Dyes and Pigments 3 (1982) 49–58

THE CONTRIBUTION OF SINGLET OXYGEN TO THE PHOTOFADING OF TRIPHENYLMETHANE AND RELATED DYES

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(Received: 19 June, 1981)

SUMMARY

The contribution of singlet oxygen ($^1\Delta_gO_2$) to the photofading of Crystal Violet in some solvents is examined. The rates of photofading in dichloromethane or acetone are accelerated in the presence of singlet oxygen sensitizers, e.g. Methylene Blue. The rates are retarded by adding effective singlet oxygen quenchers such as β-carotene or nickel dimethyldithiocarbamate. It seems that Crystal Violet is mainly photo-oxidized to give Michler's ketone and p-*dimethylaminophenol via the reaction with singlet oxygen, which can be generated by the dye itself or by an added sensitizer. The effect of various singlet oxygen quenchers on the photostability of coloured materials derived from colour formers, such as Crystal Violet Lactone and 3-diethylamino-6-methyl-7-anilinofluoran, is examined also on silica gel.*

1. INTRODUCTION

Several studies of the photofading behaviour of triphenylmethane dyes in solution or on textile materials have been reported.[1–8] Henriquez[3] proposed that in aqueous solutions of Crystal Violet and Malachite Green, dealkylation of dimethylamino groups on the phenyl rings occurred to form Parafuchsine or Doebner's Violet. On the other hand, Iwamoto[5] isolated Michler's ketone [4,4'-bis(dimethylamino)benzophenone] from the photofading products of Crystal Violet in the

Dyes and Pigments 0143-7208/82/0003-0049/$02·75

presence of air. Porter and Spears[6] exposed Malachite Green to a carbon arc source in aqueous solution or on carboxylated cellulose film, and isolated 4-dimethylaminobenzophenone, 4-methylaminobenzophenone, *p*-dimethylaminophenol and an additional product, the carbinol form of Malachite Green.

In recent years, the contribution of singlet oxygen to the photofading of some dyes has been examined. For example, it has been reported that arylazonaphthols,[9,10] indigo,[11] quinophthalones[12] and aminoanthraquinone dyes[13] undergo self-sensitized or dye-sensitized photo-oxidation in solution. Furthermore, the contribution of singlet oxygen to catalytic fading in dye mixtures has been reported recently.[14,15]

In the present work, we wish to report the photofading behaviour of Crystal Violet (**1**) in some solvents under aerobic conditions, together with the mechanism of the photo-decompositions. We have also examined the effect of singlet oxygen quenchers on the photostability of coloured materials derived from colour formers such as Crystal Violet Lactone and 3-diethylamino-6-methyl-7-anilinofluoran.

2. EXPERIMENTAL

2.1. *Materials*

The chloride of Crystal Violet (CI Basic Violet 3, λ_{max} 588 nm) (**1**) and Malachite Green (CI Basic Green 4, λ_{max} 420 and 616 nm) (**2**) were commercial reagents (Tokyo Kasei Co. Ltd). Compounds (**1**) and (**2**) were considered chromatographically pure. Crystal Violet Lactone (**8**) and 3-diethylamino-6-methyl-7-anilinofluoran (**10**) were obtained from commercial products.

2.2. *Procedure for photofading of* (**1**)

Solutions ($2{\cdot}0 \times 10^{-5}$ mol litre^{-1}) of **1** in 400 ml of dichloromethane, acetone or methanol were prepared. These air-saturated solutions were placed in an inside-irradiation-type flask (500 ml) equipped with a thermometer, condenser and magnetic stirrer and were irradiated at 22–25 °C with a 100W high-pressure mercury lamp (Ushio Electric Inc., UM-102). A Pyrex glass filter was used for filtered radiation ($\lambda > 300$ nm).

Dye solutions (400 ml, $2{\cdot}0 \times 10^{-5}$ mol litre^{-1}) containing Methylene Blue (3 mg), β-carotene (107 mg), nickel dimethyldithiocarbamate (NMC) (9·6 mg), 1,4-diazabicyclo[2.2.2]octane (DABCO) (890 mg) or 2,6-di-*t*-butyl-*p*-cresol (440 mg) were irradiated in a similar manner.

The absorption spectra of the dye solutions were measured before and after irradiation using a Shimadzu recording spectrophotometer (UV-201 type), and the relative percentage fading was determined at the absorption maximum of **1**.

Similar experiments were carried out with **2**.

2.3. *Identification of products*

A 285 mg/500 ml solution of Crystal Violet (**1**) in dichloromethane was irradiated for 10 h with filtered radiation ($\lambda > 300$ nm). After irradiation, most of the solvent was reduced in volume to 10 ml using a rotary evaporator under reduced pressure. The resulting residue was put on an activated alumina column, and then eluted using benzene and dichloromethane–acetone (9:1, v/v). Four fractions were taken. The UV spectrum and tlc analysis of the first fraction coming off the column revealed *p*-dimethylaminophenol together with smaller amounts of minor products. A compound in the second fraction coming off the column was identified as 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) by comparing its melting point (172–173·5 °C), R_f values [methanol–acetone (1:1, v/v) 0·80, benzene–acetone (4:1, v/v) 0·58 and chloroform–acetone (7:3, v/v) 0·64] and UV-spectrum (λ_{max} 245 and 370 nm) with those of an authentic sample. The visible spectrum of the third fraction showed absorption maxima at 538 nm (shoulder) and 586 nm. The former was nearly identical to one of Parafuchsine, and the latter was identical with one of unchanged starting dye. The analysis of the fourth fraction showed the unchanged starting dye.

In addition, the formation of *p*-dimethylaminophenol could be also observed in the aqueous alkaline solution extracted from the reaction mixture. Therefore the irradiated solution was extracted with aqueous sodium hydroxide. The extract was neutralized with hydrochloric acid solution and once again was extracted with benzene. The benzene extract was evaporated under reduced pressure, and the crude crystal-like residue was recrystallized once from ligroin. The material obtained was identified as *p*-dimethylaminophenol by comparison of its melting point (72–75 °C) and R_f value with those of an authentic sample prepared by a method described in the literature.[6]

2.4. *Competitive photo-oxygenation*

A solution of **1** ($2{\cdot}5 \times 10^{-5}$ mol litre^{-1}) in 100 ml acetone was prepared and 4 ml of the solution was mixed with 1 ml of NMC solution at various concentrations. The solutions (5 ml) were sealed in a Pyrex cell (10 × 10 × 60 mm) with a stopper, and irradiated with filtered radiation ($\lambda > 300$ nm) through the Pyrex glass filter from outside of the vessel. After irradiation, the relative percentage fading of dye was determined spectrophotometrically, and the relationship between the reciprocal of the rate of decomposition of the dye and the concentration of NMC was plotted (Fig. 3).

2.5. *Photofading of colour formers on silica gel*

A solution containing 238 mg of 3-diethylamino-6-methyl-7-anilinofluoran (**10**) in 200 ml of acetone–chloroform (1:1, v/v) was prepared. Nickel bis(dithiobenzil) (NBDB, 27·2 mg or 2·72 mg), nickel dibutyldithiocarbamate (NBC, 23·4 mg), DABCO (5·6 mg), 2,6-di-*t*-butyl-*p*-cresol (HP, 11 mg) or NBDB–HP (27·2 mg and

5·5 mg) were added to 20 ml aliquots. The solutions (20 μl) were spotted on silica gel tlc plates using a microcylinder and dried for 30 minutes at room temperature. The plates were exposed to air and light through a Pyrex glass filter from a 100W mercury lamp *ca* 5 cm from the plate. The apparatus was kept at 30–33 °C. After irradiation for 20 h, plates were developed with methanol. The spot of separated dye was scanned using a dual-wavelength chromatoscanner (Shimadzu, CS-900). The conversion (%) was calculated from the integration values obtained by the scanning.

Similar operations with the solutions of Crystal Violet Lactone (**8**) were carried out using nickel dibutyldithiocarbamate, nickel bis(dithiobenzil) and 2,6-di-*t*-butyl-*p*-cresol.

3. RESULTS AND DISCUSSION

3.1. *Photofading behaviour in different solvents*

A solution of Crystal Violet (**1**) in dichloromethane was faded in the presence of oxygen on exposure to filtered radiation ($\lambda > 300$ nm) from a high-pressure mercury lamp source. Figure 1 shows the photofading behaviour of **1** in the presence of various additives on exposure to filtered radiation. The rate of the photofading was accelerated by adding a singlet oxygen sensitizer such as Methylene Blue. On the other hand the rate was retarded in the presence of β-carotene or NMC, which act as quenchers of singlet oxygen. Furthermore, the rate of the photofading was only

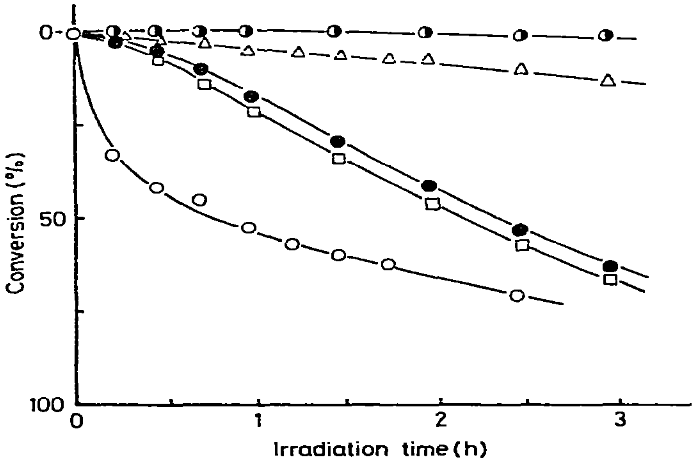


Fig. 1: Effect of additives on the photofading of Crystal Violet (**1**) in dichloromethane. Dye solution, 400 ml of $2{\cdot}0 \times 10^{-5}$ M. 100W internal high-pressure mercury lamp. Pyrex glass filter ($\lambda > 300$ nm). Additives: ●, none; ◑, nickel dimethyldithiocarbamate ($8{\cdot}0 \times 10^{-5}$ M); △, β-carotene ($5{\cdot}0 \times 10^{-4}$ M); ○, Methylene Blue ($2{\cdot}0 \times 10^{-5}$ M); □, 2,6-di-*t*-butyl-*p*-cresol ($5{\cdot}0 \times 10^{-3}$ M).

slightly altered by the addition of 2,6-di-*t*-butyl-*p*-cresol, a good free-radical scavenger. These results suggest the involvement of singlet oxygen (presumably $^1\Delta_g$) in the photochemical oxidation of **1**.

The photofading behaviour of Malachite Green **2** was similar to that of **1**.

Figure 2 shows the relative rates of the photofading of **1** in various solvents without a sensitizer. The rate of reaction depended on the solvent, apparently as a function of singlet oxygen lifetime.[16–19]

To obtain additional evidence for the intermediacy of singlet oxygen, a competitive photo-oxygenation experiment with two different substrates, as described by Wilson[20] and our previous papers,[11,12,15] was performed. Crystal Violet (**1**) and nickel dimethyldithiocarbamate (NMC) were used as acceptors (NMC acts as a quencher only, while **1** undergoes oxidation as well as acting as its own sensitizer).

For steady-state concentrations of **1*** and $^1O_2$ the reciprocal of the rate of dye decomposition should be linearly dependent on NMC concentration. Figure 3 shows the result in this case, and NMC was shown to react faster than **1** with $^1O_2$ by a factor of *ca* 11.

When **1** was irradiated with filtered radiation ($\lambda > 300$ nm) in dichloromethane,

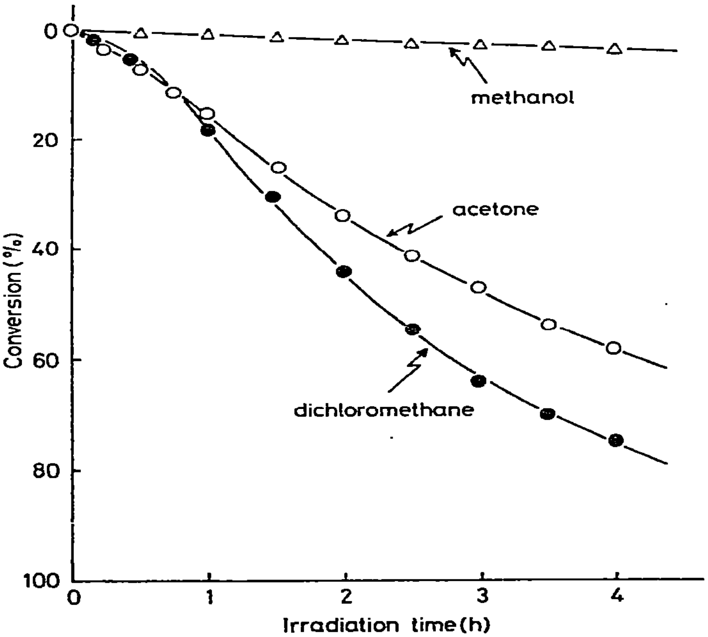


Fig. 2. Photofading behaviour of Crystal Violet (**1**) in various solvents. Dye solution, 400 ml of 2·0 × 10^{-5} M. 100W internal high-pressure mercury lamp. Pyrex glass filter ($\lambda > 300$ nm).

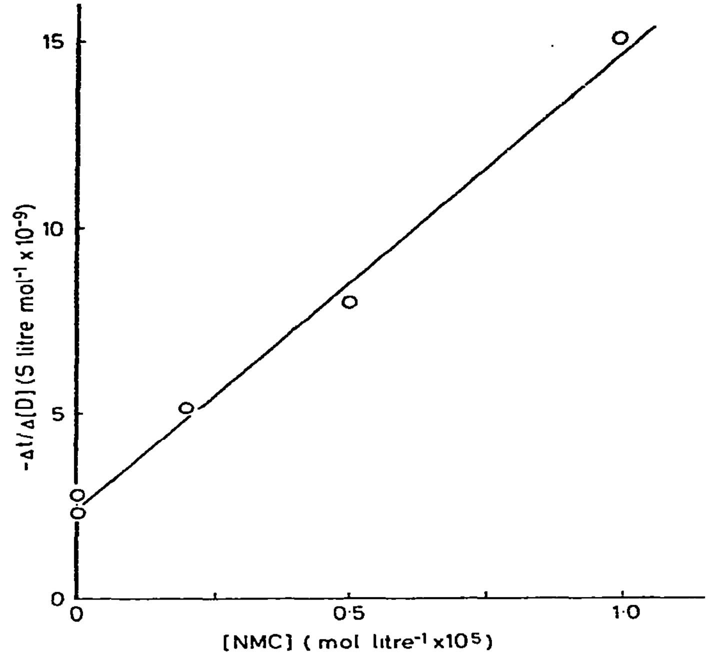


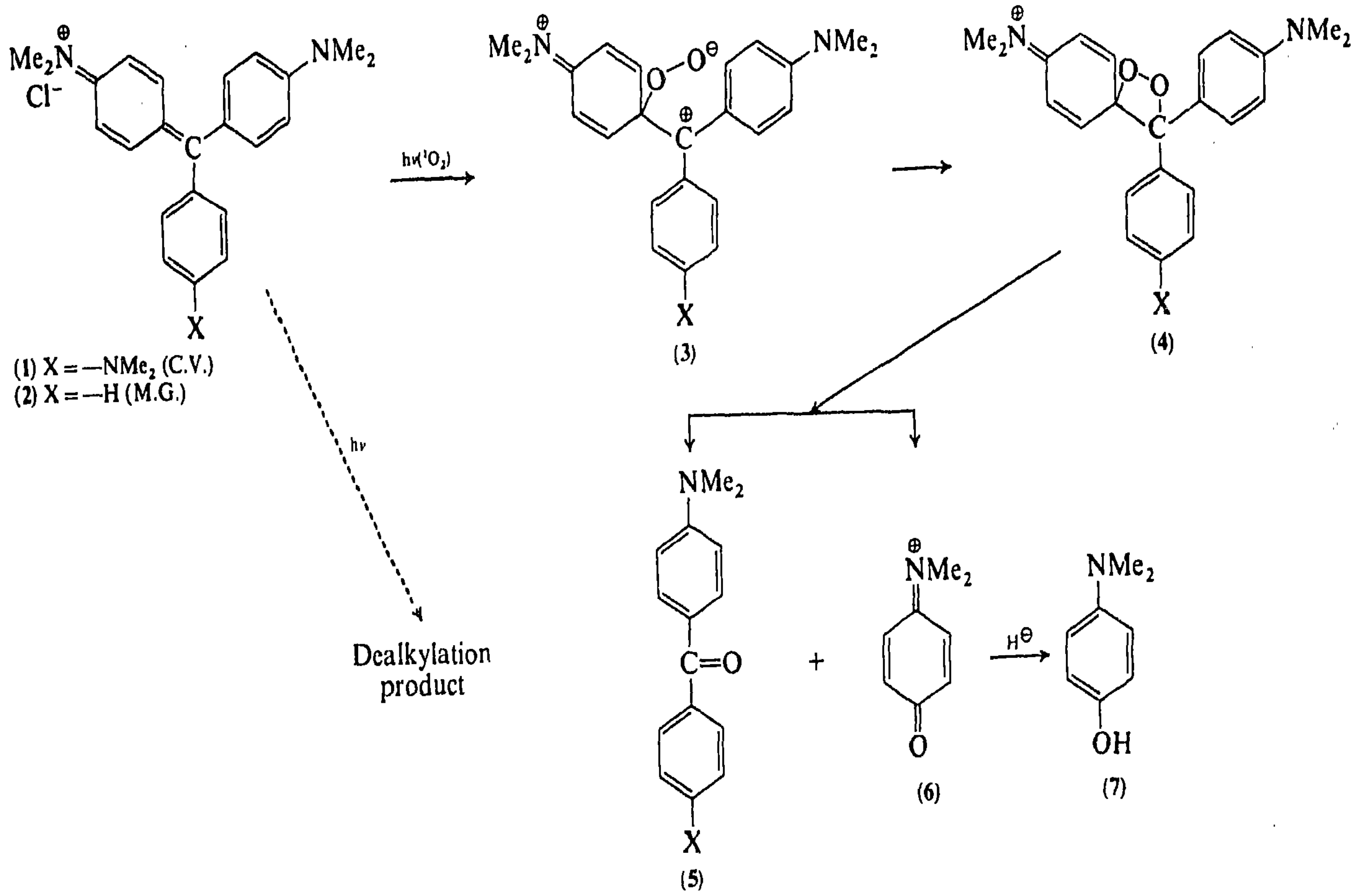
Fig. 3. Inverse of the rate of decomposition of Crystal Violet (1) ($-\Delta t/\Delta[D]$) as a function of NMC concentration. Initial concentration of (1), $2{\cdot}0 \times 10^{-5}$ M in acetone. Self-sensitized (filtered radiation, $\lambda > 300$ nm for 3 h).

the products were Michler's ketone [4,4′-bis(dimethylamino)benzophenone], *p*-dimethylaminophenol and Parafuchsine, which were identified by comparison with authentic samples.

On the other hand, the photodecomposition products of Malachite Green (2) have been identified by many workers.[3–6] From irradiation of **2** in aqueous solution or on carboxylated cellulose, Porter and Spears[6] isolated oxidative products such as 4-dimethylaminobenzophenone, 4-methylaminobenzophenone and *p*-dimethylaminophenol, together with the carbinol form of **2** as the minor product. Iwamoto[5] also obtained the same two ketones from the photofading mixture.

3.2. *Mechanism of the photofading of Crystal Violet and Malachite Green*

The most probable mechanism of the photofading and the formation of the products is shown in Scheme 1. Attack of singlet oxygen on Crystal Violet should lead to the unstable dioxetan intermediate, which could produce dimethylaminobenzophenones and dimethylaminophenol. The structure of the dioxetan intermediate was supported also by the calculation of the π-electron density of


Me₂N⊕
Cl⁻
NMe₂
C
X
(1) X = —NMe₂ (C.V.)
(2) X = —H (M.G.)
hν(¹O₂)
hν
Dealkylation product
Me₂N⊕
O–O⊖
C⊕
NMe₂
(3)
O-O
C
(4)
NMe₂
C=O
(5)
+
⊕NMe₂
O
(6)
H⊖
OH
(7)

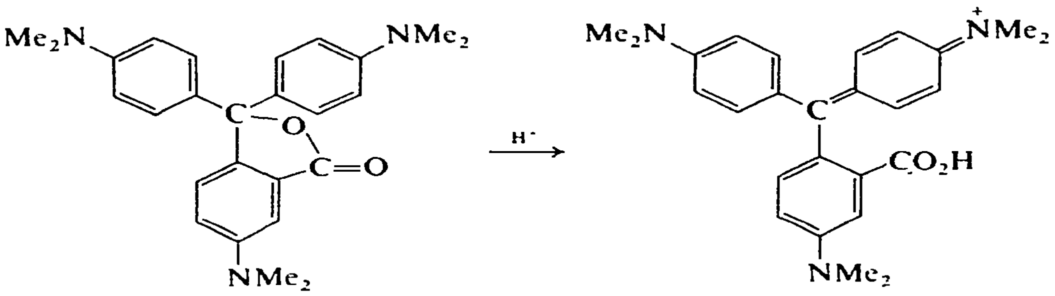
Scheme 1

Crystal Violet using a Pariser–Parr–Pople molecular orbital calculation (PPPMO) method.[21] The mechanism is appropriate also for the photofading of Malachite Green.

In the case of Crystal Violet, the contribution of dealkylation was also suggested, since small amounts of Parafuchsine could be detected in the reaction mixture. The extent of the contribution of the dealkylation, however, was very much smaller than that of the singlet oxygen mechanism. Similarly, it is known that Malachite Green gives Doebner's Violet by the dealkylation of the dimethylamino group.[6]

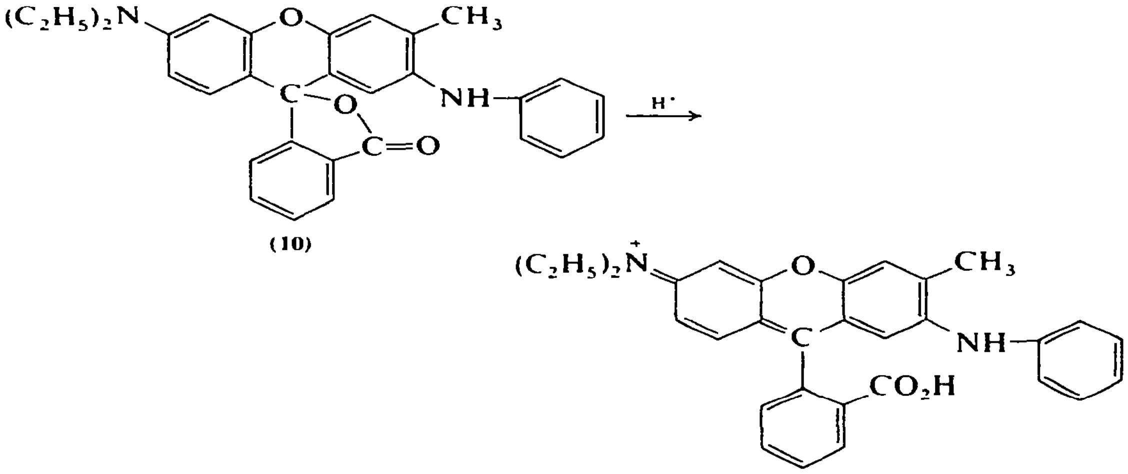
3.3. *Effect of singlet oxygen quenchers to the photostability of colour formers*

Crystal Violet Lactone (**8**) and 3-diethylamino-6-methyl-7-anilinofluoran (**10**) are extensively used for technical reproduction, e.g. business forms for register or computer. The colour materials derived from these colour formers show a blue-tinged violet colour (**9**) and black (**11**). Generally, the dyes derived from the colour



(8)

(9)



(10)

(11)

formers have a poor fastness to light, and an improvement of the properties is required.[22] In this work, the effect of various additives on the photostability of the dyes **9** and **11** derived from **8** or **10** was examined on silica gel plate.

The parent structure of **9** resembles that of Crystal Violet (**1**). Therefore it is assumed that the photofading of **9** on silica gel may involve the contribution of singlet oxygen. The influence of some additives on the photostability of **9** is summarized in Table 1. When **9** on silica gel plate was exposed for 10 h to filtered radiation ($\lambda > 300$ nm) and air, it showed 47·7 % conversion, and in the presence of equivalent molar amounts of NBC or NBDB, good singlet oxygen quenchers[23-26] showed 16 % and 13 % conversion, respectively. On the other hand, 2,6-di-*t*-butyl-*p*-cresol had no influence on the rate of photofading. These results indicate that the photo-oxidation of **9** on silica gel plate also takes place predominantly via the singlet oxygen mechanism.

TABLE 1

EFFECT OF ADDITIVES ON THE PHOTOSTABILITY OF **9** AND **11** ON SILICA GEL[a]

Run no.	*Dye*	*Additive*[d]	*Conversion* (%)[g]
1	9[b]	None	47·7
2		NBC	16·0
3		NBDB	13·0
4		HP	48·5
5	11[c]	None	54·1
6		DABCO	38·0
7		NBC	28·8
8		NBDB[e]	24·7
9		NBDB	8·3
10		HP	54·3
11		NBDB–HP[f]	10·7

[a] In all runs, tlc silica gel plates bearing 20 μl of the dye solutions [$2{\cdot}5 \times 10^{-3}$ M, in 20 ml acetone–chloroform (1:1, v/v)] were exposed to air and light ($\lambda > 300$ nm).

[b] The dye was exposed for 10 h.

[c] The dye was exposed for 20 h.

[d] As additives, DABCO, nickel dibutyldithiocarbamate (NBC), nickel bis(dithiobenzil) (NBDB) and 2,6-di-*t*-butyl-*p*-cresol (HP) were used. Additive/dye = 1·0 (mol ratio).

[e] NBDB/dye = 0·1 (mol ratio).

[f] NBDB and HP were added.

[g] From tlc analysis.

The fading behaviour of **11** derived from **10** on silica gel plates was examined in the same manner as above. Although the photo-reaction mechanism of **11** has not been defined yet, similar effects of the additives were observed on silica gel. Thus it was found that the transition metal complexes have suppressing effects on the photofading of **11**.

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