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Photoinduced Dark Reactions of Some Cationic Dyes

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SUMMARY

The poor lightfastness of many cationic dyes restricts the range of application which their otherwise attractive spectral properties would predict. Fading mechanisms are varied and complex The present preliminary account of the photolysis of aerated cyclohexanone solutions of Malachite Green, Rosaniline or Rhodamine B for relatively short periods (up to 120 seconds) followed by a longer-term (up to 60 minutes) photoinduced dark bleaching reaction presents a further complication. Some mechanistic possibilities are suggested

1. INTRODUCTION

Although the outstanding brilliance and variety of the colours of triphenylmethane dyes led to their early commercial exploitation their application in the dyeing of textile fibres in more recent times has been severely limited by their poor lightfastness. In the case of Malachite Green, (MG^+), C.I. 42 000, which is representative of the group, fading can result from a variety of photoprocesses of which (a) successive dealkylation of the *N* substituents,[1] (b) cleavage of a central Ar–C bond forming amino substituted benzophenones,[2,3] and (c) reduction of the dye to the leuco form[4] are the most documented. The latter seems to be the favoured process under anaerobic conditions. In spite of considerable interest which has been shown in recent years details of the mechanisms by which these photoproducts are formed remain incompletely understood. Evidence from several sources[1,4,5] suggests that ejection of an

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electron from the dye cation in its triplet excited state ($^3D^+$) (reaction 1) may be an important primary process although no direct evidence for the existence of the hydrated electron has been obtained. Reactions of D^{2+} with oxygen and of the solvated electron with the dye (D^+) have been suggested as the main secondary reactions leading to the formation of colourless products which include H_2O_2.

$$^3D^+ \longrightarrow D^{2+} + e^-(\mathrm{solv}) \qquad (1)$$

Zweig and Henderson[6] have shown that TPM dyes are efficient sensitisers of singlet oxygen formation and that although they undergo a fading reaction at the same time there appears to be no simple relationship between the rates of fading and of singlet oxygen production In a closely related study of the possible role of singlet oxygen in the fading of MG^+, Stevens and Kaplan[7] concluded that despite the very efficient quenching of singlet oxygen by leuco Malachite Green the dye cation appeared to be unreactive and that triplet MG^+ reacts with oxygen in the ground state to produce photooxidation products

Under anaerobic conditions when the dyes are reduced to their leuco form the molecular rigidity of the environment and the extent of interaction with a substrate seem to be important controlling factors Electron transfer to the dye cation occurs in this case the donor being either the dye gegenion[8, 9] (eqn 2), or some reactive portion of the substrate such as a carboxyl group[10]

$$^3Ar_3C^+ + X^- \longrightarrow Ar_3C + X \qquad (2)$$

$$(X = Cl, Br, I)$$

Direct evidence for the presence of free radicals obtained from Crystal Violet (CV^+), C I. 42 555, and MG^+ was obtained from flash photolysis of isopropanol solutions of the dyes[11] and from esr measurements of CV^+ in deoxygenated aqueous solutions or poly(vinyl alcohol) films[12] The situation is complicated by the extreme photosensitivity of the radicals towards light of wavelengths longer than about 400 nm

We have investigated a photoinduced dark reaction of some cationic dyes in cyclohexanone solvent, in which radicals appear to play an important part, and present typical results for MG^+, Rosaniline (Ro^+), C I. 42 510, and Rhodamine B (RB^+), C.I. 45 170

2. EXPERIMENTAL

2.1. Materials

The dyes used were of the best quality available and were used without further purification. Cyclohexanone was distilled twice before use

2.2. Photolysis

Cyclohexanone solutions of the dyes were photolysed using unfiltered light from an Osram ME/D medium pressure mercury source

3 RESULTS

3.1. Malachite Green in cyclohexanone

Dilute ($\sim 10^{-5}$ M) aerated cyclohexanone solutions of MG^+ were irradiated for various time intervals between 20 and 120 s. Immediately following the short photolysis the intensity of the characteristic absorption of MG^+ at 624 nm (A_{624}) was monitored for a further period of about 20 min. During the photolysis period the absorbance changed very little but decreased in a subsequent dark reaction. Figure 1 illustrates the changes in A_{624} which occurred following 20, 40, 60 and 120 s periods of photolysis.

A linear relationship between $1/A_{624}$ and t (min) was apparent at least for a substantial portion of the reaction and especially for those samples irradiated for longer than 60 s. Shorter periods of irradiation led to induction periods and more complicated relationships (Fig. 2). Pseudo second order rate constants calculated from the slopes of the linear portions of the graphs in Fig 2 depended on the irradiation time (Fig. 3). When degassed solutions were irradiated a fast photobleaching occurred and the dark reaction was inhibited. The dark reaction was also greatly inhibited when solutions were irradiated through a 6 mm-thick pyrex filter which prevented direct absorption by the solvent but absorption by the dye was unaffected. When the solvent alone (3 ml) was irradiated for 3 min then 1 ml of MG^+ solution (4×10^{-5} M) added, the absorbance at 624 nm decreased in a dark reaction over the next 60 min (Fig. 4a) but when the experiment was repeated but without pre-irradiation of the solvent the dark reaction was much slower (Fig. 4b).

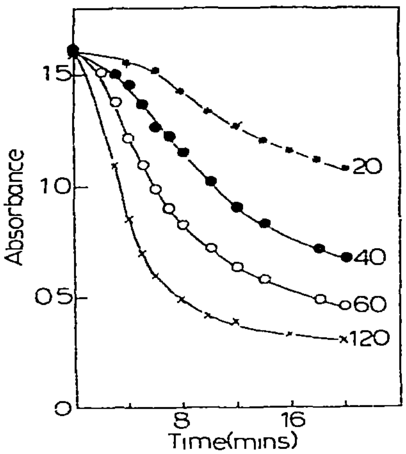


Fig. 1. Changes in absorbance at 624 nm of Malachite Green solutions following irradiation for 20, 40, 60 and 120 s

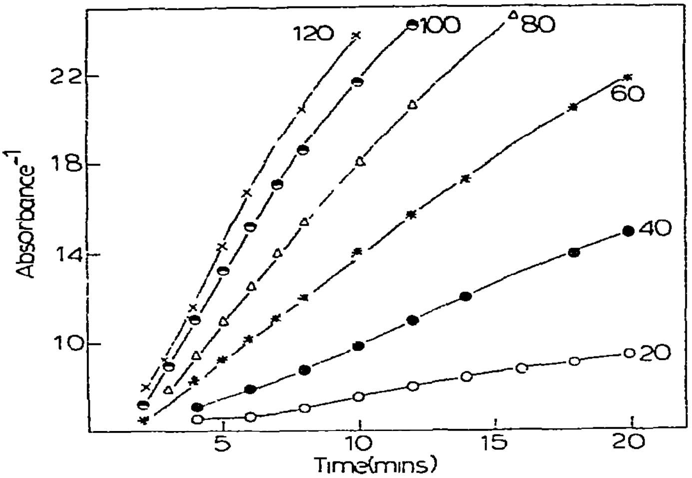


Fig. 2. Relation between absorbance^{-1} and time for dark reaction of Malachite Green solutions following irradiation for times between 20 and 120 s

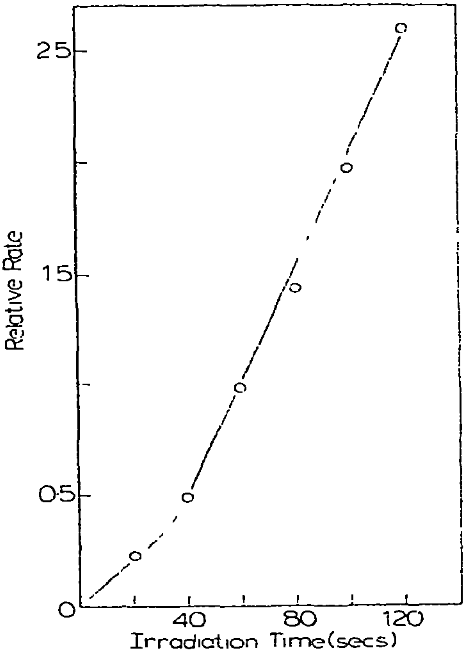


Fig. 3. Relative slopes of linear portions of graphs of Fig 2

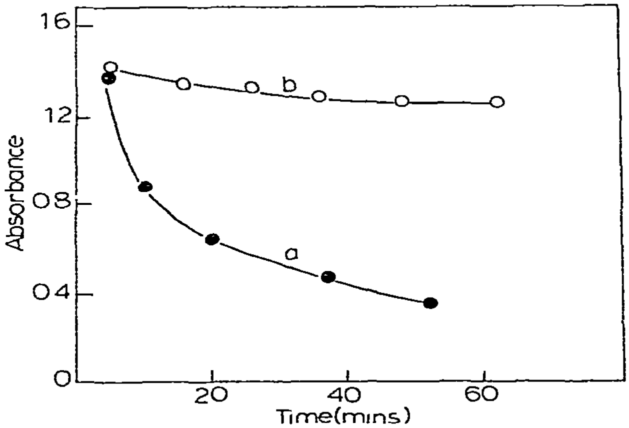


Fig. 4. Changes in absorbance at 624 nm for Malachite Green solution added (a) to pre-irradiated solvent and (b) to non-pre-irradiated solvent

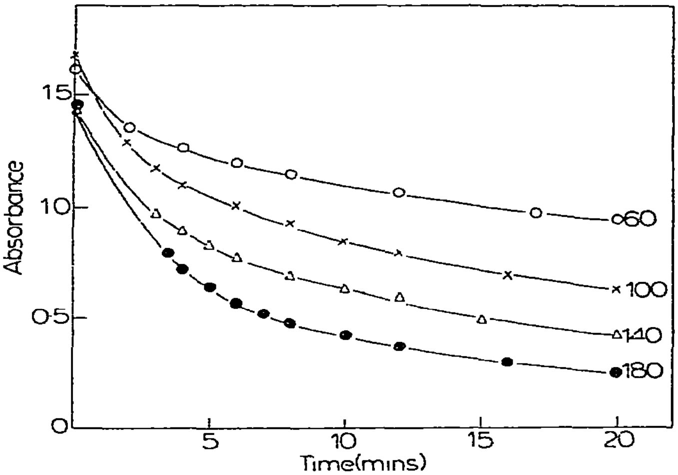


Fig. 5. Changes in absorbance at 550 nm of Rosaniline solutions following irradiation for 60, 100, 140 and 180 s

3.2. Rosaniline in cyclohexanone

Solutions of Rosaniline (Ro^+), C.I. 42 510, in cyclohexanone behaved in essentially the same way as MG^+ (Fig. 5) except that the dependence of relative rate on irradiation time was not linear (Fig. 6).

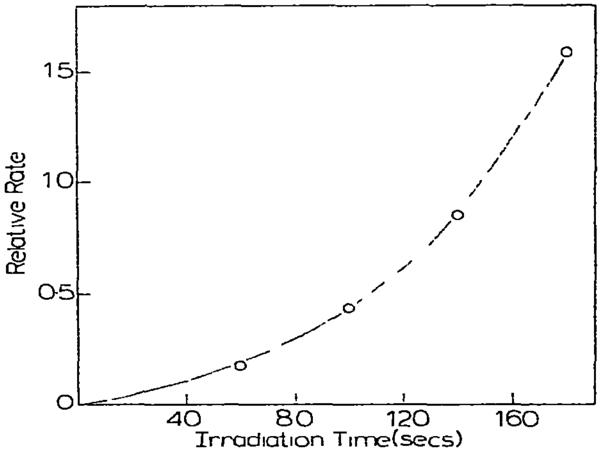


Fig. 6. Relative slopes of absorbance^{-1} versus time curves for data of Fig 5

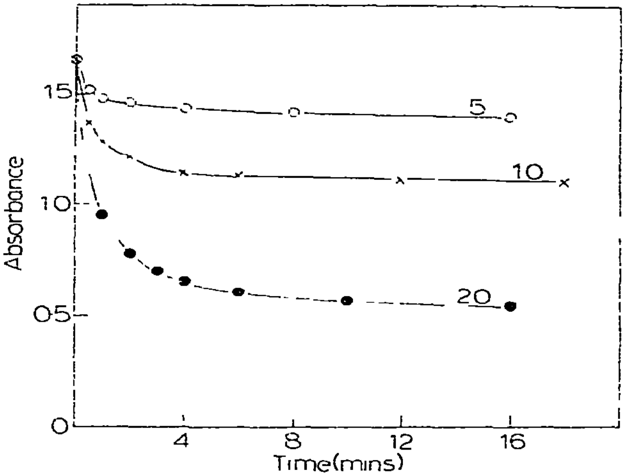


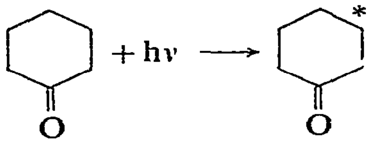
Fig. 7. Changes in absorbance at 550 nm of Rhodamine B solutions following irradiation for 5, 10 and 20 s

3.3. Rhodamine B in cyclohexanone

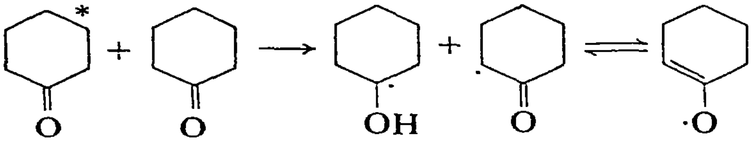
Solutions of Rhodamine B (RB^+), C.I. 45 170, in cyclohexanone also underwent a photoinduced dark reaction (Fig. 7) but the changes in absorbance which occurred during the photolysis were greater than for the two dyes previously described and the extent of the dark reaction was smaller

4 DISCUSSION

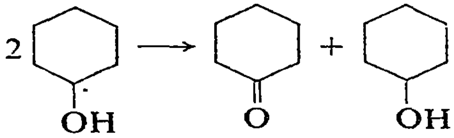
The occurrence of a slow, dark reaction taking place over about 20 min implies either the photochemical formation of a reactive species with a lifetime of this order of magnitude, or of a chain process in which the same or some equivalent species is continuously produced in a chain reaction. The following sequence of reactions which involves the photoformation of a resonance-stabilised free radical from the solvent (eqns 1 and 2), and formation of the radical by hydrogen transfer from the solvent to the dye radical (eqn. 4) takes both possibilities into account and includes both photoreductive (eqn. 4) and photooxidative routes (eqns 5 and 6).



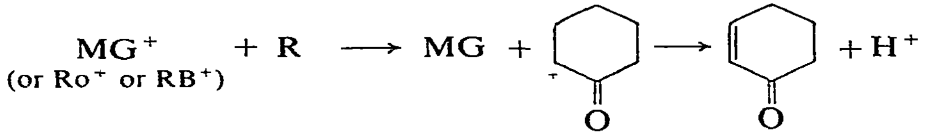
(1)



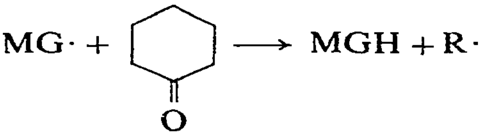
(2)



(3)

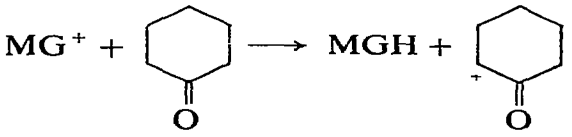


(4)



(5)

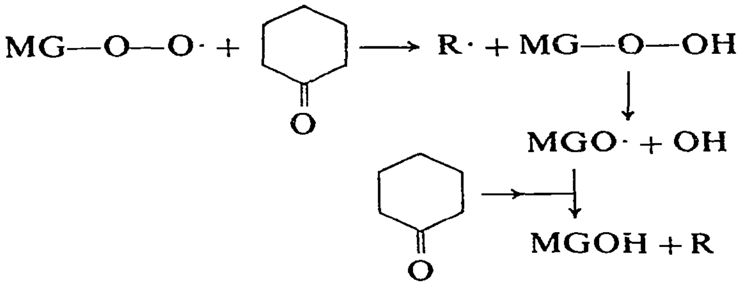
The overall result of reactions 4 and 5 (reaction 6) is reminiscent of an analogous but reverse process, namely the photosensitised oxidation of leuco crystal violet to Crystal Violet dye (CV^+), which proceeds by a sequential series of electron/proton/electron transfer reactions.[13]



(6)

The presence of oxygen in the system may result in oxidative degradation of the dye (eqns 7–8) and explain the induction period (eqn 9) which is a feature of the observed kinetics, especially in the case of MG^+ at short photolysis time

$$MG\cdot + O_2 \longrightarrow MG{-}O{-}O \qquad (7)$$



(8)

$$MG \; + O_2 \longrightarrow MG^+ + O_2^{\cdot -} \qquad (9)$$

The mechanism resembles that suggested by Allen *et al*[5] for the photofading of TPM dyes, except that in our systems electron transfer takes place from a radical (R) which has an appreciable lifetime or whose concentration is maintained in a chain process. It is consistent with other electron transfer processes suggested previously[9] for TPM dyes It is possible that photoinduced dark reactions, in some cases less obvious than the ones we have described, may be more numerous than has been realised previously and may be a complicating factor in many processes by which dyes undergo photodegradation.

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