ELSEVIER

Dyes and Pigments **25** (1994) 179–204

0143-7208/94/$7.00

The Sensitized Fading of Triphenylmethane Dyes in Polymer Films. Part 2

Debra F. Duxbury

c/o Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA

(Received 21 January 1994; accepted 23 February 1994)

ABSTRACT

Investigations were performed on four acid triphenylmethane dyes, viz. Acid Blue 1, Acid Green 9, Acid Blue 15, and Acid Violet 17, in order to elucidate the complex photochemical reactions occurring on a dyed-wool/water/air system, upon exposure to ultraviolet radiation. The studies were performed using model systems of dyed poly(vinyl alcohol), methylcellulose and gelatin films. In Part 1 of this work, compounds which model protein-bound amino acids, present in wool, were examined for their ability to promote or retard dye fading on protein substrates. Part 2 focuses on three amino acids, L-arginine, L-glutamic acid and L-aspartic acid and examines the role of the amino and carboxylate groups present in these compounds in promoting dye fading. The work compares the ability of the amino acids to promote dye fading when they exist alone in the presence of dye, and when they participate in peptide bonds. The guanidino, α-amino and carboxylate groups of these compounds appear to photosensitize dye fading.

The dye fading mechanism appears to involve an excited triplet-state dye molecule and, in the presence of a photosensitizer, possibly an excited triplet-state exciplex. It also appears to be governed by (a) the ability of the substrate, or residual solvent within the substrate, to donate electrons or hydrogen atoms to the dye, (b) the degree of dye aggregation, which may be partially determined by (c) the chemical and physical structure of the substrate, and (d) the position of the water solubilizing SO_3^- group on the dye.

Eight kinetic mechanisms are proposed and discussed in terms of their likelihood of occurring for dye fading in the presence of guanidino and carboxylate groups.

1 INTRODUCTION

Triphenylmethane dyes characteristically exhibit low lightfastness on many substrates, particularly on natural fibres such as silk, cotton and wool. Consequently, the textile application of these dyes has been limited to dyeing poly(acrylonitrile), where moderate lightfastness can be attained.[1,2]

Due to their outstanding tinctorial strength and brilliant shades of red, blue and green, this class of dye possesses commercial potential to compete with the bright, fast colours available for acrylic fibres, provided they can be rendered less fugitive to light on natural fibres. This necessitates that a clear understanding of the photochemical reactions promoting dye fading be achieved.

In Part 1 of this work,[3] certain amino acid residues present in the protein fibre wool were identified as being responsible for sensitizing dye fading, whereas other amino acid-residues appeared to have little effect or retard dye fading. In particular, it was proposed that guanidino groups and carboxylate groups promote dye fading by respectively donating hydrogen atoms and electrons to the dye. Part 2 of this work focuses more closely on the amino acids L-arginine, L-aspartic acid and L-glutamic acid, which appear to promote dye fading on protein substrates. In particular, the role of the amino and carboxylate groups in promoting dye fading is examined. Evidence is sought for the possible involvement of excited triplet-state species, exciplexes and electron transfer processes. Kinetic analysis considers the likelihood of eight possible kinetic mechanisms occurring. Since the dyed wool system is expected to promote complex photochemical reactions, the studies presented here have been performed on model polymer systems based on methylcellulose (MC), poly(vinyl alcohol) (PVA) and gelatin.

2 MATERIALS AND METHODS

The four water soluble triphenylmethane dyes selected for study were Acid Blue 1 (C.I. 42045; Lissamine Turquoise VN 150, ICI), Acid Green 9 (C.I. 42100; Sandolan Brilliant Green E-6B 300%, Sandoz), Acid Blue 15 (C.I.42645; Coomassie Blue FF, ICI), and Acid Violet 17 (C.I. 42650; Coomassie Violet R 200, ICI). The purification procedure and structures of all dyes relevant to this paper are given in Part 1.[3]

Methylcellulose (Fluka) was specified as having a methoxy content of 27·5 to 32·0% and a viscosity of 350 to 550 mPa . s for a 2% concentration at 20°C. PVA (Polyscience) was specified as 99% hydrolyzed, with a molecular weight of 133 000 and a viscosity of 28 to 32 mPa . s for a 4%

aqueous solution at 20°C. Gelatin was obtained from Ajax Chemicals. All were employed without further purification and all films were prepared, stored and irradiated as described in Part 1.[3]

The film additives L-arginine (Fluka), methylguanidine sulphate (Eastman Kodak Organic Chemicals, USA), L-arginine methylester dihydrochloride (Fluka), L-glutamic acid (BDH Poole, Dorset, UK), sodium acetate (BDH Chemicals, Australia), sodium azide (Fluka), zinc sulphate heptahydrate (AnalaR, BDH Chemicals, Australia), cadmium sulphate octahydrate (Merck Pro Analyst), manganese sulphate monohydrate (Ajax Chemicals, Sydney, Australia) were used without further purification. None of these additives absorb radiation of wavelengths greater than 270 nm. All were present at concentrations of ($3{\cdot}3 \times 10^{-5} \pm 7\%$) mol/g polymer unless otherwise indicated.

Dye fading was assessed in terms of the quantum yield of dye fading Q and relative quantum yield of dye fading Q_{rel} in the same manner as described in Part 1.[3]

3 RESULTS AND DISCUSSION

3.1 The role of the α-carboxyl and α-amino groups in free amino acids

Under physiological conditions, the pH of wool is approximately 6, and the α-amino group and the α-carboxyl group of the amino acids participate in the formation of a peptide bond, except at the ends of the protein chain. Thus, the photochemistry of the dye in the presence of free amino acid may differ from when it is in a protein-bound state. This factor was overlooked in previous photochemical studies on triphenylmethane dyes in the presence of the free amino acid histidine.[4] However, the work presented by Mason *et al.*[5] provides a good illustration that this may occur.

Table 1 provides a comparison for dye fading in the presence of the free amino acids L-arginine and L-glutamic acid and structurally related derivatives in order to elucidate the role of the α-amino and α-carboxyl groups in dye fading.

It is noted that L-glutamic acid does not sensitize the fading of Acid Green 9, Acid Blue 15 or Acid Violet 17 more than sodium acetate. At first this result seems surprising, given that L-glutamic acid has twice the number of carboxylate groups than sodium acetate. However, it must be remembered that in a solid substrate the spatial distribution of a dye and additive are fixed, and therefore L-glutamic acid should not be expected to act bifunctionally, except at very high concentrations.

TABLE 1
Dye Fading in MC in the Presence of Sodium Acetate, Sodium Azide and L-Glutamic Acid and L-Arginine and their Derivatives

Film composition	$Q \times 10^5 \pm 15\%$ *α-band*[a]	$Q_{rel} \pm 8\%$ *α-band*[a]
Acid Blue 1	6·3	1·0
Acid Blue 1 + L-arginine	20·2	3·2
Acid Blue 1 + L-arginine methylester dihydrochloride	13·9	2·2
Acid Blue 1 + methylguanidine sulphate[b]	8·2	1·3
Acid Blue 1 + L-glutamic acid	15·1	2·4
Acid Blue 1 + sodium acetate	6·5	1·03
Aeid Blue 1 + sodium azide	17·6	2·8
Acid Green 9	20·0	1·0
Acid Green 9 + L-arginine	30·0	1·5
Acid Green 9 + L-arginine methylester dihydrochloride	24·0	1·2
Acid Green 9 + methylguanidine sulphate[b]	24·0	1·2
Acid Green 9 + L-glutamic acid	27·0	1·35
Acid Green 9 + sodium acetate	26·0	1·3
Acid Green 9 + sodium azide	Very large	Very large
Acid Blue 15	3·6	1·0
Acid Blue 15 + L-arginine	7·2	2·0
Acid Blue 15 + L-arginine methylester dihydrochloride	4·3	1·2
Acid Blue 15 + methylguanidine sulphate[b]	4·0	1·12
Acid Blue 15 + L-glutamic acid	6·5	1·8
Acid Blue 15 + sodium acetate	5·8	1·6
Acid Blue 15 + sodium azide	28.8	8.0
Acid Violet 17	4·3	1·0
Acid Violet 17 + L-arginine	8·2	1·9
Acid Violet 17 + L-arginine methylester dihydrochloride	5·2	1·2
Acid Violet 17 + methylguanidine sulphate[b]	5·15	1·2
Acid Violet 17 + L-glutamic acid	6·9	1·6
Acid Violet 17 + sodium acetate	7·1	1·65
Acid Violet 17 + sodium azide	30.1	7.0

The molar ratio for dye:additive is 1:12; in all cases [dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mol/g MC and [additive] = $(3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mol/g MC.
[a] See Table 1 in Part 1[3] for the wavelengths at which fading was monitored.
[b] [Methylguanidine sulphate] = 1/2[guanidino groups] (see text).

Interestingly, Acid Blue 1 is the dye most affected by L-glutamic acid, but is the dye least affected by the electron donors, sodium azide and sodium acetate, also examined in Part 1.[3] This seemingly anomalous result may be explained by examining the structures of sodium acetate and L-glutamic acid and the way each compound interacts with each dye. Examination of the dye structures reveals that only Acid Blue 1 has a

TABLE 2
Dye Fading of Acid Blue 1 in MC in the Presence of Methylguanidine Sulphate and Sodium Acetate.

Molar ratio	$Q \times 10^5 \pm 15\%$ *α-band*[a]	$Q_{rel} \pm 8\%$ *α-band*[a]
Acid Blue 1 : methylguanidine sulphate[b]		
1:0	6·3	1·0
1:10	8·6	1·36
1:12	8·3	1·32
1:15	8·6	1·37
1:20	9·4	1·49
1:25	9·6	1·53
1:30	10·8	1·72
1:35	10·4	1·65
1:40	11·1	1·76
Acid Blue 1 : sodium acetate		
1:0	6·3	1·00
1:12	6·5	1·03
1:18	8·6	1·36

[Dye] = (2·7 ± 0·2) $\times 10^{-6}$ mol/g MC.
[a] Fading was monitored at the wavelength corresponding to the peak of the α-band (see Table 1 in Part 1).[3]
[b] [Methylguanidine sulphate] = ½[guanidino groups] (see text).
Note: for a 1% dyeing of Acid Blue 1 on wool, the molar ratios for dye:guanidino groups and dye:carboxyl groups are approximately 1:28·3 and 1:66·8 (ignoring asparagine and glutamine), respectively.[9,20,22]

SO_3^- group *ortho* to the central carbon atom. This SO_3^- group will tend to stabilize the carbonium form of the dye in which the central carbon atom is positively charged. Thus, when sodium acetate is added to the dyed polymer system, the carboxylate groups will be prevented from approaching the central positive carbon atom of the dye by the negatively charged *ortho* SO_3^- group, and this may prevent the dye from abstracting an electron. However, it may be expected that if the concentration of carboxylate groups is increased for a fixed dye concentration, the SO_3^- groups of the dye may not prevent all of the carboxylate groups from being in close proximity to the electron abstracting centre of the dye. In keeping with this argument, Q_{rel} was observed to increase when the sodium acetate concentration was increased to $4{\cdot}86 \times 10^{-5}$ mol/g MC (Table 2). Conversely, if the α-amino group of L-glutamic acid interacted with the *ortho* SO_3^- group of the dye, the positively charged central carbon atom of the dye would be more accessible to carboxylate groups. This interaction would also allow the γ-carboxyl group of the free amino

acid to lie in close proximity to the *para*-nitrogen atom (which has been reported to become electron deficient in the excited state[6,7]) of the dye. Thus, if either the central carbon atom or *para*-nitrogen atoms become electron deficient upon irradiation, electron abstraction will be facilitated. Since L-glutamic acid does not appear to act bifunctionally, there may only be one electron abstracting centre in the dye molecule.

Table 1 reveals that, when the α-carboxyl group is blocked by methylation, as is the case for L-arginine methylester dihydrochloride, then sensitization is reduced from the value obtained using L-arginine. In addition, L-arginine methylester dihydrochloride produced the same sensitization as methylguanidine sulphate for all dyes except Acid Blue 1. It should be noted here that methylguanidine sulphate has the molecular formula $(CH_3NHC:NHNH_2)_2 . H_2SO_4$ and so all films containing this compound have twice the number of guanidino groups as those films containing the additives L-arginine $HN:C(NH_2)NH(CH_2)_3CH(NH_2)COOH$ and L-arginine methylester dihydrochloride $HN:C(NH_2)NH(CH_2)_3CH(NH_2)COOCH_3 . 2HCl$. However, examination of Table 2 reveals that Q_{rel} is essentially constant for mole of dye to mole of methylguanidine sulphate ratios below 1 : 20. Consequently, all tables presented in the text have been interpreted based on this and that the observed trends are not attributable to differences in the concentrations of groups modelling amino-acid residues. The results therefore show that the α-carboxyl group of L-arginine is capable of sensitizing dye fading. In the case of Acid Blue 1, not only is it apparent that blocking the α-carboxyl group removes some of the sensitization observed in the presence of L-arginine, it is also apparent that the α-amino group sensitizes dye fading. Here it is seen that Q_{rel} in the presence of the methylester is larger than in the presence of methylguanidine sulphate. Again, the most plausible explanation involves the interaction of the positively charged α-amino group with the SO_3^- groups of the dye. It is proposed that when the interaction between a positively charged group of the additive and the *ortho*-sulphonate group is strong, the positive charge on the dye spends more time on the *para*-nitrogen atom than when the interaction is weak, since in the latter case the *ortho* SO_3^- group would tend to stabilize the carbonium form of the dye.

In contrast to the situation for Acid Blue 1, L-arginine methylester dihydrochloride would not be expected to sensitize the fading of the other dyes more than methylguanidine sulphate, because the interaction between the positive groups of the additives and the SO_3^- groups on these dyes does not favour any particular resonance structure of the dye.

For Acid Green 9, Acid Blue 15 and Acid Violet 17, the reduction in Q_{rel} caused by blocking the carboxyl group of L-arginine is essentially the

same magnitude as the increase in Q_{rel} caused by the presence of sodium acetate (Table 1). This implies that the zwitterionic and guanidino moieties of L-arginine act independently and additively when sensitizing dye fading and that L-arginine, unlike L-glutamic acid, is able to act bifunctionally. This difference may arise firstly, because the probability of L-arginine being located in close proximity to the dye during the film drying process could be greater than for L-glutamic acid (owing to more favourable ionic attraction), and secondly, because the interaction between the dye and L-glutamic acid involves one mechanism, whereas with L-arginine two different mechanisms could be involved. In order to examine this point further, sodium acetate was added to MC films containing L-arginine methylester dihydrochloride or methylguanidine sulphate in the presence of dye (Table 3).

The results of this experiment (Table 3) confirm that L-arginine sensitizes the fading of Acid Green 9, Acid Blue 15 and Acid Violet 17 to essentially the same degree as L-arginine methylester dihydrochloride and methylguanidine sulphate, each in the presence of sodium acetate. The result for Acid Blue 1 in the presence of L-arginine methylester dihydrochloride and sodium acetate also confirms the result that the zwitterionic moiety and the guanidino group in arginine act independently when sensitizing dye fading. This result and that obtained for the fading of Acid Blue 1 in the presence of both methylguanidine sulphate and sodium acetate indicate that, at this concentration, sodium acetate is able to sensitize dye fading. This seems to contradict the result obtained for dye fading in the presence of sodium acetate alone (Table 3). However, it may be argued that both model amino-acid compounds, containing guanidino groups, possess at least one positive charge and so they may attract the negatively charged acetate ion or interact with the SO_3^- groups on the dye, while the film is still in the liquid state. By virtue of either interaction, the local concentration of the acetate groups in the proximity of the dye molecules (after film solidification) may be higher than that in the absence of these positively charged model amino-acid compounds, or the relative spatial orientation of the compounds may help promote sensitized dye fading.

3.2 A test for electron transfer processes occurring between compounds sensitizing dye photodegradation and dyes in MC

In order to test the proposal that electron transfer processes are occurring between the dye and a sensitizing group, cadmium sulphate octahydrate was incorporated into films containing dye in the presence of sensitizer. Where such electron transfer processes occur, Q_{rel} would be

TABLE 3

Dye Fading in MC in the Presence of Sodium Acetate and Either L-Arginine Methylester Dihydrochloride or Methylguanidine Sulphate Compared to Dye Fading in the Presence of L-Arginine or Sodium Acetate

Film composition	$Q \times 10^5 \pm 15\%$ *α-band*[a]	$Q_{rel} \pm 8\%$ *α-band*[b]
Acid Blue 1	6·3	1·0
Acid Blue 1 + L-arginine	20·2	3·2
Acid Blue 1 + sodium acetate	6·5	1·03
Acid Blue 1 + L-arginine methylester dihydrochloride + sodium acetate	18·9	3·0
Acid Blue 1 + methylguanidine sulphate[b] + sodium acetate	11·4	1·8
Acid Green 9	20·0	1·0
Acid Green 9 + L-arginine	30·0	1·5
Acid Green 9 + sodium acetate	26·0	1·3
Acid Green 9 + L-arginine methylester dihydrochloride + sodium acetate	29·0	1·45
Acid Green 9 + methylguanidine sulphate[b] + sodium acetate	31·0	1·55
Acid Blue 15	3·6	1·0
Acid Blue 15 + L-arginine	7·2	2·0
Acid Blue 15 + sodium acetate	5·8	1·6
Acid Blue 15 + L-arginine methylester dihydrochloride + sodium acetate	6·8	1·9
Acid Blue 15 + methylguanidine sulphate[b] + sodium acetate	6·7	1·85
Acid Violet 17	4·3	1·0
Acid Violet 17 + L-arginine	8·2	1·9
Acid Violet 17 + sodium acetate	7·1	1·65
Acid Violet 17 + L-arginine methylester dihydrochloride + sodium acetate	7·8	1·8
Acid Violet 17 + methylguanidine sulphate[b] + sodium acetate	9·0	2·1

The molar ratios for dye : sodium acetate : additives are 1:12:12. The molar ratio for dye: L-arginine (or sodium acetate) for films containing L-arginine (or sodium acetate) is 1:12. [Dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mol/g MC and [additives] = $(3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mol/g MC.

[a] See Table 1 Part 1[3] for the wavelengths at which fading was monitored.

[b] [Methylguanidine sulphate] = 1/2[guanidino groups] (see text).

expected to be reduced more than can be accounted for by the effect of cadmium sulphate octahydrate scavenging electrons from the MC/H_2O system.

The Q_{rel} values obtained for dye fading in the presence of both sensitizer and cadmium sulphate octahydrate are presented in Table 4. A comparison between Tables 1 and 4 reveals that for all dyes cadmium sulphate octahydrate reduces the sensitization caused by L-arginine

TABLE 4
The Effect of Cadmium Sulphate on Dye Fading in MC and in the Presence of Dye Fading Sensitizers

Film composition	*Column 1*		*Column 2*
	$Q \times 10^5 \pm 15\%$ *α-band*[a]	$Q_{rel} \pm 8\%$ *α-band*[a]	*Reduction in* Q_{rel}[b] *α-band*[a]
Acid Blue 1	6·3	1·0	—
Acid Blue 1 + cadmium sulphate	5·2	0·83	0·17 ± 0·07
Acid Blue 1 + sodium acetate + cadmium sulphate	5·5	0·87	0·16 ± 0·15
Acid Blue 1 + L-arginine methylester dihydrochloride + cadmium sulphate	10·4	1·65	0·55 ± 0·30
Acid Blue 1 + methylguanidine sulphate[c] + cadmium sulphate	6·6	1·05	0·25 ± 0·20
Acid Green 9	20·0	1·00	—
Acid Green 9 + cadmium sulphate	12·4	0·62	0·38 ± 0·05
Acid Green 9 + sodium acetate + cadmium sulphate	14·5	0·73	0·57 ± 0·15
Acid Green 9 + L-arginine methylester dihydrochloride + cadmium sulphate	17·2	0·86	0·34 ± 0·15
Acid Green 9 + methylguanidine sulphate[c] + cadmium sulphate	16·0	0·80	0·40 ± 0·15
Acid Blue 15	3·6	1·00	—
Acid Blue 15 + cadmium sulphate	1·95	0·54	0·46 ± 0·04
Acid Blue 15 + sodium acetate + cadmium sulphate	2·3	0·63	0·97 ± 0·20
Acid Blue 15 + L-arginine methylester dihydrochloride + cadmium sulphate	3·0	0·84	0·36 ± 0·15
Acid Blue 15 + methylguanidine sulphate[c] + cadmium sulphate	3·1	0·87	0·25 ± 0·15
Acid Violet 17	4·3	1·0	—
Acid Violet 17 + cadmium sulphate	1·7	0·40	0·60 ± 0·03
Acid Violet 17 + sodium acetate + cadmium sulphate	1·9	0·43	1·22 ± 0·15
Acid Violet 17 + L-arginine methylester dihydrochloride + cadmium sulphate	3·0	0·69	0·51 ± 0·15
Acid Violet 17 + methylguanidine sulphate[c] + cadmium sulphate	3·0	0·70	0·50 ± 0·15

The molar ratios for dye : fading sensitizer : Cd^{2+} are 1:12:12. [Dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mol/g MC. [Dye fading sensitizer] = $[Cd^{2+}] = (3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mol/g MC.

[a] See Table 1 in Part1[3] for the wavelengths at which fading was monitored.

[b] This corresponds to the amount Q_{rel} is reduced from its value for dye fading in the presence of sensitizer alone.

[c] [Methylguanidine sulphate] = ½[guanidino groups] (see text).

methylester dihydrochloride, methylguanidine sulphate and sodium acetate. Each result presented in column 2 of Table 4 has been calculated by substracting each value of Q_{rel} presented in column 1 of Table 4 from its corresponding value of Q_{rel} for dye fading in the presence of sensitizer alone (Table 1).

The evidence does not prove conclusively that electron transfer occurs between each dye and each compound containing guanidino groups. This conclusion is reached because, in view of the experimental errors, most reductions in Q_{rel} must be considered to have the same magnitude as those observed for dye fading in the presence of cadmium sulphate octahydrate alone (Table 4), and in the latter case it is believed that cadmium sulphate octahydrate scavenges electrons from the substrate/H_2O system, as examined in Part I of this work[3].

The results for Acid Blue 1 in the presence of both L-arginine methylester dihydrochloride and cadmium sulphate octahydrate, and Acid Blue 15 in the presence of both methylguanidine sulphate and cadmium sulphate octahydrate appear to show that cadmium sulphate octahydrate scavenges more and less electrons, respectively, than in the presence of dye alone. However, these trends must be considered to be barely significant in view of the experimental errors.

Similarly the results do not show unequivocally that electron transfer occurs between sodium acetate and the dyes Acid Blue 1 and Acid Green 9. In contrast, the results for Acid Blue 15 and Acid Violet 17 (Table 4) indicate that this process takes place, because each Q_{rel} for these dyes in the presence of sodium acetate is reduced more by the addition of cadmium sulphate octahydrate than can be accounted for by the ability of Cd^{2+} to scavenge electrons from the substrate/H_2O system.

3.3 Excited triplet state quenching

Triphenylmethane dyes are characterized by an exceptionally high absorptivity in the visible region of their spectrum. Such strong absorption implies very short radiative lifetimes, and accordingly these molecules are almost entirely non-fluorescent in fluid media.[8] The weak fluorescence is attributed to an extremely rapid non-radiative deactivation process which is brought about by intramolecular rotation of the flexible aryl groups. This process has been recently reviewed.[9] There are a number of ways in which the molecular motion may be suppressed, e.g. by introducing bulky substituents into the dye structure, or a high molecular weight polymer to which the dye can bind, or, as is relevant here, by incorporating the dye into a solid substrate. The latter will also reduce collisional quenching of the excited states.

Reduced molecular motion will diminish the competitive radiationless internal conversion process and enhance fluorescence. The increased lifetime of the first excited singlet state will similarly enhance intersystem crossing to the excited triplet state, perhaps resulting in increased dye photodegradation or phosphorescence to regenerate the ground-state dye molecule. Fluorescence of certain triphenylmethane dyes has been observed in solid polymeric media such as nylon.[10] On the basis of this, the involvement of the excited singlet-state dye or exciplex is possible. However, no reports could be found for a specific excited singlet-state quencher of triphenylmethane dyes, and tests to determine whether a number of known singlet-state quenchers were able to quench this excited state could not be performed due to lack of available facilities to measure dye luminescence. Instead, attention was directed towards the involvement of excited triplet-state species.

Paramagnetic metal ions and heavy atoms have been reported to quench triplet states.[11–16] Of these species, the metal ions, Zn^{2+},Cd^{2+} and Mn^{2+} have been reported as poor singlet-state quenchers.[11] In particular, only Mn^{2+} is paramagnetic and it has been reported to quench the triplet state of the triphenylmethane dye Acid Blue 7, when in the form of manganese sulphate.[5] Accordingly, in order to ascertain whether dye fading in MC occurred via the excited triplet-state dye molecule, the effect of manganese sulphate monohydrate on dye fading was examined. The results are reported in Table 5 and show that, for all dyes, manganese sulphate monohydrate reduces Q_{rel} from the value obtained in the absence of quencher. This implies that the excited triplet-state dye is involved in dye photodegradation.

The reduction in Q_{rel} for Acid Green 9 is not as large as that observed for the other dyes. This may suggest that the triplet state of the dye is not significantly involved in the photodegradation and that perhaps the excited singlet state is more important. Alternatively, since this dye fades the fastest of all dyes in the absence of additives (Table 5) there may be insufficient manganese sulphate monohydrate in the film to observe an effect on fading. This latter hypothesis is supported in view of the fact that when a higher concentration of Mn^{2+} ($(6{\cdot}6 + 0{\cdot}5) \times 10^{-5}$ mol/g MC) was incorporated into the film a significant reduction of Q_{rel} was observed (see results in parentheses in Table 5).

By comparing the results in Table 5, it can be seen that the electron scavenger cadmium sulphate octahydrate reduces the fading of Acid Green 9 and Acid Violet 17 more efficiently than the triplet-state quencher manganese sulphate monohydrate.

By analogy with the quenching effect manganese sulphate monohydrate exerts on the triplet-state dye monomers in MC, Mn^{2+} may be

TABLE 5
Dye Fading in MC in the Presence of Cd^{2+}, Mn^{2+} and Zn^{2+}, and Dye Fading in PVA in the Presence of Cd^{2+} and Mn^{2+}

Film composition	*Substrate*	$Q \times 10^5 \pm 15\%$		Q_{rel}	
		α-band[a]	*β-band*[a]	*α-band*[a]	*β-band*
Acid Blue 1	MC	6·3	—	1·0	—
Acid Blue 1 + Cd^{2+}	MC	5·2	—	0·83 ± 8%	—
Acid Blue 1 + Mn^{2+}	MC	5·0	—	0·79 ± 8%	—
Acid Blue 1 + Zn^{2+}	MC	4·6	—	0·73 ± 8%	—
Acid Blue 1	PVA	7·0	—	1·0	—
Acid Blue 1 + Mn^{2+}	PVA	6·5	—	0·93 ± 8%	—
Acid Green 9	MC	20·0	—	1·0	—
Acid Green 9 + Cd^{2+}	MC	12·4	—	0·62 ± 8%	—
Acid Green 9 + Mn^{2+}	MC	17·6	—	0·88 ± 8%	—
Acid Green 9 (+ Mn^{2+})[b]	MC	(14·6)[b]	—	(0·73 ± 8%)[b]	—
Acid Green 9 + Zn^{2+}	MC	13·8	—	0·69 ± 8%	—
Acid Green 9	PVA	14·2	—	1·0	—
Acid Green 9 + Mn^{2+}	PVA	12·8	—	0·90 ± 8%	—
Acid Blue 15	MC	3·6	—	1.0	1·0
Acid Blue 15 + Cd^{2+}	MC	1·95	—	0·54 ± 8%	—
Acid Blue 15 + Mn^{2+}	MC	2·2	—	0·62 ± 8%	—
Acid Blue 15 + Zn^{2+}	MC	2·15		0·6 ± 8%	—
Acid Blue 15	PVA	2·65	6·1	1·0	1·0
Acid Blue 15 + Mn^{2+}	PVA	1·70	3·7	0·64 ± 8%	0·61 ± 8%
Acid Violet 17	MC	4·3	—	1·0	—
Acid Violet 17 + Cd^{2+}	MC	1·7	—	0·40 ± 8%	—
Acid Violet 17 + Mn^{2+}	MC	2·6	—	0·61 + 8%	—
Acid Violet 17 + Zn^{2+}	MC	2·1	—	0·49 ± 8%	—
Acid Violet 17	PVA	2·4	6·8[c]	1.0	1·0
Acid Violet 17 + Mn^{2+}	PVA	1·7	4·8	0·70 ± 8%	0·71 ± 8%[c]

[a] See Table 1 in Part 1[3] for the wavelengths at which fading was monitored.
[b] For this film the molar ratio for dye : Mn^{2+} was 1:24 and $[Mn^{2+}] = (6·6 \pm 0·5) \times 10^{-5}$ mol/g MC.
[c] For fading at 35 min exposure to radiation (see text).
[Dye] = $(2·7 \pm 0·2) \times 10^{-6}$ mol/g polymer, [additive] = $(3·2 \pm 0·2) \times 10^{-5}$ mol/g polymer; thus, the molar ratio for dye : additive was 1:12.

expected to quench triplet-state dimers. Part 1 of this work[3] revealed that the triaminotriphenylmethane dyes Acid Blue 15 and Acid Violet 17 show a propensity to dimerize, particularly in PVA and gelatin. Unequivocal evidence for the participation of the dimer in photodegradative mechanisms of Acid Blue 15 and Acid Violet 17 is difficult to obtain without spectrally deconvoluting the dye spectra to monitor fading at the

TABLE 6
Quantum Yields and Relative Quantum Yields of Dye Fading in Gelatin in the Presence of Various Metal Ions

Film composition	*α-band*[a]		*β-band*[a]	
	$Q \times 10^5 \pm 15\%$	$Q_{rel} \pm 10\%$	$Q \times 10^5 \pm 15\%$	$Q_{rel} \pm 10\%$
Acid Blue 1	14·6[b]	1	—	—
Acid Blue 1 + Cd^{2+}	11·8[b]	0·81[b]	—	—
Acid Blue 1 + Mn^{2+}	11·7[b]	0·80[b]	—	—
Acid Blue 1 + Zn^{2+}	12·3[b]	0·84[b]	—	—
Acid Green 9	20·0[b]	1	—	—
Acid Green 9 + Cd^{2+}	16·6[b]	0·83[b]	—	—
Acid Green 9 + Mn^{2+}	16·4[b]	0·82[b]	—	—
Acid Green 9 + Zn^{2+}	16·0[b]	0·80[b]	—	—
Acid Blue 15	3·6	1	4·2	1
Acid Blue 15 + Cd^{2+}	2·8	0·78	3·3	0·79
Acid Blue 15 + Mn^{2+}	3·0	0·84	3·7	0·88
Acid Blue 15 + Zn^{2+}	2·6	0·73	3·3	0·79
Acid Violet 17	3·5	1	4·7[b]	1
Acid Violet 17 + Cd^{2+}	2·6	0·73	3·2	0·69[b]
Acid Violet 17 + Mn^{2+}	2·5	0·72	3·5	0·75[b]
Acid Violet 17 + Zn^{2+}	2·2	0·64	3·4	0·72[b]

The molar ratio for dye : additive is 1 : 96. [Metal ion] = $(2{\cdot}6 \pm 0{\cdot}2) \times 10^{-4}$ mol of metal/g gelatin; [dye] = $(2{\cdot}7 \pm 0{\cdot}2) \times 10^{-6}$ mol of dye/g gelatin.
[a] See Table 1 in Part 1[3] for the wavelength at which fading was monitored.
[b] For fading at 35 min exposure to radiation (see text).

α-band (where monomeric dye absorbs) independently of the β-band (where the dimer absorbs). Nevertheless, these preliminary results do show that Q_{rel} measured at the β-band is reduced by the presence of Mn^{2+} in both PVA (Table 5) and gelatin (Table 6). This suggests that excited triplet-state dye dimers may participate in the photodegradation mechanism, as suggested in Part 1 of this work.[3]

For Acid Blue 1 and Acid Green 9 (the two fastest fading dyes) in PVA the values of Q_{rel} show that, at the concentration employed, manganese sulphate monohydrate does not significantly reduce either quantum yield of dye fading.

Furthermore, Tables 5 and 6 show that Q_{rel} is also reduced by the transition metal ion Zn^{2+}. This result is interesting from the perspective that Zn^{2+} is less toxic than Cd^{2+} and Mn^{2+} [17–19] and so, if it can be applied to wool in a suitable manner, it may represent a basis for a commercial treatment to retard dye fading on wool.

3.4 Excited triplet state quenching in the presence of photosensitizers

3.4.1. Sensitized dye fading in MC

To ascertain whether photosensitization occurs via an excited triplet-state dye molecule or excited triplet-state exciplex formed between the dye and the photosensitizer, manganese sulphate monohydrate was incorporated into MC films containing dye and various photosensitizers. The results for this experiment are shown in Table 7. A comparison between these results and those presented in Table 1 indicates that for every dye-addi-

TABLE 7

The Effect of Metal Ion on Dye Fading in MC in the Presence of Dye Fading Sensitizers

Film composition before addition of metal ion	Cd^{2+}		Mn^{2+}		Zn^{2+}	
	$Q \times 10^5$ ± 15% α-band[a]	Q_{rel} ± 8% α-band[a]	$Q \times 10^5$ ± 15% α-band[a]	Q_{rel} ± 8% α-band[a]	$Q \times 10^5$ ± 15% α-band[a]	Q_{rel} ± 8% α-band[a]
(Acid Blue 1)[b]	6·3	1·00	6·3	1·00	6·3	1·00
Acid Blue 1 + LAMED	10·4	1·65	7·0	1·11	9·5	1·50
Acid Blue 1 + MGS[c]	6.6	1·05	6·7	1·07	6·7	1·07
Acid Blue 1 + NaAc	5·5	0·87	5·5	0·87	4·6	0·73
(Acid Green 9)[b]	20·0	1·00	20·0	1·00	20·0	1·00
Acid Green 9 + LAMED	17·2	0·86	23·4	1·17	19·0	0·94
Acid Green 9 + MGS[c]	16·0	0·80	19·6	0·98	16·0	0·80
Acid Green 9 + NaAc	14·5	0·73	[18·0][d]	[0·90][d]	16·0	0·80
(Acid Blue 15)[b]	3·6	1·00	3·6	1·00	3·6	1·00
Acid Blue 15 + LAMED	3·0	0·84	2·8	0·79	2·8	0·78
Acid Blue 15 + MGS[c]	3·1	0·87	3·0	0·83	2·2	0·61
Acid Blue 15 + NaAc	2·3	0·63	1·9	0·54	2·2	0·61
(Acid Violet 17)[b]	4·3	1·00	4·3	1·00	4·3	1·00
Acid Violet 17 + LAMED	3·0	0·69	3·5	0·82	3·3	0·77
Acid Violet 17 + MGS[c]	3·0	0·70	3·6	0·83	3·3	0·77
Acid Violet 17 + NaAc	1·9	0·43	3·8	0·88	1·85	0·43

The symbols LAMED, MGS and NaAc refer to L-arginine methylester dihydrochloride, methylguanidine sulphate and sodium acetate, respectively.

The molar ratios for dye : dye fading sensitizer : metal ion are 1 : 12 : 12. [Dye] = (2·7 ± 0·2) × 10^{-6} mol/g MC; [dye fading sensitizer] = $[Cd^{2+}]$ = $[Mn^{2+}]$ = $[Zn^{2+}]$ = (3·3 ± 0·2) × 10^{-5} mol/g MC.

[a] Fading was monitored at the wavelength corresponding to the peak of the α-band (see Table 1 in Part 1[3]).

[b] These values correspond to dye fading in the absence of any additives.

[c] [Methylguanidine sulphate] = 1/2[guanidino groups] (see text).

[d] For this film the molar ratios for dye : sodium acetate : Mn^{2+} are 1 : 12 : 24 with $[Mn^{2+}]$ = (6·6 ± 0·5) × 10^{-5} mol/g MC.

tive combination tested (except Acid Green 9 in the presence of both L-arginine methylester dihydrochloride and manganese sulphate monohydrate), manganese sulphate monohydrate reduces Q_{rel} from the value obtained in the presence of photosensitizer alone (compare Tables 1 and 7). These results show that in all cases except one, dye photodegradation occurs via a triplet-state species in the presence of the additives which model protein-bound amino acids in wool. However, since Q_{rel} was reduced by the same amount as it was in the absence of these additives (compare Tables 5 and 7), an increase in triplet-state species was not observed.

For Acid Green 9 in the presence of L-arginine methylester dihydrochloride, the addition of manganese sulphate monohydrate does not reduce the sensitization caused by the methylester (compare Tables 1 and 7). In this case it would seem that there may be insufficient Mn^{2+} present to observe a reduction in Q_{rel}, or that a triplet-state species is not involved in the photodegradation process. In the presence of methylguanidine sulphate, however, the sensitization is reduced by manganese sulphate monohydrate, and this therefore suggests that protein-bound arginine would sensitize dye fading via an excited triplet-state species.

In three notable instances, namely Acid Blue 1 in the presence of L-arginine methylester dihydrochloride and Acid Blue 15 and Acid Violet 17 both in the presence of sodium acetate, Q_{rel} is reduced more by the addition of Mn^{2+} than for dye fading in the absence of photosensitizer (compare Tables 5 and 7). Assuming that Mn^{2+} has the same quenching potential in the presence and absence of photosensitizer, then in these three cases a higher concentration of excited triplet-state species is generated in the presence of photosensitizer than in its absence. An increase in the concentration of excited triplet-state species suggests that, in these cases, dye fading may proceed via an exciplex mechanism. In an exciplex mechanism the extra excited triplet-state species may be either the excited triplet-state exciplexes formed between the dye and the photosensitizer, or excited triplet-state dye molecules whose formation is facilitated by the dissociation of the excited triplet-state exciplex.

3.4.2 Sensitized dye fading in gelatin

Part 1 of this work revealed that both electron transfer and hydrogen atom transfer would be expected to occur simultaneously in gelatin and that the substrate promotes dye aggregation.[3] The results presented in Table 6 further reveal that electron transfer processes and excited triplet-state species are involved in dye degradation in the protein substrate, since the respective metal ions Cd^{2+} and Mn^{2+} reduce the fading of each

dye. Furthermore, they also show that Zn^{2+} is successful in reducing dye fading in gelatin and may reduce dye fading in wool if it can be appropriately applied to the fibre. It is to be noted here that, when the same concentration of moles of metal ion/g substrate as used in MC and PVA (e.g. $(3{\cdot}2 \pm 0{\cdot}2) \times 10^{-5}$ mol metal ion/g substrate) was incorporated into gelatin, no reduction in dye fading was observed. This is believed to be due to the fact that in gelatin, the number of moles of amino acid residues sensitizing dye fading is larger than the number incorporated into the other films. Thus, it would appear that insufficient metal ion is present in gelatin to overcome the sensitizing effect of the amino acid residues. For example in gelatin there is at least $1{\cdot}7 \times 10^{-3}$ mol of sensitizer/g of dry substrate,[20] whereas in MC and PVA films $(3{\cdot}3 \pm 0{\cdot}2) \times 10^{-5}$ mol of sensitizer was added per gram of substrate. In accordance with this, the metal ion concentration needed to be increased to $(2{\cdot}6 \pm 0{\cdot}2) \times 10^{-4}$ mol of metal ion/g gelatin in order to observe the trends presented in Table 6.

3.5 Elucidation of the kinetics of dye fading in MC in the presence of photosensitizers

It has become apparent that in MC, the monomeric form of the dye predominates, and that during dye photodegradation in the presence of photosensitizers, the dye monomer is able to abstract either an electron or a hydrogen atom from the photosensitizer. In addition, the dye can abstract an electron, and possibly also a hydrogen atom, from the substrate/residual solvent system. In each case, it appears that the excited triplet-state dye molecule is involved in the reaction, and possibly an excited triplet-state exciplex formed between the dye and the photosensitizer, since this may be quenched in a similar manner as the excited triplet-state of the dye.

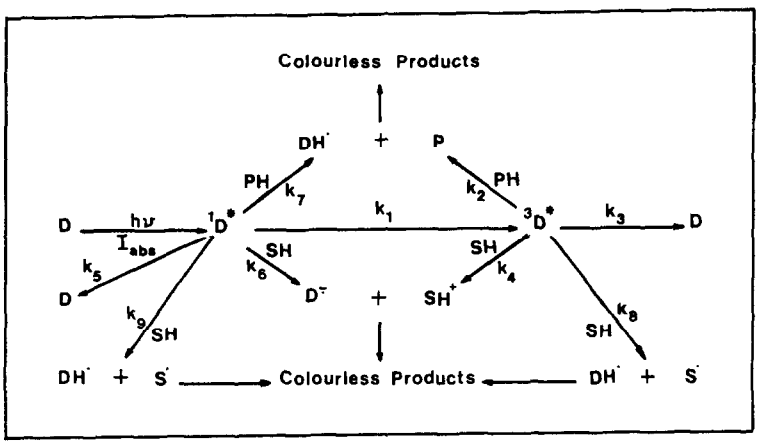
Since the photosensitizers used in this study did not absorb radiation above 270 nm, the fluorescence spectrum of the dye and the absorption spectrum of the photosensitizer will not overlap. This precludes energy transfer processes between the dye and the additive.

There are, however, eight possible mechanisms which may be proposed to explain the observed photodegradation of the dye monomer. They are presented in Figs 1–4. In these mechanisms it has been assumed that the primary photochemical reactions lead directly to the formation of colourless photoproducts. Reactions in which the highly reactive dye–radical species replenish the dye concentration have been considered negligible by comparison, because linear fading curves were observed for all dye–photosensitizer systems studied in MC.

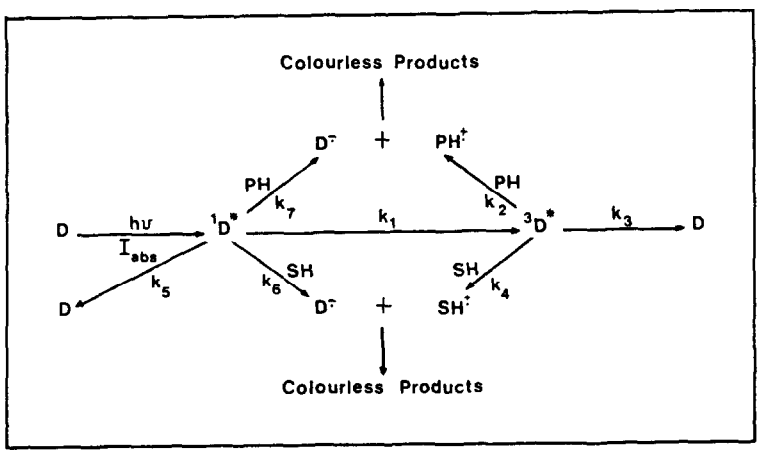
Kinetic analysis of mechanism 1 reveals that the rate of dye loss $-\mathrm{d}[D]/\mathrm{d}t$ is given by eqn (1):

$$R_0 = -\frac{\mathrm{d}[D]}{\mathrm{d}t} = I_{\mathrm{abs}}\left[1 - \frac{1}{k_7[\mathrm{PH}] + k_1 + k_5 + K_{96}}\left(k_5 + \frac{k_1 k_3}{k_3 + k_2[\mathrm{PH}] + K_{84}}\right)\right] \quad (1)$$

where $K_{84} = (k_8 + k_4)[\mathrm{SH}]$ and $K_{96} = (k_6 + k_9)[\mathrm{SH}]$, (because the concentration of the substrate or residual solvent within the film [SH] may be

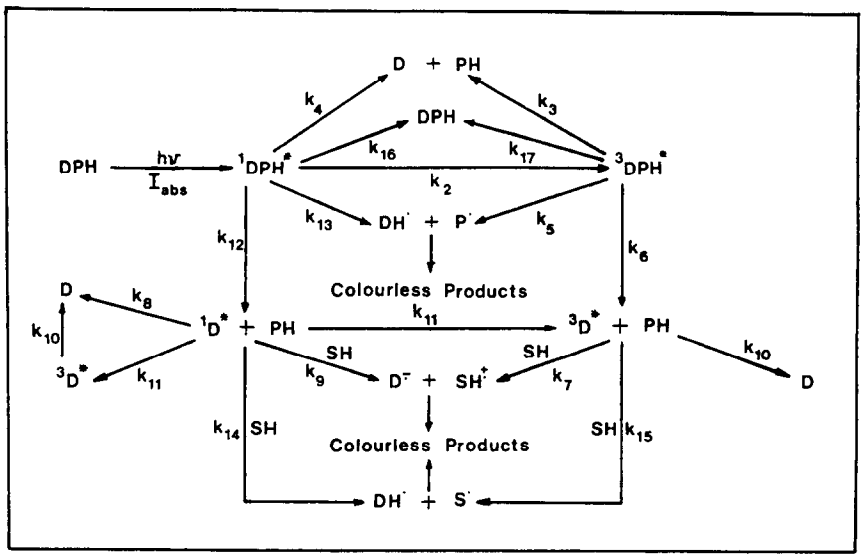


(a)

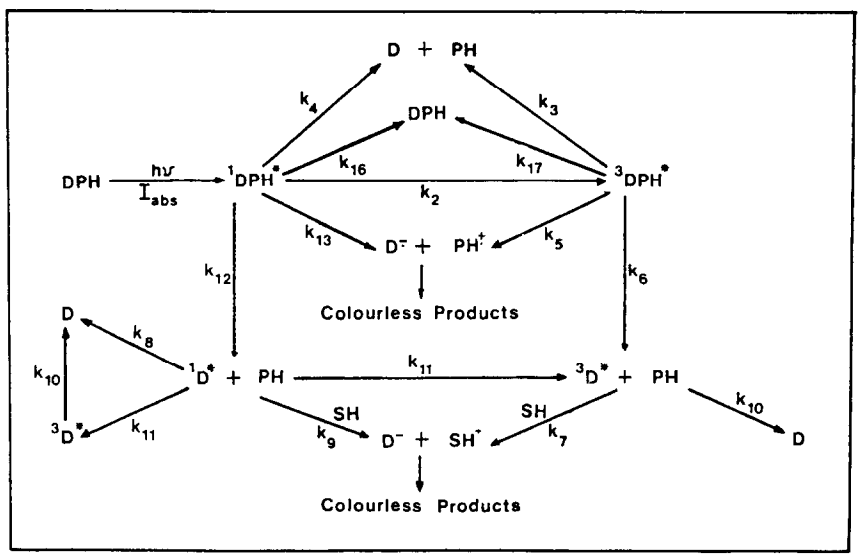


(b)

Fig. 1. One-step electron and hydrogen atom transfer. (a) Mechanism 1: one-step hydrogen atom transfer; (b) mechanism 2: one-step electron transfer. D represents the ground-state dye molecule, PH the photosensitizer, SH the substrate and/or residual solvent in the film. I_{abs} is the rate of light ($h\nu$) absorption and k is used for the rate constant of each process.



(a)



(b)

Fig. 2. Hydrogen atom and electron transfer involving exciplex formation via excitation of a ground-state complex. (a) Mechanism 3: hydrogen atom transfer involving exciplex formation via excitation of a ground-state complex; (b) mechanism 4: electron transfer involving exciplex formation via excitation of a ground-state complex. D represents the ground-state dye molecule, PH the photosensitizer, SH the substrate and/or residual solvent in the film and DPH is the ground-state complex. I_{abs} is the rate of light ($h\nu$) absorption, and k is used for the rate constant of each process.

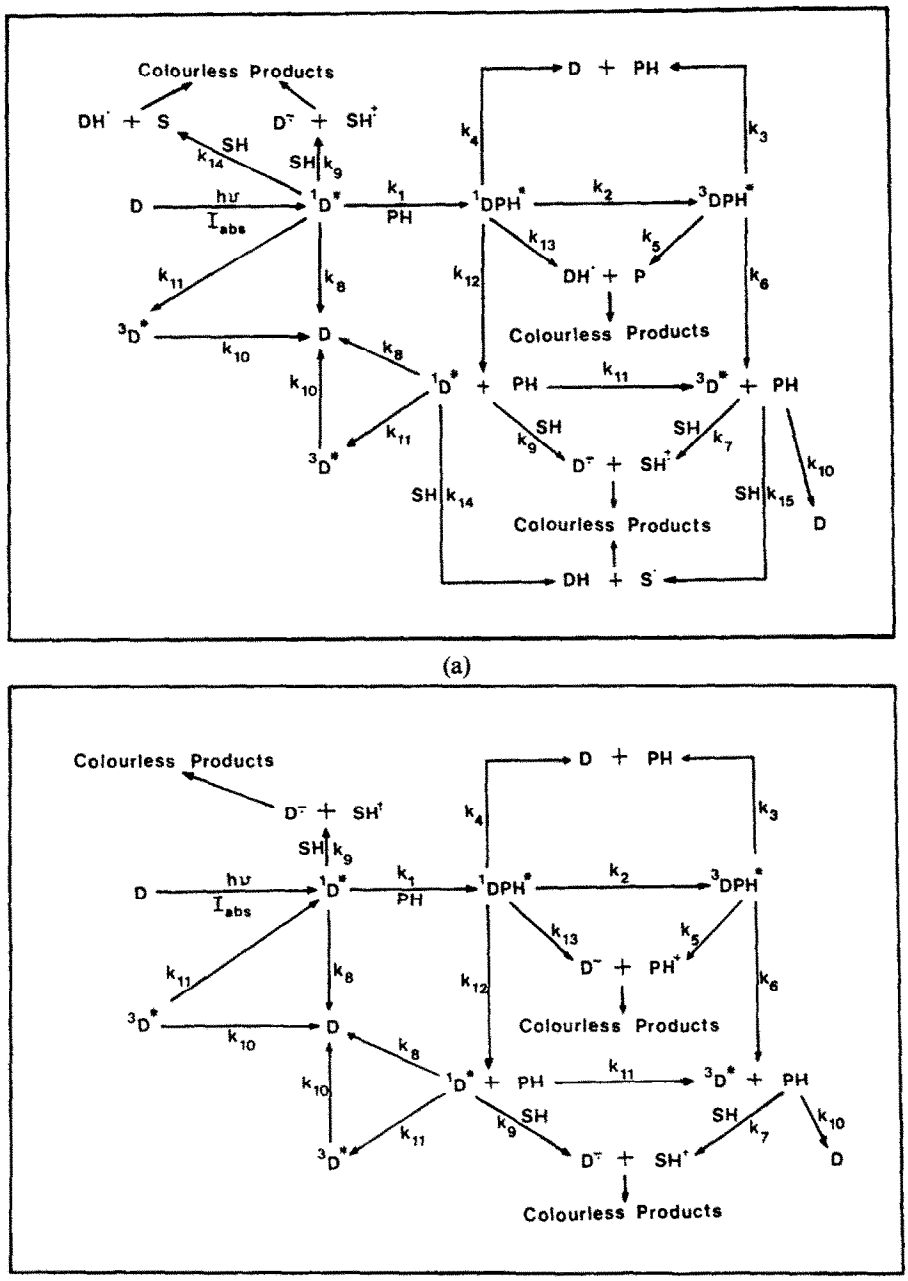
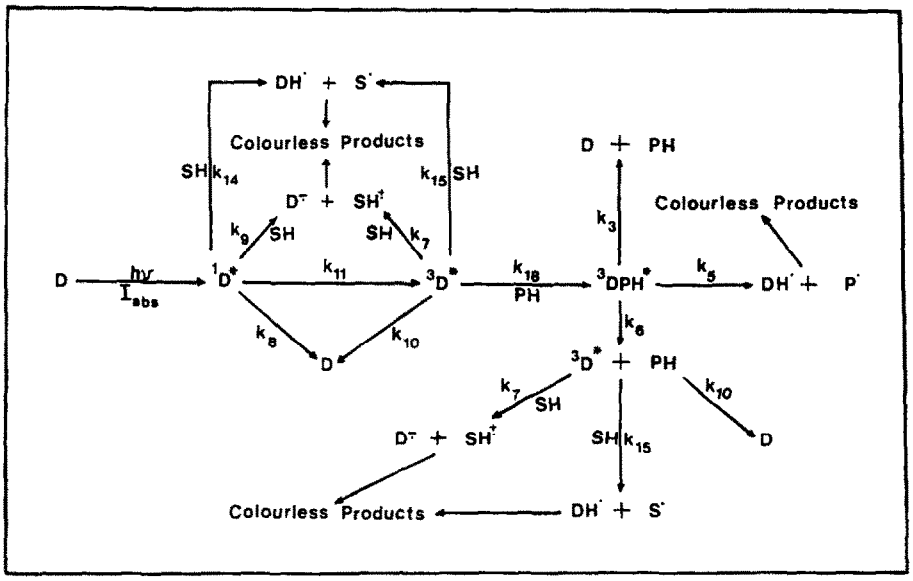
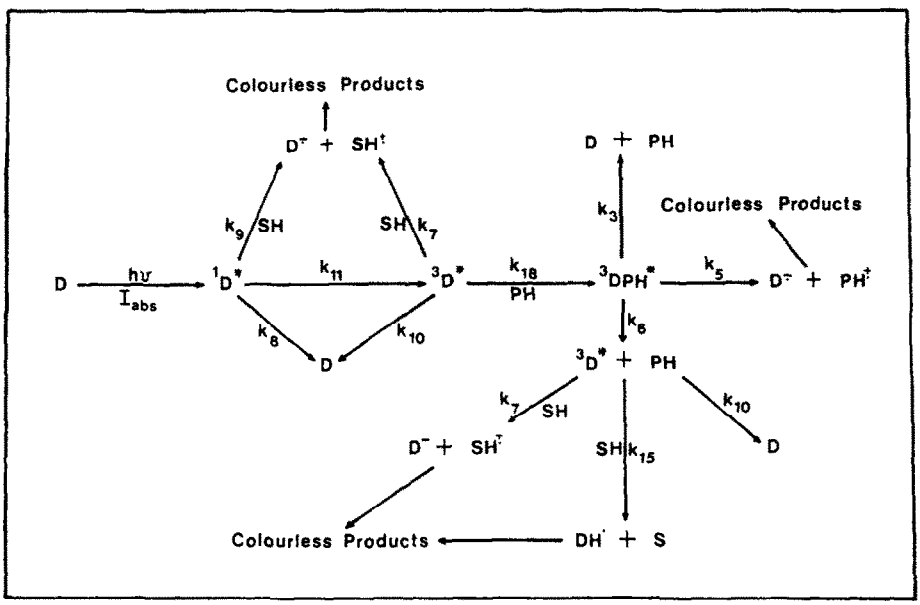


Fig. 3. Hydrogen atom and electron transfer involving exciplex formation via the excited singlet-state dye molecule. (a) Mechanism 5: hydrogen atom transfer involving exciplex formation via the excited singlet-state dye molecule; (b) mechanism 6: electron transfer involving exciplex formation via the excited singlet-state dye molecule. D represents the ground-state dye molecule, PH the photosensitizer, SH the substrate and/or residual solvent in the film. I_{abs} is the rate of light ($h\nu$) absorption, and k is used for the rate constant of each process.



(a)



(b)

Fig. 4. Hydrogen atom and electron transfer involving exciplex formation via the excited triplet-state dye molecule. (a) Mechanism 7: hydrogen atom transfer involving exciplex formation via the excited triplet-state dye molecule; (b) mechanism 8: electron transfer involving exciplex formation via the excited triplet-state dye molecule. D represents the ground-state dye molecule, PH the photosensitizer, SH the substrate and/or residual solvent in the film. I_{abs} is the rate of light ($h\nu$) absorption, and k is used for the rate constant of each process.

considered constant), if steady state approximations are applied to the excited-state species.

Since I_{abs} may be shown to be essentially constant for dye degradation down to 10% dye loss, and that the initial rate of fading, $R_0 = -\mathrm{d}[D]/\mathrm{d}t = I_{abs}Q$ (see Part 1[3]), then it is evident that as the concentration of photosensitizer [PH] increases, the rate of dye loss (and hence Q and Q_{rel}) increases.

The kinetic analysis for mechanism 2 is analogous to that for mechanism 1 and it yields the following expression for the rate of dye loss:

$$R_0 = -\frac{\mathrm{d}[D]}{\mathrm{d}t} = I_{abs}\left[1 - \frac{1}{k_1 + k_5 + K_6 + k_7[\mathrm{PH}]}\left(k_5 + \frac{k_1k_3}{k_3 + K_4 + k_2[\mathrm{PH}]}\right)\right] \tag{2}$$

where $K_4 = k_4[\mathrm{SH}]$ and $K_6 = k_6[\mathrm{SH}]$. Thus, it is again apparent that as [PH] increases, the rate of dye loss (and hence Q and Q_{rel}) increases.

Apart from the one-step transfer mechanisms discussed, dye loss may occur via an exciplex mechanism. In mechanisms 3 and 4 the exciplex is formed via excitation of a ground-state complex. Such mechanisms may be applicable to anionic dye fading in the presence of positively charged species. In the kinetic analysis of these mechanisms it is proposed that the photosensitizer (PH) complexes with the dye D via the ionized SO_3^- groups on the dye and so the ground-state complex DPH is assumed to absorb radiation in a similar wavelength region to the dye. Thus, the observed rate of dye loss is given by eqn (3):

$$\begin{aligned} R_0 = -\frac{\mathrm{d}[D]}{\mathrm{d}t} &= -\frac{\mathrm{d}[\mathrm{DPH}]}{\mathrm{d}t} \\ &= I_{abs}\left[1 - \left(\frac{(k_4 + k_{16})ACE + (k_3 + k_{17})k_2AE}{ABCE}\right.\right. \\ &\qquad \left.\left. + \frac{k_8k_{12}CE + 2k_{10}(k_2k_6A + 2k_{11}k_{12}C)}{ABCE}\right)\right] \end{aligned} \tag{3}$$

where $A = k_8 + 2k_{11} + K_9 + K_{14}$, $B = k_2 + k_4 + k_{12} + k_{13} + k_{16}$, $C = k_3 + k_{17} + k_5 + k_6$, $E = 2k_{10} + K_7 + K_{15}$, with $K_7 = k_7[\mathrm{SH}]$, $K_9 = k_9[\mathrm{SH}]$, $K_{14} = k_{14}[\mathrm{SH}]$, $K_{15} = k_{15}[\mathrm{SH}]$ for mechanism 3, and the equivalent expression for mechanism 4 except that $k_{14} = k_{15} = 0$. The expressions for mechanisms 3 and 4 thus illustrate that the rate of dye loss is a constant, independent of the photosensitizer concentration.

Mechanisms 5–8 involve exciplex formation via interaction between the ground state photosensitizer PH and either the excited singlet-state dye molecule $^1\mathrm{D}^*$ or the excited triplet-state dye molecule $^3\mathrm{D}^*$. The

kinetic analysis of mechanisms 5–8 is very complex. For example, the rate of dye loss for mechanism 5 is given by eqn (4):

$$R_0 = -\frac{d[D]}{dt} = I_{abs}\left[1 - \frac{1}{X}\left(2k_8F + \frac{Y}{G(H+K_{15})} + k_1k_4[PH] + \frac{Z}{G}\right)\right] \quad (4)$$

where

$$F = k_2 + k_4 + k_{12} + k_{13},\ G = k_3 + k_5 + k_6,\ H = 3k_{10} + K_7 \text{ with } K_7 = k_7[SH]$$

$$J = 2k_8 + 3k_{11} + 2K_9 \text{ with } K_9 = k_9[SH] \text{ and } K_{14} = k_{14}[SH] \text{ and } K_{15} = k_{15}[SH]$$

$$X = F(2K_{14} + J + k_1[PH]) - k_1k_{12}[PH],\ Y = 3k_{10}(k_1k_2k_6[PH] + 3k_{11}FG)$$

$$Z = k_1k_2k_3[PH]$$

From eqn (4) it is evident that, without a detailed knowledge of the relative values of the many rate constants involved, it is not possible to predict the functional behaviour of the initial rate of dye loss as the initial concentration of the photosensitizer is varied. Similarly, kinetic analysis of mechanisms 6–8 did not elucidate the dependence of the initial rate of dye loss on the initial photosensitizer concentration.

However, the work presented in Table 2 clearly indicates that the relative quantum yield of dye fading (and hence $R_0 = -d[D]/dt$, see Part 1[3]) increases as the concentration of both methylguanidine sulphate and sodium acetate increases. This allows mechanisms 3 and 4 to be eliminated from the list of possible mechanisms by which the dyes may fade, and indicates that dye fading in the presence of sodium acetate may proceed via mechanism 2, whilst mechanism 1 is likely for dye fading in the presence of methylguanidine sulphate. Furthermore, it is to be noted that, on the basis of the kinetic analysis of mechanisms 5–8, it is not possible to eliminate the possibility that dye fading occurs via an exciplex mechanism. Thus, mechanisms 6 and 8 must also be considered as possible pathways for dye degradation in the presence of sodium acetate, whilst in the presence of methylguanidine sulphate, mechanisms 5 and 7 are likely. In support of the proposal that exciplex formation may occur during sensitized dye fading it has been noted (during the presentation of the manganese sulphate monohydrate work (Table 7)) that the fading of Acid Blue 1 in the presence of L-arginine methylester dihydrochloride, and that of Acid Blue 15 and Acid Violet 17, both in the presence of sodium acetate, appear to proceed via an exciplex mechanism.

Table 8 summarizes the kinetic behaviour for mechanisms 1–8 and their relevance to fading in the presence of acetate and guanidino groups.

TABLE 8
Summary of the Kinetic Behaviour for Mechanisms 1–8

Number	*Mechanism*	*Equation that gives* R_0	*Predicted dependence of* R_0, Q *and* Q_{rel} *on [PH]*	*Most likely sensitizers of dye fading*
1	1 step H˙ transfer	1	All increase as [PH] increases	Guanidino groups
2	1 step e^- transfer	2	All increase as [PH] increases	Acetate groups
3	H˙ transfer involving exciplex formed via excitation of a ground state complex	3	All are constant	—
4	e^- transfer involving exciplex formed via excitation of a ground state complex	3 with $k_{14} = k_{15} = 0$	All are constant	—
5[a]	H˙ transfer involving exciplex formed via $^1D^*$	4	R_0 a complex function of [PH]	Guanidino groups
6[a]	e^- transfer involving exciplex formed via $^1D^*$	Not shown	R_0 a complex function of [PH]	Acetate groups
7[a]	H˙ transfer involving exciplex formed via $^3D^*$	Not shown	R_0 a complex function of [PH]	Guanidino groups
8[a]	e^- transfer involving exciplex formed via $^3D^*$	Not shown	R_0 a complex function of [PH]	Acetate groups

[a] The text indicates that exciplex mechanisms may be involved for: (a) Acid Blue 1 in the presence of L-arginine methylester dihydrochloride; (b) Acid Blue 15 in the presence of sodium acetate; (c) Acid Violet 17 in the presence of sodium acetate.
Mechanisms 6 and 8 are possible for cases (b) and (c), and mechanisms 5 and 7 are likely for case (a). In general, exciplex mechanisms for Acid Blue 1 may be facilitated by the presence of the positively charged α-amino and guanidino groups.

4 SUMMARY

The free amino acids L-arginine and L-glutamic acid were able to sensitize the photodegradation of all four triphenylmethane dyes studied in MC. However, caution must be exercised when extrapolating the effect to protein substrates where the amino acids participate in peptide bonds, as the α-amino and α-carboxyl groups are not available for reaction (except at the ends of the peptide chains).

L-Arginine was more effective than methylguanidine sulphate in sensitizing dye fading in MC. The studies performed revealed that both the

guanidino group and the α-carboxyl group in L-arginine are capable of sensitizing dye fading independently and additively.

In contrast to the functional groups in L-arginine, the α-carboxyl and γ-carboxyl groups in L-glutamic acid do not sensitize dye fading additively. This difference appears to arise firstly, because the probability of L-arginine being located in close proximity to the dye during the film drying process could be greater than for L-glutamic acid (owing to more favourable ionic attraction), and secondly, because the interaction between the dye and L-glutamic acid involves one mechanism, whereas with L-arginine two different mechanisms could be involved.

The α-amino group of both amino acids was able to sensitize the fading of Acid Blue 1, but not the fading of the other dyes. This sensitization was observed only when the α-amino group was attached to a carboxyl group (such as in L-glutamic acid) or a guanidino group (such as in L-arginine) and appeared to suggest that the *ortho* phenyl ring substituent on the dye molecule, SO_3^-, facilitates fading by interacting with the positively charged α-amino group.

It has been suggested that, in the presence of protein-bound amino acids which are capable of sensitizing dye fading, the fading of triphenylmethane dyes, in the most general sense, apparently involves hydrogen atom or electron transfer, the excited triplet-state dye molecule and possibly an excited triplet-state exciplex (see mechanisms 1, 2 and 5–8 and Table 8).

Kinetic studies were performed in which the concentration of methylguanidine sulphate (a photosensitizer) was varied, and the effect of an excited triplet-state quencher, Mn^{2+}, and an electron scavenger, Cd^{2+}, were examined. It was found that the observed kinetic behaviour of dye fading in the presence of methylguanidine sulphate could be explained by a one-step hydrogen atom transfer mechanism (mechanism 1). However, it was not possible on the basis of these kinetic studies to exclude the possibility that dye fading proceeded via an exciplex mechanism (5 and 7). Consequently, in the presence of protein-bound arginine, the fading of triphenylmethane dyes appears to involve hydrogen atom transfer.

In the presence of protein-bound glutamic and aspartic acids, it is proposed that sensitized dye fading occurs via a one-step electron transfer process, since the observed kinetic behaviour of model systems could be explained by mechanism 2. However, on the basis of these kinetic studies it was not possible to exclude the possibility that dye fading proceeded via the alternative exciplex mechanisms 6 and 8. Such mechanisms may, in fact, prove to be particularly relevant for the fading of Acid Blue 15 and Acid Violet 17 in the presence of protein-bound aspartic and

glutamic acids, as indicated by the work presented for dye fading in the presence of sodium acetate (Table 7). Here, it is important to note that these proposals refer to the acidic forms of protein-bound glutamic and aspartic acids.

These studies highlight the complexity of dye fading on protein substrates and have indicated which functional groups are likely to promote or retard dye fading. They have suggested that, if relatively safe metal ions such as Zn^{2+} can be incorporated appropriately into wool, fading may be retarded. Similarly, it has been further verified that if carboxylate and guanidino groups are removed, fading may be retarded in the wool fibre. The position of water solubilizing groups, such as SO_3^-, has also been shown to influence the lightfastness of dyes. In particular, terminal α-amino groups attached to guanidino or carboxylate residues in the protein chain may photosensitize dyes like Acid Blue 1, which has an *ortho* SO_3^- group on one phenyl ring.

Many questions remain to be answered if this complex process is to be fully understood. For example, future studies could be directed toward elucidating the role of radical species in fading mechanisms where electron and hydrogen atom transfer is occurring. Detailed luminescence and quenching studies may reveal the relative contribution of the singlet- and triplet-state dye or exciplex species to dye fading in solid substrates. Nevertheless, the work presented here represents an important and useful preliminary step in elucidating the complex fading mechanisms present on solid natural and synthetic polymers for this class of dye.

ACKNOWLEDGMENTS

I would like to acknowledge that the work presented in this paper was performed at the School of Textile Technology, University of New South Wales, PO Box 1, Kensington, NSW, Australia. In addition, I would like to express my sincere appreciation to Drs M. T. Pailthorpe and J. V. Brancik and Mrs C. M. Wilson for their help at various stages of the work and to Associate Professor A. Datyner and Miss E. Heaton for providing English translations of several published articles. In particular, Associate Professor C. H. Nicholls is gratefully acknowledged for suggesting this topic for study and guidance throughout the course of the project. Special thanks go to Professor P. M. Duxbury, my husband, for support in innumerable ways. Finally, the Australian Wool Corporation is gratefully acknowledged for the award of a postgraduate scholarship.

REFERENCES

1. Harper, S. H., Aromatic compounds. In *Rodds Chemistry Of Carbon Compounds. A Modern Comprehensive Treatise*, 2nd edn, Vol. III, Part F, ed. S. Coffey. Elsevier, New York, 1974, Ch. 21, p. 129.
2. Grewal, N. & Balakrishnaiah, B., *Man-Made Text. India*, **29**(3) (1986) 134.
3. Duxbury, D. F., *Dyes and Pigments*, **25** (1994) 131.
4. Cumming, J. W., Giles, C. H. & McEachran, A. E., *J. Soc. Dyers Colour*, **72** (1956) 373.
5. Mason, R. E., Nicholls, C. H. & Pailthorpe, M. T., *Polym. Photochem.*, **2** (1982) 23.
6. Meier, H., In *The Chemistry of Synthetic Dyes*, Vol. 4, ed. K. Venkataraman. Academic Press, New York, 1971, Ch. 7, p. 389.
7. van Beek, H. C. A. & Heertjes, P. M., *Studies Conserv.*, **11** (1966) 123.
8. Leaver, I. H., In *Photochemistry of Dyed and Pigmented Polymers*, ed. N. S. Allen & J. F. McKellar. Elsevier Applied Science, London, 1980, Ch. 4, p. 161.
9. Duxbury, D. F., *Chem. Rev.* **3**(1) (1993) 381.
10. Nakamura, R. & Hida, M., *Sen-i Gakkaishi*, **39** (1983) T-125.
11. Guilbault, G. G., *Practical Fluorescence Theory. Methods and Techniques.* Marcel Dekker, New York, 1973, p. 121.
12. Chanduri, J. N. & Basu, S., *Trans. Faraday Soc.*, **54** (1958) 1605.
13. Hill, C. O. & Lin, S. H., *J. Chem. Phys.*, **53**(2) (1970) 608.
14. Linschitz, H. & Pekkarinen, L., *J. Am. Chem. Soc.*, **82** (1960) 2411.
15. Linschitz, H. & Sarkanen, K., *J. Am. Chem. Soc*, **80** (1958) 4826.
16. Porter, G. & Wright, M. R., *Dis. Faraday Soc.*, **27** (1959) 18.
17. Budavari, S. (ed.), *The Meck Index—An Encyclopedia of Chemicals, Drugs and Biologicals*, 11th edn. Merck, Rahway, NJ, USA, 1989.
18. Browning, E., *Toxicity of Industrial Metals*, 2nd edn. Butterworth, London, 1969.
19. Friberg, L., Nordberg, G. F. & Vouk, V. B. (eds), *Handbook on the Toxicology of Metals.* Elsevier/North-Holland Biomedical Press, New York, 1979.
20. Roff, W. J. & Scott, J. R., *Fibres Films Plastics and Rubbers—A Handbook of Common Polymers.* Butterworth, London, 1971, p. 207.
21. Yakatan, G. J. & Schulman, S. G., *J. Phys. Chem.*, **76**(4) (1972) 508.
22. Maclaren, J. A. & Milligan, B., The chemical reactivity of the wool fibre. In *Wool Science.* Science Press, Marrickville, NSW, Australia, 1981, p. 137.