Dyes and Pigments 2 (1981) 133–141

MECHANISM OF THE PHOTOFADING OF DYE: CONTRIBUTION OF SINGLET OXYGEN TO THE PHOTOFADING OF AMINOANTHRAQUINONE DYES

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SUMMARY

The contribution of singlet oxygen ($^1\Delta_gO_2$) to the photofading of some animoanthraquinone dyes in solution is examined. The rates of the photofading are accelerated in the presence of sensitizers of singlet oxygen, e.g. Rose Bengal or Methylene Blue. The rates are retarded by adding effective singlet oxygen quenchers, such as DABCO or nickel dimethyldithiocarbamate (NMC). Additional evidence for the intermediacy of singlet oxygen is obtained by examining the effect of deuterium solvent, the effect of chemical sources of singlet oxygen, and the competitive photo-oxygenation with the dyes and NMC.

1. INTRODUCTION

Despite extensive investigations[1–9] into the photofading of anthraquinone dyes in solution or on textile materials, there is no clear understanding of the mechanism involved.

In recent years, the contribution of singlet oxygen to the photofading of some dyes has been reported. For example, Griffiths and Hawkins[10,11] reported the photochemical oxidation of 4-arylazo-1-naphthols and their analogous dyes, and we showed that 1-arylazo-2-naphthols,[12] indigo[13] and quinophthalone dyes[14] undergo the self-sensitized or dye-sensitized photooxidation in solutions. Zweig and Henderson[15] have also reported that some aminoanthraquinone dyes should be able to produce singlet oxygen. Furthermore, the contribution of singlet oxygen to catalytic fading by some aminoanthraquinone dyes in dye mixtures has been recently reported.[16,17] However no work has been reported in which aminoanthraquinone dyes are decomposed via reaction with singlet oxygen by a self-sensitized process.

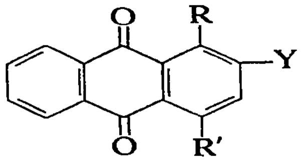
Dyes and Pigments 0143-7208/81/0002–0133/$02.50—
Printed in Northern Ireland

In the present work, we wish to report the photofading behaviours of some aminoanthraquinone dyes in solvents under aerobic conditions, together with evidence for the mechanism of the photofading.

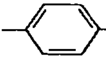
2. EXPERIMENTAL

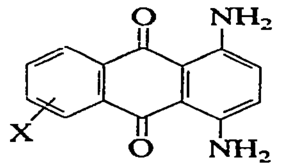
2.1. *Source of materials*

Dye Nos. **2**, **9** and **13** were prepared according to the literature.[18] Dye Nos. **1**, **3**–**6** and **11** were commercial reagents. Dye Nos. **7**, **8**, **10** and **12** were obtained by Soxhlet-extraction with benzene–acetone (1:1, v/v) from the commericial products.



1 R = R' = OH, Y = H (λ_{max} 481 nm in acetone)
2 R = R' = OCH$_3$ Y = H (λ_{max} 425 nm)
3 R = NH$_2$, R' = Y = H (λ_{max} 474 nm)
4 R = NH—C$_4$H$_9$(n), R' = Y = H (λ_{max} 514 nm)
5 R = R' = NH$_2$, Y = H (λ_{max} 550 and 590 nm)
6 R = NH$_2$, R' = OH, Y = H (λ_{max} 525 and 560 nm)
7 R = NH$_2$, R' = OH, Y = OCH$_3$ (λ_{max} 510 and 546 nm)
8 R = NH$_2$, R' = NHCH$_3$, Y = H (λ_{max} 570 and 614 nm)
9 R = R' = NHCH$_3$, Y = H (λ_{max} 596 and 643 nm)
10 R = NHCH$_3$, R' = NHC$_2$H$_4$OH, Y = H (λ_{max} 593 and 640 nm)

11 R = R' = NH——CH$_3$, Y = H (λ_{max} 602 and 638 nm)



12 X = 5,8-(NH$_2$)$_2$ (λ_{max} 598 and 641 nm)
13 X = 5,6-benzo (λ_{max} 583 and 624 nm)

All dyes were purified by repeated recrystallization followed by chromatography over activated-alumina(benzene–acetone = 9:1, v/v).

2.2. *Procedures for photofading of anthraquinone compounds in solvent*

The following method typifies the procedure used to examine the photofading behaviour: A solution ($1{\cdot}0 \times 10^{-4}$ mole litre^{-1}) of the anthraquinone compound in 200 ml of acetone containing or not containing the additive Rose Bengal (20 mg), 1,4-diazabicyclo[2.2.2]octane (DABCO, 890 mg), β-carotene (50 mg) or nickel dimethyldithiocarbamate (NMC) (6 mg, $1{\cdot}0 \times 10^{-4}$ mole litre^{-1}) was prepared. This solution, placed in a 250 ml quartz flask equipped with a thermometer, condenser and magnetic stirrer, was irradiated at 21–25°C with a 500 W high-pressure mercury lamp (Ushio Electric Inc., UI-501 type) from outside the vessel in an aerobic atmosphere. The vessel was kept at a distance of approximately 25 cm from the light source. To exclude undesirable wavelengths of light, coloured glass filters (Toshiba, manufacturer's number UV-39, V-V42, V-Y42 or V-052 filters) were used.

The absorption spectra of the dye solutions were measured before and after irradiation using a Shimadzu recording spectrophotometer (UV-200 type), and the relative percentage fading was determined at the absorption maximum of each dye.[12,13]

In the cases where Rose Bengal or β-carotene was added, the relative percentage fading was determined using thin layer chromatography (t.l.c), i.e., the reaction mixture was developed on a silica gel plate (solvent: benzene–acetone = 9 : 1), and the spot of separated anthraquinone compound was scanned at the absorption maximum of each dye by means of a thin layer chromatoscanner (Shimadzu, CS-900 type). The relative percentage fading was calculated from the integration values obtained by scanning.

2.3. *Indentification of product*

In the present work, phthalic acid was formed as the main product of photofading.

Solutions ($2{\cdot}0 \times 10^{-4}$ mole litre^{-1}) of **1**, **9** or **11** in 500 ml of acetone were irradiated under an oxygen atmosphere (O_2 gas, 10 ml min^{-1}) through a Pyrex glass filter with a 100 W inside high-pressure mercury lamp. After irradiation for several hours (7–20 h), the solvent was removed by careful evaporation under reduced pressure. A colourless crystal, isolated by sublimation from the residue, was identified as phthalic anhydride by comparing its m.p., u.v.- and i.r.-spectra with those of an authentic sample. The yield of phthalic acid was determined by g.l.c. analysis. It was detectable as phthalic anhydride under high column temperature conditions (at 180°C, 10% silicon OV-17 column). Phthalic acid from **9** was obtained in 80–85% yields (based on reacted dyes). Phthalic acid from **1** or **11** was obtained in 50–60% yields.

2.4. *Competitive photo-oxygenation experiments*

A solution ($5{\cdot}0 \times 10^{-5}$ mole litre^{-1}) of aminoanthraquinone dye in 200 ml of acetone was prepared. Four millilitres of this solution were mixed with 1 ml of the NMC solution with various concentrations. The mixed solutions (5 ml) were sealed in Pyrex-cells ($10 \times 10 \times 60$ mm) with a stopper, and irradiated with filtered radiation ($\lambda > 420$ nm) from outside the vessel. After the irradiation in each case, the relative percentage fading of dye was determined spectrophotometrically. The irradiation time was kept constant (5 h) for a given concentration of NMC, and the relative percentage fading was kept to less than 10%.

The relationships between the reciprocal of the rate of decomposition of used dyes and the concentration of NMC were determined.

2.5. *Comparison of the rates of photo-oxidation in methanol–water and in tetradeuteriomethanol–deuterium oxide*

A solution of **9** (3·0 mg) and Rose Bengal in methanol–water (1 : 1, v/v) was prepared. Samples (1·0 ml) were added to oxygenated mixtures of CH_3OH (1·0 ml) and H_2O (1·0 ml) or CD_3OD (1·0 ml) and D_2O (1·0 ml) in sealed Pyrex cells. The absorbances of the solutions ($1{\cdot}3 \times 10^{-5}$ mole litre^{-1}) were recorded directly at the absorption maximum of **9**, and the solutions were then immersed in a bath containing a filter solution (5% $NaNO_2$ aq.). The dye-solutions were irradiated at 15–16°C through the filter solution which cut out the wavelengths below 430 nm, using a 100 W high-pressure mercury lamp, with uniform exposure of the samples. After 5 h the absorbance values were determined, and the relative percentage fading (conversion) was calculated. The deuterated solution showed 43·1% conversion, whereas the nondeuterated solution showed 5·7% conversion.

Similar experiments with compounds **5** and **13** were carried out and the results are summarized in Table 2 (see later).

2.6. *Chemical oxidation of anthraquinone compounds with hydrogen peroxide–sodium hypochlorite*

A solution ($2{\cdot}0 \times 10^{-4}$ mole litre^{-1}) of 5·3 mg **9** in 100 ml of methanol was cooled to 0°C and aqueous hydrogen peroxide ($6{\cdot}0 \times 10^{-5}$ mole of H_2O_2 in 1·0 ml distilled water) was added. The solution was stirred and 20 ml of sodium hypochlorite solution ($5{\cdot}0 \times 10^{-5}$ mole amounts in 20 ml of distilled water) was added dropwise over 90 min. The absorption spectra of the dye solutions were measured, and the relative percentage fading (48·2%) was determined by the method described in Section 2.2. When the reaction was repeated in the presence of DABCO (0·12 M), the extent of oxidation of **9** was greatly reduced (7·2% conversion).

Similar experiments with the other compounds were carried out, and the results are summarized in Table 1 (see later).

2.7. *Influence of superoxide ion in the photofading of aminoanthraquinone dyes*

A solution of epinephrine ($2{\cdot}5 \times 10^{-3}$ mole litre^{-1}) and **9** ($4{\cdot}0 \times 10^{-5}$ mole litre^{-1}) in 200 ml of CH_3CN–0·024N aq. HCl (9 : 1, v/v) was prepared. The solution was irradiated under an aerobic condition with filtered radiation ($\lambda > 520$ nm) from outside the vessel. But in this case, a new absorption band (based on adrenochrome) in the visible spectrum did not appear.

Similar results were also observed when sets of solutions containing **6**, **10** or **11** in place of **9** were irradiated.

3. RESULTS AND DISCUSSION

3.1. *Photo-oxidation of aminoanthraquinone dyes in some solvents*

The solutions of **1**–**13** in organic media such as acetone, dichloromethane–methanol (4:1, v/v) or dimethylsulphoxide (DMSO) were faded in the presence of oxygen on exposure to unfiltered radiation from a high-pressure mercury lamp source. Phthalic acid was obtained as a main product. The solutions of **6**–**13** were faded also by exposure to filtered visible radiation but solutions of **2**–**5** were relatively stable under these conditions.

Table 1 shows the relative percentage fading of **1** and **6**–**12** in the presence of various additives on exposure to filtered visible radiation. The rates of photofading were increased by the addition of singlet oxygen sensitizers such as Rose Bengal or Methylene Blue. On the other hand these rates were retarded in the presence of DABCO or NMC, which act as quenchers of singlet oxygen. In general, the rates of the photo-reactions were more rapid in dipolar aprotic solvents than in protic solvents. These results suggest the involvement of singlet oxygen (presumably $^1\Delta_g$) in the photochemical oxidation of the dyes **6**–**12**.

Additional evidence for the intermediacy of singlet oxygen was obtained by examining the effect of chemical sources of singlet oxygen on these dyes. Thus the dyes **6**–**12** were oxidized by singlet oxygen formed from hydrogen peroxide and sodium hypochlorite,[19] and the reactions were suppressed by DABCO as shown in Table 1. The dyes **2**–**5**, which were stable to exposure of visible radiation, were not oxidized even in the presence of a chemical source of singlet oxygen.

Moreover, convincing physical evidence for the involvement of singlet oxygen was obtained by the deuterium isotope method described by Merkel *et al.*[20,21] and Griffiths and Hawkins.[10] these authors noted that the lifetime of singlet oxygen ($^1\Delta_g$) in D_2O–CD_3OD (1:1) was increased ten-fold as compared with H_2O–CH_3OH, and the resultant increase in photo-oxidation rate could be used diagnostically for singlet oxygen. When solutions of **9** ($1{\cdot}3 \times 10^{-5}$ M) in 1:1 D_2O–CD_3OD and in 1:1 H_2O–CH_3OH containing equivalent amounts of Rose Bengal were irradiated ($\lambda > 430$ nm) under identical conditions, it was found that after 300 min the deuterated solutions showed 43·1% conversion, whereas the undeuterated solutions showed only 5·7% conversion. A similar result with **13** ($2{\cdot}5 \times 10^{-4}$ M) was observed (Table 2). Thus the photo-oxidation

TABLE 1

FADING OF ANTHRAQUINONE DYES IN SOME SOLVENTS

		Photofading (%) with the visible light[a]						*Fading (%) with H_2O_2–NaOCl*[b]		
			Additive[c]						*Additive*	
Dye-compound	*Solvent*	*Light (nm)*	*None* 5 h	*None* 8 h	*RB* 5 h	*RB* 8 h	*DABCO or NMC*[d] 5 h	*Solvent*	*None*	*DABCO*[e]
1	CH_2Cl_2–MeOH	>390	0		32·0	53·2				
	DMSO	>390	0·8	2·9	33·6					
2–4	CH_2Cl_2–MeOH	>520		0		0		MeOH	0	
	Me_2CO									
5	CH_2Cl_2–MeOH	>520		0		0		MeOH	0	
	Me_2CO	>520								
	DMSO	>520								
6	Me_2CO	>520		1·0	30·2	50·3	0			
7	Me_2CO	>420	1·2	2·4	67·3	94·7				
8	CH_2Cl_2–MeOH	>520	1·6	1·9	13·7	23·0	0			
	Me_2CO	>520	0·7	1·1	11·9	18·4		MeOH	49·5	0
	DMSO	>520	1·3	2·0	16·2	26·8				
9	CH_2Cl_2–MeOH	>520	0·7	1·4	11·7	18·2				
	Me_2CO	>520	0·7	1·6	28·1	38·0	0[d]	MeOH	48·2	7·1
	DMSO	>520	1·8	3·0	57·0	72·0				
10	DMSO	>520	0·5	0·8	20·2	33·0		MeOH	37·3	2·6
11	CH_2Cl_2–MeOH	>520		0·7	5·3	10·6				
	Me_2CO	>520		0·7	6·0	12·6		MeOH	17·9	7·0
	DMSO	>520		1·2	(75·4)[g]		7·9[f]			
12	CH_2Cl_2–MeOH	>520	2·0	2·8	13·4	21·2				
	Me_2CO	>520	1·2	1·4	16·4	26·0		MeOH	97·1	11·6
	DMSO	>520	11·2	16·5	(87·1)[g]		0			

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[a] The solutions (200 ml of $1{\cdot}0\times10^{-4}$ M) were irradiated with filtered light (a 500 W high-pressure mercury lamp source) from outside at 22–25°C under an oxygen atmosphere (O_2 gas, 10 ml min^{-1}).

[b] Each solution (100 ml of $2{\cdot}0\times10^{-4}$ M) was allowed to react for 2 h at 0°C with singlet oxygen formed from hydrogen peroxide and sodium hypochlorite.

[c] Rose Bengal (20 mg/200 ml of solution), DABCO (890 mg) or nickel dimethyldithiocarbamate (NMC, 6 mg) were used.

[d] NMC (6 mg) was added.

[e] DABCO (1·33 g) was added.

[f] Rose Bengal (20 mg) and DABCO (890 mg) were added.

[g] After irradiation for 2 h.

of these dyes proceeds predominantly by a singlet oxygen mechanism. However, the dye **5** did not react in either the deuterated or the undeuterated media, as much as when a chemical source of singlet oxygen was present.

When a mixture of **6** with quinophthalone [2-(2-quinolyl)indane-1,3-dione, λ_{max} 418 and 442 nm] was irradiated with filtered radiation ($\lambda > 520$ nm, which

TABLE 2

DEUTERIUM EFFECTS ON THE PHOTOFADING OF SOME ANTHRAQUINONE DYES[a]

Dye compounds	*Conversion (%)* CH_3OH–H_2O (1 : 1)	CD_3OD–D_2O (1 : 1)	*Ratio*
5[b]	0	0	—
9[c]	5·7	43·1	7·6
13[d]	8·7	44·5	5·1
Azo-dye[e]	14	64	4·6

[a] Dye solutions containing Rose Bengal (mole ratio, Rose Bengal: Dye = 0·2) were irradiated with filtered radiation ($\lambda > 430$ nm) at 15–16°C.

[b] Dye concentration, $5{\cdot}0 \times 10^{-5}$ M, irradiation for 150 min.

[c] Dye concentration, $1{\cdot}3 \times 10^{-5}$ M, irradiation for 300 min.

[d] Dye concentration, $2{\cdot}5 \times 10^{-4}$ M, irradiation for 100 min.

[e] Results for 1-p-tolylazo-2-naphthol (Sensitizer: Methylene Blue) were cited from reference 10.

only **6** absorbs) in acetone, the phenomenon of catalytic fading of quinophthalone by **6** was observed and this was suppressed by the presence of a singlet oxygen quencher such as DABCO or NMC. The relative percentage fading of **6** was much less in the mixture than in the single case. Similar catalytic fading was also observed in a mixed system with 1-(*p*-aminophenylazo)-2-naphthol (λ_{max} 435 and 478 nm) and **9**. These results indicate that the catalytic fading may be caused by sensitized photo-oxidation according to the singlet oxygen mechanism, where aminoanthraquinone dyes act as sensitizers.

3.2. *Photofading of some hydroxyanthraquinones in alkaline solution*

Figure 1 shows the photofading behaviour of 1-amino-4-hydroxyanthraquinone **6** on exposure to visible filtered radiation ($\lambda > 520$ nm) in methanol. A solution of **6** in methanol did not show any significant photochemical change on exposure to visible filtered radiation. On the other hand, the solutions containing sodium hydroxide faded rapidly. In alkaline solutions hydroxy groups in some hydroxyanthraquinones are capable of giving rise to phenoxy anions, thus increasing the electron density on the anthraquinone ring system. It is well-known that singlet oxygen has a mild electrophilic property[22] and consequently it is possible that the greater reactivity of hydroxyanthraquinones in alkaline solution is due to contribution of singlet oxygen.

The rates of photofading of **1** and **7**, having a hydroxy group, were also accelerated in alkaline methanolic solution.

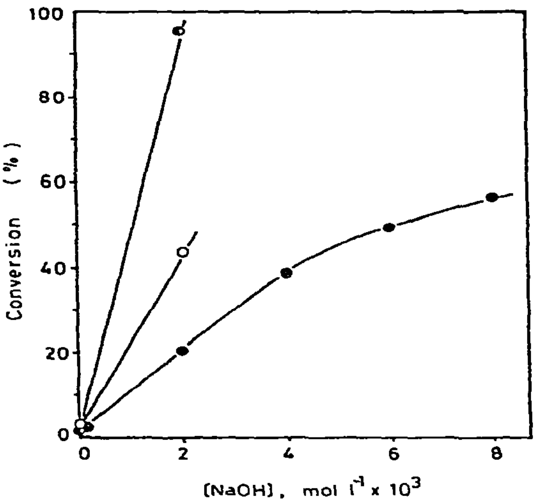

Fig. 1. Photofading behaviours of 1,4-dihydroxyanthraquinone (**1**), 1-amino-4-hydroxyanthraquinone (**6**) and 1-amino-2-methoxy-4-hydroxyanthraquinone (**7**) in alkaline methanolic solution. The solutions containing these dyes ($1{\cdot}0 \times 10^{-4}$ mole litre^{-1}) and sodium hydroxide in 200 ml of methanol were irradiated for 3 h with filtered radiation from outside the vessel at 21–23°C under an oxygen atmosphere (O_2 gas, 10 ml min^{-1}). —◐—Dye No. (**1**), filtered radiation ($\lambda > 390$ nm); —●—Dye No. (**6**), filtered radiation ($\lambda > 520$ nm); —○—Dye No. (**7**), filtered radiation ($\lambda >$ 420 nm).

3.3. *Competitive photo-oxygenation experiments with dye and NMC as acceptors*

Several methods are described in the literature to determine whether photo-oxygenation takes place via singlet oxygen.[15,16,23–25] To obtain additional evidence for the intermediacy of singlet oxygen, a method of competitive photo-oxygenation with two different substrates as described by Wilson[25] was applied. In this work, an aminoanthraquinone dye (D) and NMC (Q) were used as acceptors (NMC acts as a quencher only, while the dye undergoes an oxidation reaction as well as acting as its own sensitizer).

Assuming steady states for D* and $^1O_2$ concentrations, the reciprocal of the rate of decomposition of dye and the concentration of NMC were found to have a linear relationship, which leads to a value of k_Q/k_D (relative rate constant for the reactions with singlet oxygen[13,17]) of 16·4 for **6** and 8.7 for **9**.

This it is reasonable to assume that the photochemical oxidation of these dyes in the solvent proceeds entirely via singlet oxygen by a self-sensitized process.

3.4. *Contribution of the superoxide ion*

The photochemical formation of singlet oxygen from sensitizers such as Rose Bengal or Methylene Blue is well-known, and these sensitizers have been used for many years as the source of singlet oxygen in dye-sensitized photooxygenation. Recently, however, Srinivasan *et al.*[26] have reported that the superoxide ion ($O_2^{\cdot -}$) may be also produced competitively with singlet oxygen from irradiated Rose Bengal in the presence of oxygen. In our preliminary study,[27] Rose Bengal and Methylene Blue were found to generate the superoxide ion competitively with singlet oxygen on irradiation of the solution. However, when solutions containing epinephrine (which is oxidized to adrenochrome by the superoxide ion[28,29]) and **6**, **9**, **10** or **11** were irradiated with filtered radiation, the new absorption peak (λ_{max} 480 nm) of adrenochrome in visible spectra did not appear in all cases. Thus it seems that aminoanthraquinone dyes largely lack the ability to generate the superoxide ion.

REFERENCES

1. G. S. Egerton and A. G. Morgan, *J. Soc. Dyers and Colourists*, **86**, 242 (1970); **87**, 268 (1971).
2. G. H. Giles and R. S. Sinclair, ibid., **88**, 109 (1972).
3. E. McAlpine and R. S. Sinclair, *Text. Research J.*, **47**, 283 (1977).
4. M. Couper, ibid. **21**, 720 (1951).
5. G. S. Egerton, J. M. Gleadle and A. G. Roach, *J. Soc. Dyers and Colourists*, **82**, 369 (1966).
6. G. S. Egerton and N. E. N. Assaad, ibid., **83**, 85 (1967).
7. D. Wegerle, ibid., **89**, 54 (1973).
8. T. Kitao, Y. Watada, M. Matsuoka and K. Konishi, *Nippon Kagaku Kaishi*, 939 (1974).
9. T. Iijima, *Kogyo Kagaku Zasshi*, **67**, 46 (1964).
10. J. Griffiths and C. Hawkins, *J.C.S. Chem. Comm.*, 463 (1972); *J.C.S. Perkin II*, 747 (1977).
11. J. Griffiths and C. Hawkins, *J. Appl. Chem. Biotechnol.*, **27**, 558 (1977).
12. N. Kuramoto and T. Kitao, *Nippon Kagaku Kaishi*, 258 (1977).
13. N. Kuramoto and T. Kitao, *J. Soc. Dyers and Colourists*, **95**, 257 (1979).
14. N. Kuramoto and T. Kitao, *J.C.S. Chem. Comm.*, 379 (1979).
15. A. Zweig and W. A. Henderson, *J. Polymer Sci.*, **13**, 717 (1975); ibid., **13**, 993 (1975).
16. M. W. Rembold and H. E. A. Kramer, *J. Soc. Dyers and Colourists*, **94**, 12 (1978).
17. N. Kuramoto and T. Kitao, *J. Chem. Technol. Biotechnol.*, **30**, 129 (1980).
18. M. Matsuoka, T. Okamoto, T. Kitao and K. Konishi, *Nippon Kagaku Kaishi*, 1328 (1973).
19. C. S. Foote, S. Wexler, W. Ando and R. Higgins, *J. Amer. Chem. Soc.* **90**, 975 (1968).
20. P. B. Merkel, R. Nilsson and D. R. Kearns, ibid., **94**, 1030 (1972).
21. P. B. Merkel and D. R. Kearns, ibid., **94**, 7244 (1972).
22. R. W. Denny and A. Nickon, *Organic reactions*, Vol. 20, 143. New York, John Wiley & Sons (1973).
23. C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
24. C. S. Foote, R. W. Denny, L. Weaver, Y. Chang and J. Peters, *Ann. N.Y. Acad. Sci.*, **171**, 139 (1970).
25. T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).
26. V. S. Srinivasan, D. Podolski, N. J. Westrick and D. C. Neckers, ibid., **100**, 6513 (1978).
27. N. Kuramoto and T. Kitao, *J. Soc. Dyers and Colourists*, submitted for publication.
28. J. M. McCord and I. Fridovich, *J. Biol. Chem.*, **244**, 6049 (1969).
29. E. Lee-Ruff, *Chem. Soc. Rev.*, **6**, 195 (1977).