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Flash Photolysis Studies of a Sulphonated Bis-styryl Biphenyl Fluorescent Dye

K. J. Smit* & K. P. Ghiggino‡

Department of Physical Chemistry, University of Melbourne, Victoria 3052, Australia

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ABSTRACT

Long-lived (μs–ms) oxygen-insensitive transient species have been detected during laser flash photolysis of solutions of a sulphonated bis-styryl biphenyl dye. The transient species are readily quenched by the reducing agents iodide and sulphite ions but their yield is enhanced in the presence of oxidizing ions. It is proposed that the transients are dye radical cations formed following monophotonic photoionization. Transient quenching is also observed in the presence of indole, tryptophan and tryptophyl peptides and the relevance of these results to the sensitized photodegradation of the protein fibre, wool keratin, in the presence of this fluorescent whitening dye is discussed.

INTRODUCTION

Dyes which absorb in the UV spectral region and emit blue fluorescence are widely used to whiten materials including paper, plastics and textiles.[1] A major problem associated with the use of such fluorescent whitening agents on protein fibres such as wool is that dye-sensitized photodegradation of the fibre occurs.[2–6] The mechanism for the degradation process has not been resolved although oxygen and moisture appear to be important factors.[4–6] Tryptophyl residues in the protein have been shown to be particularly susceptible to photodegradation in both natural and fluorescently whitened wool.[2–9]

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* Present address: Materials Research Laboratory, DSTO Melbourne, PO Box 50, Ascot Vale, Victoria 3032, Australia.

‡ Author to whom correspondence should be addressed.

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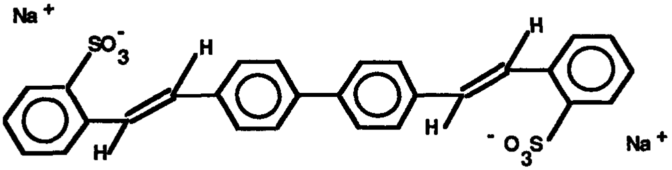

Fig. 1. Structure of the fluorescent whitening dye, **I**.

In a previous paper we reported the fluorescence and singlet-state *trans–cis* photoisomerization behaviour of stilbene-based and bis-styryl biphenyl fluorescent whitening dyes in various media and noted that energy transfer from the excited dye molecules to wool pigments may be a factor in sensitizing degradation of the fibre.[10] However, in other classes of dyes, longer-lived triplet excited states and free radicals have been implicated in sensitized photodegradation of substrates. In particular, triplet states can generate reactive singlet excited oxygen.[11,12] In the present work, laser flash photolysis measurements have been applied to investigate the possible involvement of triplet states and radical species in the photochemistry of a commercial bis-styryl biphenyl fluorescent dye **I** (Fig. 1).

EXPERIMENTAL

The laser flash photolysis system used in this work incorporated a Nd^{3+}/silicate glass laser rod pumped with a helical flash lamp in a Korad K1 housing (Union Carbide). The laser produces 15-ns (FWHM) pulses of approximately 1 J at 1062 nm when passively Q-switched with bis(4-dimethylaminodithiobenzil)nickel (Eastman) in chloroform. Frequency doubling of the fundamental in a temperature-tuned caesium dihydrogen arsenate crystal was used in conjunction with frequency mixing in an angle-tuned rubidium dihydrogen phosphate crystal (Quantum Technology) to provide pulses at 354 nm for sample excitation. A series of neutral density filters could be used to attenuate the exciting pulse intensity.

The monitoring beam from a stabilized 150 W-xenon arc lamp (Rofin), filtered to remove UV light, was passed at right angles to the excitation pulse through a 1-cm pathlength quartz cuvette containing the sample. A monochromator (Jobin-Yvon H-10) isolated the wavelength of the monitoring light. The detection system consisted of an RCA 1P28 photomultiplier (S-5 response) and a Tektronix 7633 storage oscilloscope (7A26 amplifier, 7B53A timebase). The oscilloscope trace was digitized using a video camera/microcomputer arrangement and the data analysed using non-linear least-squares iterative procedures.

To test the system the transient formation from indole in degassed aqueous solutions at pH 6 was studied. Lifetimes of 15·2 μs and 1·1 μs were obtained for the indole triplet and cation radical respectively, in agreement with published values of 15–16 μs[13] and 1 μs[14] for these species.

trans-([1,1′-Biphenyl]-4,4′-diyldi-2,1-ethenediyl)-bis[benzene-2-sulphonate], disodium salt (Uvitex NFW Ciba-Geigy, reg. no. [60317-04-6]), **I**, was recrystallized three times from ethanol/water before use. Dye concentrations of approximately 2×10^{-4} M were used for the flash photolysis studies. Indole (Hopkin and Williams, L. R.) was purified by vacuum sublimation. D,L-Tryptophan (BDH), 1-methylindole (Aldrich), 3-methylindole (Sigma), L-tryptophan-L-alanine monohydrate (Cyclochemicals), L-alanyl-L-tryptophan (Sigma), L-cystine (BDH) and D,L-serine (BDH) were used as received. Distilled water was further purified in a Milli-Q reagent water system before use, while methanol was redistilled from A.R. grade solvent. Thin films of poly(vinyl alcohol) (PVA, Polysciences) containing the dye were prepared by casting a 4% aqueous solution of the polymer onto glass plates and allowing it to dry in air.

RESULTS AND DISCUSSION

The fluorescence and photoisomerization properties of **I** in various solvents have been characterized by us previously.[10] The transient absorption spectra of **I** in air-saturated aqueous and methanol solutions recorded immediately following excitation by the laser pulse are presented in Fig. 2. Identical results were obtained in degassed solutions. Within the time resolution of the flash photolysis system (~15 ns) there was no evidence for any grow-in of the transient spectra. In aqueous solution two absorption bands were evident with maxima at 470 nm and 560 nm. The decay of transient absorption at both wavelengths could only be well fitted by a two-exponential function with decay lifetimes of the shorter-lived components of 215 μs (470 nm) and 110 μs (560 nm) (cf. Fig. 3). There was also a much longer-lived component which contributed significantly at both wavelengths (approx. 40% of the transient absorption), although the lifetime could not be measured precisely and is estimated to be several milliseconds. This absorption could be considered a positive constant baseline component for the purposes of fitting the transient decay curves over the first few hundred microseconds (Fig. 3).

In methanol only one transient absorption band is observed with a maximum at 570 nm (Fig. 2). A two-exponential function was again necessary to fit adequately the decay of the transient yielding a lifetime of 61 μs for the shorter-lived component with approximately 17% of the absorbance decaying over a much longer time-scale.

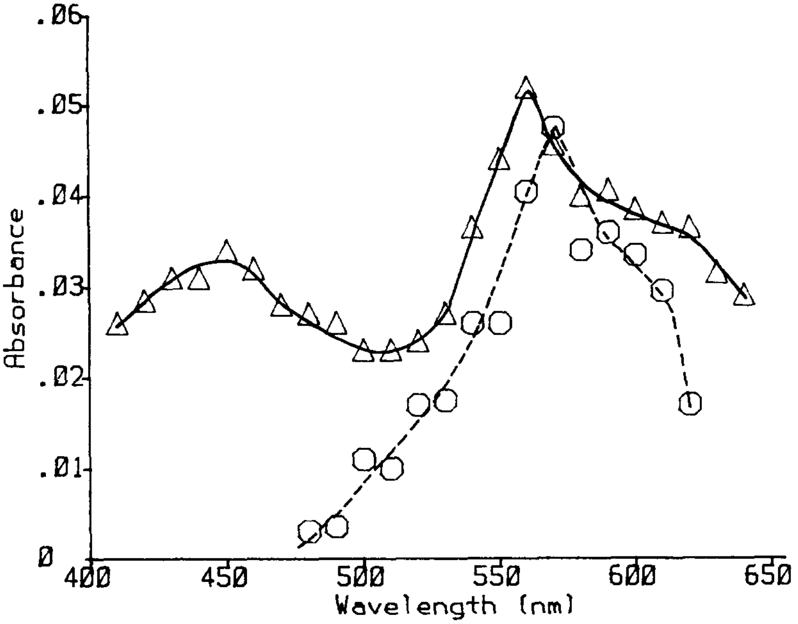

Fig. 2. Transient absorption spectra of **I** in aqueous solution (——) and methanol (– – –) recorded immediately following laser pulse excitation at 354 nm.

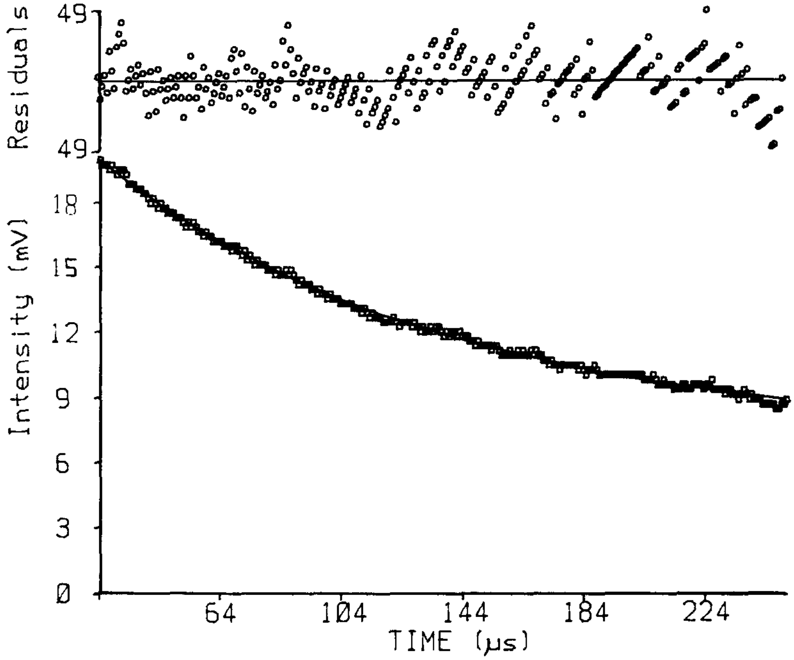

Fig. 3. Decay of transient absorption of **I** in water at 560 nm. The points represent experimental data; the solid line is a fitted curve with decay lifetime of 110 μs and positive baseline component of 36% (see text).

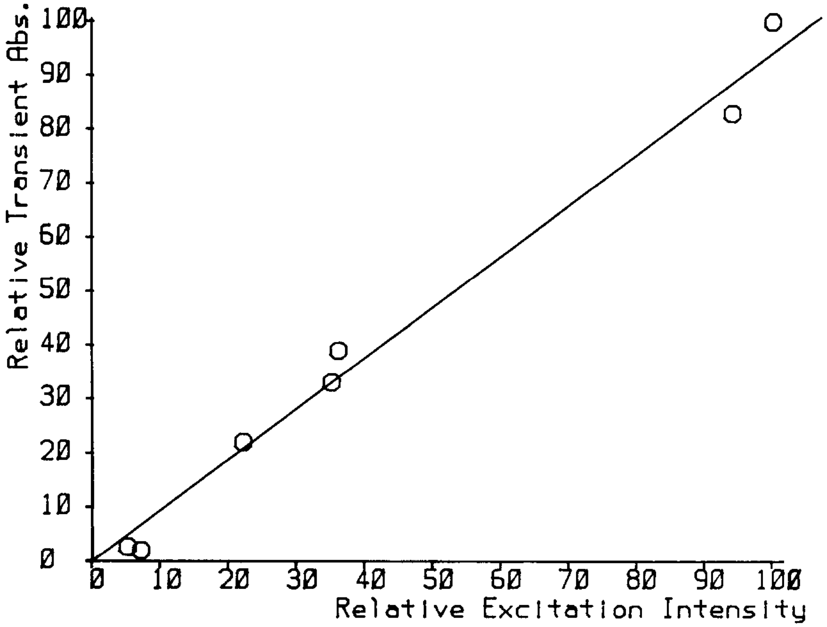

Fig. 4. Yield of transient formation in aqueous solution at 470 nm as a function of excitation intensity at 354 nm.

The absence of any quenching effect on the transients due to the presence of oxygen argues strongly against their assignment to triplet excited states or carbon-centred neutral radicals.[15] However, it is known that radical cations formed following photoionization are not very sensitive to oxygen quenching.[16,17] Attempts to detect the presence of hydrated electrons were unsuccessful although it is likely the very short-lived transient absorption of this species would be masked by the strong fluorescence signal from the solute. A linear relationship between excitation light intensity and transient absorption was determined (cf. Fig. 4). This result indicates that a monophotonic process is responsible for transient formation which has been reported for radical cation formation in other compounds,[18–21] particularly in aqueous solution.

An upper limit on the quantum yield of transient formation (ϕ_x) can be estimated from the yields of fluorescence (ϕ_f) and *trans–cis* photoisomerization (ϕ_t) determined previously[10] and assuming the total quantum yield for all processes is unity. For **I** in methanol, ϕ_f and ϕ_t are 0·95 and 0·016 respectively. Since ϕ_t represents only about one-half of the molecules undergoing initial intramolecular rotation (i.e. the photoisomerization branching ratio is approximately 0·5[10,22]), then the maximum possible ϕ_x is 0·018. For aqueous solutions ϕ_f and ϕ_t are 0·82 and 0·019 respectively and a similar calculation gives a maximum ϕ_x of 0·14.

The effect of added salts on transient formation in aqueous solution was studied in order to characterize further the nature of the transient species. Bromide and chloride ions had no effect on the transients but addition of iodide at low concentrations ($\sim 10^{-5}$ M) resulted in significant reductions in yield and lifetime. The quenching rate constants for the shorter-lived transient species with iodide ion were 4×10^{7} M^{-1} s^{-1} (470 nm) and 5×10^{7} M^{-1} s^{-1} (560 nm) whilst there was also a significant reduction in the proportion of the longer-lived transient contributing to absorbance. Similar quenching behaviour was observed in the presence of sulphite ions, suggesting that the high reducing power of iodide[23,24] and sulphite is responsible.

In contrast to the effect of reducing agents, the addition of the oxidizing ions nitrate and persulphate led to an increase in the yield and apparent lifetime of the transients. It should be noted that fluorescence from **I** was unaffected by the presence of these salts. The behaviour of the transients in the presence of oxidizing and reducing agents suggests that the species are likely to be semi-oxidized radicals formed following photoionization of the dye. These species have also been detected in similar studies on solutions of pyrazoline-based fluorescent whitening agents.[25] Strong solvent stabilization of a transient product or its hydrolysis by water may be responsible for the presence of the additional transient species present in aqueous solution with absorption maximum at 470 nm which is absent in methanol. The underlying much longer-lived transients might be attributed to photodegradation intermediates formed from the initial radical ions. Long-lived ($>300\,\mu$s) transient absorption was also observed for **I** in solid poly(vinyl alcohol) films at both 470 nm and 560 nm indicating the photochemical process also occurs in the solid state.

The photodegradation of the dye may be readily followed by absorption measurements and a number of oxidized cleavage photoproducts, including aldehyde and carboxylic acid derivatives of benzenesulphonate and biphenyl have been identified previously.[1,6] It was noted that in the presence of persulphate ions, where transient formation is enhanced, the formation of photo-oxidation products of **I** was accelerated,[26] suggesting that the transient species may be involved in the overall decomposition of the dye.

Fluorescent whitening agents are known to sensitize photodegradation of protein fibres such as wool.[2-6] Amino acid residues based on the indole chromophore (i.e., tryptophan) have been found to be particularly susceptible to photodegradation.[2-9] The interaction of the transient species of **I** with model indole compounds, tryptophan and tryptophyl peptides, was therefore examined in order to determine the possible involvement of the transients in sensitized degradation pathways.

The presence of low concentrations of indole led to significant quenching

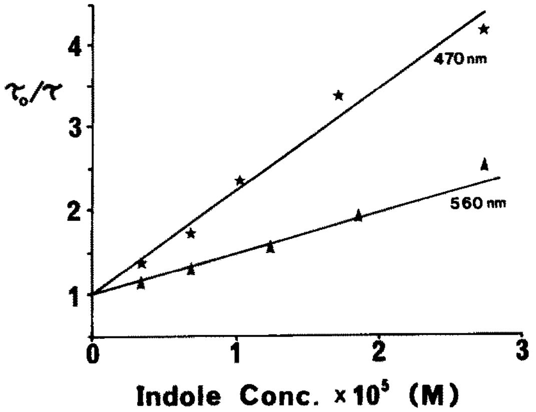

Fig. 5. Stern–Volmer type plots for the quenching of transient absorption of **I** at 470 nm and 560 nm by indole in aqueous solution.

of the transient absorption of **I**. The quenching rate constants (k_q) can be obtained from the Stern–Volmer relationship

$$\tau_0/\tau - 1 = k_q\tau_0[Q]$$

where [Q] is the quencher concentration; τ and τ_0 are the transient lifetimes in the presence and absence of quencher respectively. Stern–Volmer plots (τ_0/τ vs [Q], Fig. 5) for the quenching of the shorter-lived component by indole resulted in similar quenching rate constants of $6 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$ and $5 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$ at 470 nm and 560 nm respectively. The longer-lived dye transient absorption was also reduced in the presence of indole. 1-Methylindole and 3-methylindole also quenched the transient absorption strongly. Tryptophan and the tryptophyl peptides L-alanyl-L-tryptophan and L-tryptophyl-L-alanine were also efficient quenching species. In contrast, the amino acids D,L-serine and L-cysteine at concentrations of $10^{-4}\,\text{M}$ had no effect on dye transient absorption. There was no evidence of any interaction between indole and the ground or excited singlet state of **I**.

Indole and tryptophan are known to act as reducing agents for excited state and radical species.[27–32] It seems likely that, as observed with iodide and sulphite ions, the semi-oxidized radical ions formed through photolysis of **I** may be reduced by direct electron transfer from indole and its derivatives. Photodegradation intermediates formed from the dye radical ions are also diminished in concentration, thus decreasing the yield of the longer-lived transient species. Absorption due to oxidized indole species expected to result from the quenching of dye transients could not be detected in our experiments, probably due to the low concentration and relatively short lifetime of these species masked by the presence of a strong fluorescence signal from the dye.

The observed interaction between the transient species formed following photolysis of **I** and tryptophyl amino acid residues may be important in the dye-sensitized photodegradation of wool. Acid dyes such as **I** generally bind to proteins by a combination of electrovalent, hydrophobic and van der Waals interactions,[33] although the binding sites have generally been thought to be some distance from the protein residues susceptible to photodegradation.[34] The semi-oxidized dye radical ions formed following irradiation of the dye might promote degradation of tryptophyl and other susceptible residues by oxidation via electron transfer through the protein backbone. Long-range intramolecular electron transfer can occur through fully saturated hydrocarbon bridges over distances up to 15 Å[35–37] and within proteins intramolecular electron transfer over distances up to 20 Å has been observed.[38] Absorbed water can promote electron transfer[39] and also favours a higher yield of dye transient formation. This may be relevant to the increased photosensitized degradation of the wool fibre in the presence of moisture.[4–6]

CONCLUSION

A number of long-lived transient species are observed during flash photolysis of solutions of the sulphonated bis-styryl biphenyl dye, **I**. The yield and lifetime of the transients are insensitive to the presence of oxygen but the species readily interact with oxidizing and reducing agents. The results indicate that the initial transient species are semi-oxidized radical cations, formed following monophotonic ionization. Model indole compounds, tryptophan and tryptophyl peptides quench the dye transient species in aqueous solution. This observation suggests that oxidation of tryptophyl residues by semi-oxidized dye radical cations may make an important contribution to the sensitized photodegradation of protein fibres such as wool in the presence of fluorescent whitening agents of this type.

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