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# Role of Counter-Ions in the Photofading Reaction of Crystal Violet Lactone

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## *ABSTRACT*

*The photofading behaviour of Crystal Violet lactone was investigated in solution and in the adsorbed state and the contribution of dye counter-ions to the fading is demonstrated. A novel approach for improving the lightfastness of indicator dyes in pressure (or heat)-sensitive recording systems is proposed.*

## 1 INTRODUCTION

Several studies have been made to identify the decomposition products of triphenylmethane dyes in varied physical environments. Henriquez[1] noted that, in aqueous solutions of Malachite Green or Crystal Violet, dealkylation of the amino groups on the phenyl rings occurred to form Doebner's Violet or parafuchsine. Iwamoto[2] and other workers[3–5] showed that Malachite Green and Crystal Violet were photo-oxidised in the presence of oxygen to *p*-dimethylaminobenzophenone and Michler's ketone, respectively. Porter & Spears[4] isolated 4-methylaminobenzophenone, 4-dimethylaminobenzophenone and *p*-dimethylaminophenol as

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the decomposition products in UV-irradiated aqueous solutions of Malachite Green.

The photostabilities of cationic triphenylmethane dyes are affected by the substrate and by external agents such as oxygen and water. For example, the lightfastness of C.I. Basic Blue 18 varies from below 1 on cotton in the presence of moisture and oxygen up to 7 on Orlon in the presence of nitrogen.[6] Many proposals have been advanced to account for the roles which water and oxygen play in the photofading reaction of triphenylmethane dyes, but a definite conclusion has not yet been reached.

The reason for the higher lightfastness shown by triphenylmethane dyes on basic-dyeable polyacrylonitrile fibres (e.g. Orlon) compared with that exhibited on other substrates has been studied in some detail by several workers.[4,7-11] Zollinger[9] demonstrated that the counter-ion is a factor of primary importance in the mechanism of light fading of cationic dyes on substrates of different chemical natures. Porter & Spears[4] observed a significant increase in the photostability of Malachite Green on sulphoethylated cotton compared with carboxymethylated or untreated cotton.

In the present paper, the effect of various counter-ions has been examined as a means of improving the lightfastness of coloured material derived from Crystal Violet lactone in solution and in a solid state.

## 2 EXPERIMENTAL

### 2.1 Materials

2-Hydroxybenzophenone (HBP), nickel dimethyldithiocarbamate (NMC), 2,2′-bis(4-hydroxyphenyl)propane and *n*-hexadecyltrimethylammonium bromide were commercial reagents (Tokyo Kasei Co. Ltd). Crystal Violet lactone (**1**), tetrachlorophthalic acid monoethyleneglycol ester zinc salt and tetrachlorophthalic acid monocyclohexyl ester zinc salt were obtained from commercial products. *s*-Benzylthiuronium chloride was synthesised and recrystallised according to the procedures described in the literature.[12]

### 2.2 Procedures for photofading of Crystal Violet lactone

An air-saturated solution ($5 \times 10^{-5}$ M) of **1** was prepared in a 300 ml mixture of acetic acid–dimethylsulphoxide (DMSO) (7:3, v/v), with or without additives ($1 \times 10^{-4}$, $2 \times 10^{-4}$ or $1 \times 10^{-3}$ M) of acids, NMC, HBP or sodium perchlorate. This was placed in a 300 ml flask equipped with a thermometer, condenser and magnetic stirrer, and then irradiated at 28–30°C with a 100W internal high-pressure mercury lamp (Ushio Electric Inc., UM-102 type).

The absorption spectra of the solutions were measured before and after irradiation using a Shimadzu recording spectrophotometer (UV-180 type) and relative conversions were determined at the absorption maximum of the coloured material **2** derived from the colour former **1**.

### 2.3 Photofading of colour former in adsorbed state

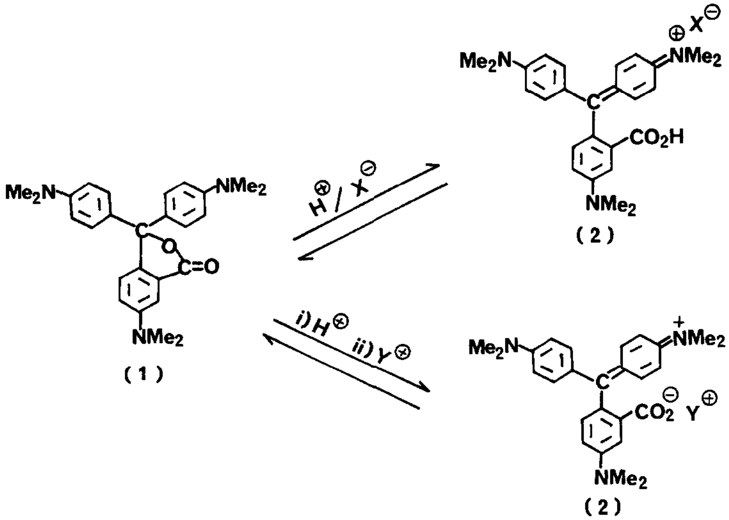
A solution of **1** ($4 \times 10^{-3}$ M) in 60% acetic acid (10 ml) with or without the additives ($4 \times 10^{-3}$ or $4 \times 10^{-2}$ M) such as acids, sodium perchlorate or HBP was prepared. Portions of the solutions (20 $\mu$l) were spotted on silica gel TLC plates and dried. NMC solution (10 $\mu$l, $2 \times 10^{-3}$ M) in chloroform was further spotted on a part of these spots and dried. The plates were held at a distance of approximately 5 cm from the light source and exposed to light ($\lambda > 300$ nm) in air. The apparatus was kept at 30 ± 2°C. After irradiation for 15 h, the plates were developed with chloroform–acetone (3:2, v/v). The spot of separated colour was scanned using a Shimadzu thin layer chromatoscanner (CS-920 type). The percentage conversion was calculated by comparison with unirradiated colour.

Similarly, solutions of **1** ($8 \times 10^{-3}$ M) in 10 ml of ethanol containing 2,2′-bis(4-hydroxyphenyl)propane ($2{\cdot}4 \times 10^{-2}$ mol) and HBP ($8 \times 10^{-4}$ mol) were prepared and the photofading with or without additive ($2 \times 10^{-2}$ M) was assessed on cellulose TLC plates.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of various carboxylic acids on the photofading of Crystal Violet lactone

The chemistry of colour formers has now become important, particularly in connection with the rapid development of information recording systems. Crystal Violet lactone (**1**) is of commercial interest as a blue indicator dye for carbonless copying paper, but this dye gradually fades and an improvement of this property is required.[13,14] Crystal Violet lactone (**1**) is a chromogenic compound in its colourless form. Acidic catalysts, e.g. acidic clay, open the lactone, thereby allowing a violet triarylmethane dye (**2**) to form (see Scheme 1). The parent structure of **2** resembles that of Crystal Violet (C.I. Basic Violet 3, $\lambda_{max}$ 586 nm). Therefore it can be expected that the contribution of dye counter-ions may be involved in the photofading reactions of **2**.[4,7–9] In a previous paper[16] the influence of various counter-ions on the photofading of colour former has been investigated in solution and in the adsorbed state.



Scheme 1.

**TABLE 1**

Effect of Dicarboxylic Acids on the Photostability of Dye **2** in the Presence of HBP[7]

| *Run* | *Additive* | *In acetic acid–DMSO*[a] | | *On silica gel*[b] | |
|---|---|---|---|---|---|
| | | *Conversion* (%) | *Relative ratio* | *Conversion* (%) | *Relative ratio* |
| 1 | None | 20 | 1·00 | 64 | 1·00 |
| | HOOC-$(CH_2)_n$-COOH | | | | |
| 2 | $n = 0$ | 13 | 0·65 | 48 | 0·75 |
| 3 | $n = 1$ | 16 | 0·80 | 50 | 0·78 |
| 4 | $n = 2$ | 13 | 0·65 | 45 | 0·70 |
| 5 | $n = 4$ | 13 | 0·65 | 39 | 0·61 |
| 6 | $n = 5$ | 12 | 0·60 | 62 | 0·97 |
| 7 | HC—COOH<br>‖<br>HC—COOH | 17 | 0·85 | 19 | 0·30 |
| 8 | $HClO_4$ | 10 | 0·50 | — | — |
| 9 | $NaClO_4$[c] | 9 | 0·45 | 22 | 0·34 |

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[a] In all runs, solution of dye ($5 \times 10^{-5}$ M) in acetic acid–DMSO (7:3, v/v) containing HBP ($1 \times 10^{-3}$ M) was irradiated for 3 h with unfiltered light ($\lambda > 300$ nm). Additive/dye = 2 (molar ratio).

[b] In all runs, TLC silica gel plates bearing 20 $\mu$l of the dye solutions ($4 \times 10^{-3}$ M, in 60% acetic acid) containing HBP ($4 \times 10^{-2}$ M) were exposed for 15 h to air and light ($\lambda > 300$ nm). Additive/dye = 1 (molar ratio).

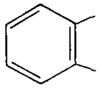
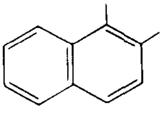
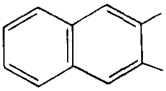
[c] Additive/dye = 10 (molar ratio).

It was found that the counter-ion plays a very important role in the retardation of that fading. In this work, the effect of various carboxylic acids on the photofading of the dye **2** derived from **1** was examined in the presence of *o*-hydroxybenzophenone (HBP), a good UV absorber, in solution and on silica gel. The influence of aliphatic dibasic acids on the fading of **2** is shown in Table 1. A solution of dye **2** in acetic acid–DMSO was faded in air on exposure to unfiltered light ($\lambda > 300\,\mathrm{nm}$) from a high-pressure mercury lamp. However, the addition of a series of aliphatic dibasic acids in the photofading system afforded considerable protection against fading. A similar protecting effect was observed also in the adsorbed state on silica gel, and maleic acid in particular showed an excellent suppressing effect against the fading. The protecting effect is apparently superior to that of perchlorate ion and this suggests that the dye counter-ion, forming such intramolecular hydrogen bonds as does maleic acid, is very effective in suppressing the fading of Crystal Violet lactone. This effect, with carboxylic acids capable of forming intramolecular hydrogen bonds, was examined in solution and on silica gel. The results are summarised in Tables 2 and 3, respectively.

As shown in Table 2, the majority of the hydroxy acids examined retarded the photofading of dye **2**. Salicyclic acid was found to be especially effective and the retarding effect in solution was appreciably higher than that of perchlorate ion. However, the addition of 1-hydroxy-2-naphthoic acid in

TABLE 2

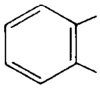
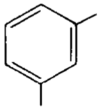
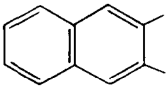
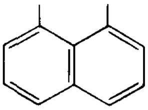
Effect of Hydroxy Acids on the Photostability of Dye **2** in the Presence of HBP[a]

| *Run* | *HO—X—COOH* *X* | *In acetic acid–DMSO* | | *On silica gel* | |
|---|---|---|---|---|---|
| | | *Conversion (%)* | *Relative ratio* | *Conversion (%)* | *Relative ratio* |
| 1 | None | 20 | 1·00 | 64 | 1·00 |
| 2 | —$CH_2$— | 14 | 0·70 | 49 | 0·77 |
| 3 |  | 7 | 0·35 | 35 | 0·55 |
| 4 |  [b] | 62 | 3·10 | 40 | 0·63 |
| 5 |  | 14 | 0·70 | 34 | 0·53 |

[a] Experimental conditions are identical to those described in Table 1.

[b] 1-Hydroxy-2-naphthoic acid.

**TABLE 3**
Effect of Aryl Dicarboxylic Acids on the Photostability of Dye **2** in the Presence of HBP[a]

| *Run* | *HOOC—Ar—COOH* *Ar* | *In acetic acid–DMSO* | | *On silica gel* | |
|---|---|---|---|---|---|
| | | *Conversion (%)* | *Relative ratio* | *Conversion (%)* | *Relative ratio* |
| 1 | None | 20 | 1·00 | 64 | 1·00 |
| 2 |  | 13 | 0·65 | 17 | 0·27 |
| 3 |  | 17 | 0·85 | 43 | 0·67 |
| 4 |  | 16 | 0·80 | 33 | 0·52 |
| 5 |  | 28 | 1·40 | 35 | 0·55 |

[a] Experimental conditions are identical to those described in Table 1.

**TABLE 4**
Effect of Additives on the Photostability of Dye **2** in the Presence of HBP[a]

| *Run* | *Additive* | *In acetic acid–DMSO* | | *On silica gel* | |
|---|---|---|---|---|---|
| | | *Conversion (%)* | *Relative ratio* | *Conversion (%)* | *Relative ratio* |
| 1 | None | 20 | 1·00 | 64 | 1·00 |
| 2 | HC—COOH<br>‖<br>HC—COOH | 17 | 0·85 | 19 | 0·30 |
| 3 | + NMC[b] | 0 | — | 9 | 0·14 |
| 4 | $o$-$C_6H_4$—$(COOH)_2$ | 13 | 0·65 | 17 | 0·27 |
| 5 | + NMC[b] | 0 | — | 9 | 0·14 |
| 6 | $o$-HO—$C_6H_4$—COOH | 7 | 0·35 | 35 | 0·55 |
| 7 | + NMC[b] | 0 | — | 28 | 0·44 |
| 8 | $NaClO_4$ | 9 | 0·45 | 22 | 0·34 |
| 9 | + NMC[b] | 0 | — | 0 | — |
| 10 | NMC[b] | 4 | 0·20 | 34 | 0·53 |

[a] Experimental conditions are identical to those described in Table 1.
[b] Additive/dye = 4 (molar ratio).

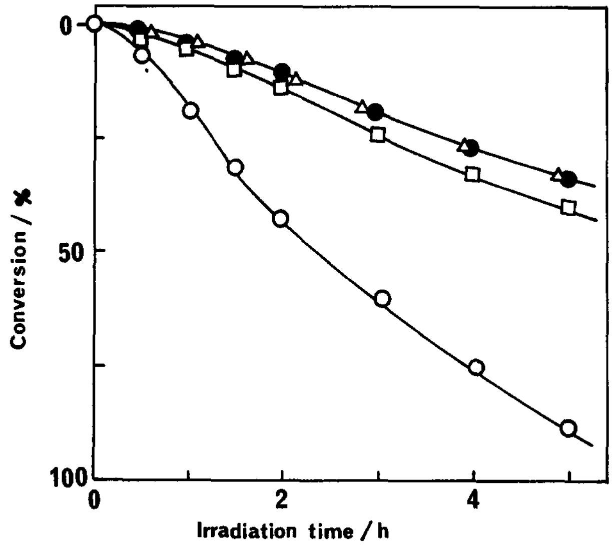


Fig. 1. Effect of additives on the photostability of dye **2** in acetic acid–DMSO mixture (7:3, v/v) in the presence of HBP ($1 \times 10^{-3}$ M). Initial concentrations: (**2**) $5 \times 10^{-5}$ M; additive $5 \times 10^{-5}$ M. ●, No additive; □, 1-naphthol; △, 2-naphthoic acid; ○, 1-hydroxy-2-naphthoic acid.

solution accelerated the fading of dye **2**. Such an enhanced photodegradation of **2** has also been observed on addition of 1-naphthol, but 2-naphthoic acid had no influence on the rate of fading (see Fig. 1). Reasons for this anomalous behaviour in solution are unclear. Table 3 also shows that some aryl dicarboxylic acids are very effective for the retardation of the photofading of dye **2**. On the other hand, the addition of isophthalic acid gave less efficient protection against the fading than phthalic acid, not only in solution but also in the adsorbed state on silica gel. This behaviour indicates that carboxylic acids capable of forming intramolecular hydrogen bonds may provide more marked improvements in the lightfastness properties of colour formers than do conventional acids.

## 3.2 Effect of simultaneous use of acids and singlet oxygen quencher on the photostability of colourant

On the basis of the above results, representative compounds, viz. maleic acid, phthalic acid and salicylic acid, were selected in each series, and the effect of the combined use of an acid and a singlet oxygen quencher on the photofading of dye **2** was examined in solution and on silica gel. As shown in Table 4, the retardation effect of the representative acids of each series on the fading of dye **2** compared favourably with that of nickel dimethyldithiocarbamate (NMC), a good singlet oxygen quencher,[17,18] in the adsorbed state on silica gel. The addition of these acids together with NMC significantly suppressed the rate of photofading of dye **2** not only in solution but also in the adsorbed state. These findings apparently imply that the combined use of such an acid, e.g. maleic acid or phthalic acid, and a singlet oxygen quencher is very effective for protecting the fading of colour formers such as Crystal Violet lactone.

### 3.3 Action of various cations on the photostability of Crystal Violet lactone on cellulose

In a previous paper,[16] it was found that the *s*-benzylthiuronium cation was very effective in retarding the photofading of Crystal Violet lactone in solution. Therefore, with various types of related cation, the effectiveness of these compounds was examined in the presence of HBP on cellulose. The influence of some additives on the photostability of dye **2** derived from **1** is summarised in Table 5. When dye **2** on a cellulose plate was exposed for 5h to unfiltered radiation ($\lambda > 300$ nm) and air, it showed 59% conversion, and in the presence of tetrachlorophthalic acid monoethyleneglycol ester zinc salt or the cyclohexyl derivative, it showed 30% and 44% conversion, respectively. The fading on the addition of *n*-hexadecyltrimethylammonium bromide was 35% conversion. However, when *s*-benzylthiuronium chloride was added to the photofading system, dye **2** still showed 57% conversion, in contrast to that in solution. These results indicate that zinc salts or long-chain alkyl cations are very useful counter-ions in the retardation of the photofading of Crystal Violet lactone.

TABLE 5
Effect of Various Additives on the Photostability of Dye **2** in the Presence of HBP[a]

| *Run* | *Additive* | *Conversion*[b] (%) |
|---|---|---|
| 1 | None | 59 |
| 2 | $(HOCH_2CH_2OOCC_6Cl_4COO)_2Zn$ | 30 |
| 3 | $(C_6H_{11}OOCC_6Cl_4COO)_2Zn$ | 44 |
| 4 | $[BzSC(NH_2)_2]^+Cl^-$ | 57 |
| 5 | $[CH_3(CH_2)_{15}N(CH_2)_3]^+Br^-$ | 35 |

[a] In all runs, TLC cellulose plates bearing 10 μl of the dye solutions ($8 \times 10^{-3}$ M, in ethanol) containing 2,2′-bis-(4-hydroxyphenyl)propane ($2{\cdot}4 \times 10^{-4}$ M) and HBP ($8 \times 10^{-2}$ M) were exposed for 5 h to air and light ($\lambda > 300$ nm). Additive/dye = 5 (molar ratio).

[b] Developing solvent: 60% acetic acid.

## 4 CONCLUSION

The contribution of counter-ions to the photofading of cationic dyes has been examined by several workers.[4,7-11] However, there are few experiments in which the use of counter-ions as a means of improving lightfastness of indicator dyes in pressure (or heat)-sensitive recording systems has been examined. In this paper we have reported the influence of various counter-ions on the photofading of coloured material derived from a colour former.

The results suggested a novel approach for improving the lightfastness of colourants for imaging and data recording systems. Whilst the situation with recording paper is expected to be more complicated because of specific interactions between dye and substrate, the investigation of similar counter-ions as a means of improving lightfastness in such systems would be of particular practical interest. The counter-ions examined in this study also can be expected to improve the image stability of the system.

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