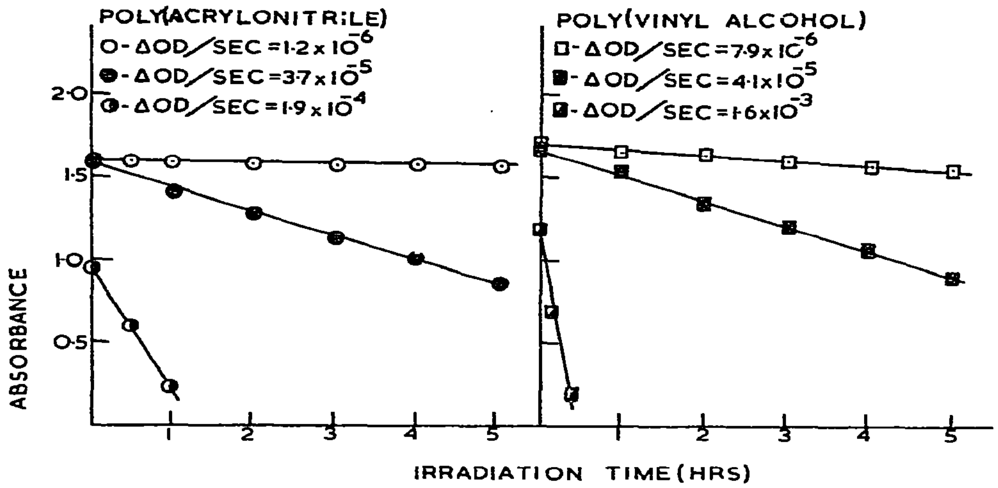

Fig. 4. Change in the optical density of the longest wavelength absorption band of Malachite Green in Orlon (617 nm) and poly (vinyl alcohol) (620 nm) films (25 μm thick) containing no sensitiser (○, □), 10^{-3} M benzhydrol (●, ■) and 10^{-3} M benzophenone (◐, ▨).

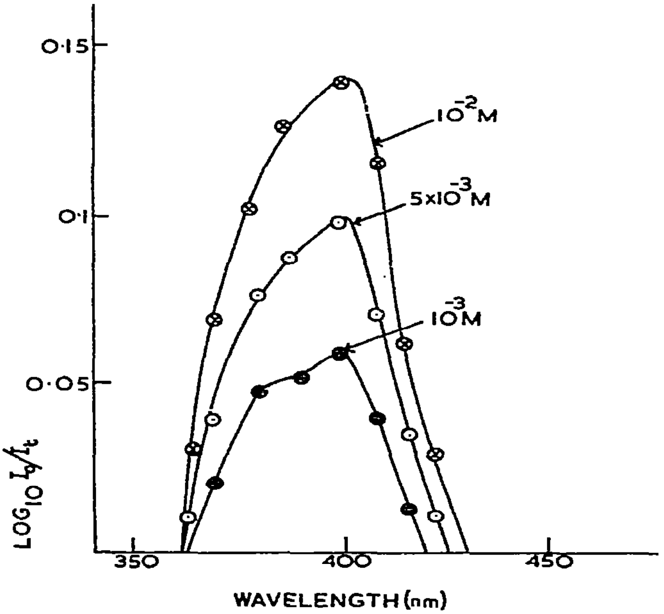

Fig. 5. Transient absorption spectra produced in the flash photolysis of nitrogen saturated (<5 ppm oxygen) 10^{-6} M solutions of Malachite Green in acetonitrile containing 10^{-3} M (●), 5×10^{-3} M (○) and 10^{-2} M (⊗) concentrations of benzhydrol.

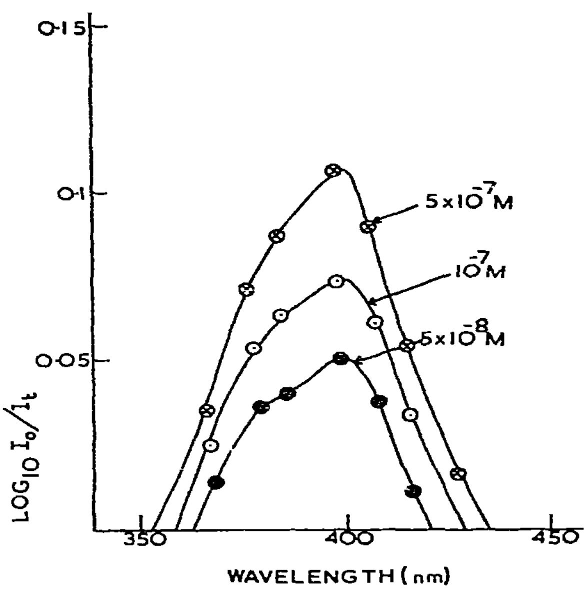

Fig. 6. Transient absorption spectra produced in the flash photolysis of nitrogen saturated (<5 p.p.m. oxygen) 10^{-6} M solutions of Malachite Green in acetonitrile containing 5×10^{-8} M (●), 10^{-7} M (○) and 5×10^{-7} M (⊗) concentration of benzophenone.

a 10^{-2} M concentration of benzhydrol was required to induce maximum transient formation from the dye (Fig. 5) only a 5×10^{-7} M concentration was required for benzophenone (Fig. 6).

Thus, as found earlier for anthraquinone disperse dyes,[7–10,14] the results of flash photolysis on the basic triphenylmethane dyes are also very useful in the interpretation of their light fastness properties in both acrylic and cotton fibres. The observation of low light fastness for the dyes in cotton fibre is paralleled by strong transient absorption in propan-2-ol whereas their higher light fastness in acrylic fibre is paralleled by a lack of transient absorption in acetonitrile. The former result indicates that the dyes are more easily photoreduced to give the triphenylmethane radical in an environment like cotton. This is supported by the observation that a powerful reducing agent, benzhydrol, induces formation of the radical and accelerates fading of the dyes in an acrylic environment. Finally, the importance of the excited triplet state of the dye in fading is demonstrated by two observations. First, the presence of oxygen inhibits transient formation and dye fading and secondly, the presence of a powerful triplet sensitiser, benzophenone, markedly accelerates these processes in an acrylic environment.

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