Oxidation by Singlet Oxygen of 2-(2-Quinolyl)indan-1,3-dione

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Self-sensitised and Methylene Blue- or Rose Bengal-sensitised photo-oxidation of 2-(2-quinolyl)indan-1,3-dione (1) in solution gives phthalic acid, quinoline-2-carbaldehyde, and quinoline-2-carboxylic acid, *via* the reaction of singlet oxygen with (1).

THE photochemistry of quinophthalones is important particularly in connection with the fading of quinophthalone dyes, an important group of dyestuffs and pigments. However little is known about the mechanisms of their photofading reactions.

In recent years, the contribution of singlet oxygen to the photofading of some dyes has been examined. For example, it has been reported that 4-arylazo-1-naphthols,[1] 1-arylazo-2-naphthols,[1,2] indigo,[3] and some aminoanthraquinonoid dyes[4] undergo self-sensitised or dye-sensitised photo-oxidation in solution.

In a preliminary study,[5] quinophthalone [2-(2-quinolyl)indan-1,3-dione] (1) was found to undergo sensitised photo-oxidation, quenching experiments suggesting a singlet oxygen mechanism. We now report additional evidence for the mechanism of this reaction.

RESULTS AND DISCUSSION

Photo-oxidation of Quinophthalone Dye.—The dye chosen for detailed study was 2-(2-quinolyl)indan-1,3-dione (1a), $\lambda_{max.}$ 418 and 442 nm, which exists in equilibrium with the tautomeric form (1b). I.r. spectra (CCl_4 and KBr) exhibit $\nu_{C=O}$ near 1 680 and 1 630 cm^{-1}, and thus suggest the predominance of the form (1a).[6]

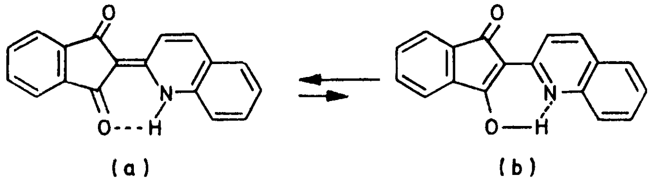
TABLE 1

Oxidation products of (1)

No.	Reaction method [a]	Solvent	Reaction time (h)	Light (nm)	Conversion (%)	Yields of products (%) [c]			
						PA	DMP	2-QC	Others
1	Self-sensitised photo-oxidation	CH_2Cl_2	39.8	>300	100	26.5		9.8	2-QA, UM
2	Sensitised photo-oxidation [b]	CH_2Cl_2–CH_3OH (9 : 1 v/v)	8	520—580	78	37.8	9.1	5.2	2-QA, UM
3	Oxidation with H_2O_2–NaOCl	CH_3OH	2		72	30.3	40.8	5.3	2-QA, UM

[a] In reactions 1 and 2, a solution (200 ml, 5.0 × 10^{-4}M) was irradiated with filtered radiation from outside at 21—23 °C under an oxygen atmosphere (O_2 gas, 10 ml min^{-1}). In reaction 3, a methanolic solution (200 ml, 4.6 × 10^{-4}M) was oxidized with hydrogen peroxide and sodium hypochlorite at 0 ± 1 °C. [b] As a sensitiser, Rose Bengal (20 mg) was added. [c] PA = Phthalic acid, DMP = dimethyl phthalate, 2-QC = quinoline-2-carboxylic acid, 2-QA = quinolino 2-carbaldehyde, UM = unidentified material.

Solutions of (1) in methanol, acetone, or dichloromethane–methanol (9 : 1 v/v) faded under oxygen upon irradiation with filtered visible radiation or unfiltered radiation from a high-pressure mercury lamp. The reaction was accelerated by the addition of Rose Bengal or Methylene Blue as the sensitiser. The photo-oxidation proceeded smoothly with filtered radiation (λ > 520 nm) which was absorbed by the sensitiser only, and analysis of the products showed that the reaction was identical to the slower self-sensitised process. When (1) was irradiated with filtered radiation (λ > 520 nm) in dichloromethane–methanol (9 : 1 v/v) containing Rose Bengal, the products were phthalic acid (3) (38%), dimethyl phthalate (5) (9%), quinoline-2-carboxylic acid (6) (5%), and quinoline-2-carbaldehyde (4) (trace), which were identified by comparison with authentic samples (m.p., u.v. spectra, and R_F values). In addition, the formation of unidentified material which seems to be identical to the compound derived from irradiation of quinoline-2-carbaldehyde alone under these conditions was observed by t.l.c. The results are shown in Table 1.



(1)

The most probable mechanism for the photo-oxidation of (1) is shown in the Scheme, and involves attack by photochemically generated singlet oxygen (presumably $^1\Delta_g$) on the central double bond in the tautomeric form (1a) in a concerted 'ene' reaction or possibly *via* a 'perepoxide' type intermediate.[7] This would lead to the hydroperoxide (2), which could decompose homolytically or heterolytically to (3) and (4).

The rate of the photo-oxidation was retarded in the presence of singlet oxygen quencher such as 1,4-diazabicyclo[2.2.2]octane (DABCO); 2,6-di-t-butylphenol, an efficient peroxide radical scavenger, had no effect on the rate of the photo-oxidation.

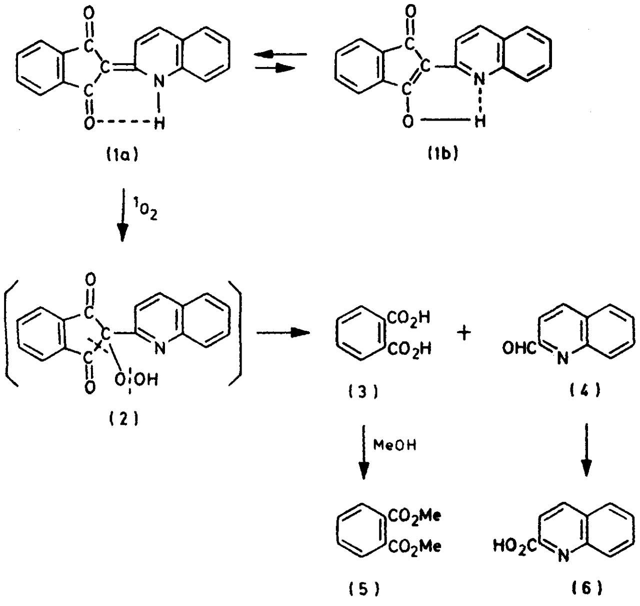
It is well known that the lifetime of singlet oxygen changes widely with solvents. The relative lifetime in some solvents has been already determined by other workers.[8-11] In the present work, the relationship between the relative lifetime of singlet oxygen and the relative rate of the photo-oxidation in some solvents was examined. The results for (1) are shown in Table 2.

TABLE 2

Solvent effects on the photo-oxidation of (1) [a]

Solvent	Relative [b] lifetime ($^1\Delta_gO_2$)	Additive	$t_{30\%}$ [c]		$t_{50\%}$ [c]	
			Time (min)	Relative ratio	Time (min)	Relative ratio
Methanol	7		1 050	1.00	1 800	1.00
Ethanol	12		1 080	0.97	1 800	1.00
Acetone	26		108	9.72	180	10.0
Chloroform	60		34	30.9	57	31.6
Chloroform		P [d]	70	15.0	120	15.0
Carbon tetrachloride	700		8	131	14	129
Carbon tetrachloride		P [d]	14	75.0	23	78.3

[a] In all runs, the solution (500 ml, 1.0×10^{-3}M) was irradiated at 23—25 °C with a 100 W high pressure mercury lamp. [b] These values were cited from refs. 9 and 11. [c] The time for conversion of 30 and 50% in photolysis, respectively. [d] 2,6-Di-t-butylphenol (2.0×10^{-2}M).



SCHEME

The broad trend apparent from these data is that a faster rate of oxidation is observed with increasing $^1O_2$ lifetime; this clearly indicates the involvement of the latter species although the variation of rate in $CHCl_3$ and CCl_4 with added 2,6-di-t-butylphenol possibly indicates some radical contribution.

When a mixture of (1) and 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15), $\lambda_{max.}$ 525 and 560 nm, was irradiated with filtered radiation ($\lambda > 520$ nm) in acetone, the phenomenon of catalytic fading of (1) by C.I. Disperse Red 15 was observed; this was suppressed in the presence of DABCO.[4]

Additional evidence was obtained by examining the effect of chemical sources of singlet oxygen on (1). Thus (1) was oxidized to phthalic acid and quinoline-2-carboxylic acid by singlet oxygen formed from hydrogen peroxide and sodium hypochlorite [12] in methanol (Table 1). The reaction was suppressed by DABCO.

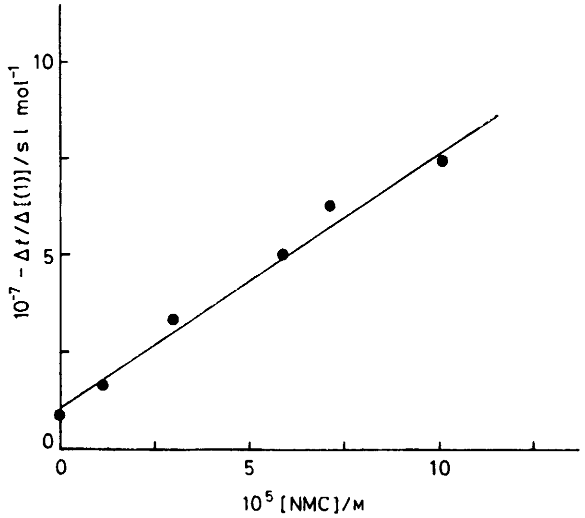
Several methods to determine if photo-oxygenation takes place *via* a singlet oxygen mechanism have been described.[13-18] To obtain additional evidence for the intermediacy of singlet oxygen, a competitive photo-oxygenation experiment with two different substrates, as described by Wilson,[18] was performed. The dye (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 sensitiser].

For steady-state concentrations of (1)* and $^1O_2$ the reciprocal of the rate of dye decomposition should be linearly dependent on NMC concentration. This was the case (Figure) and NMC was shown to react faster than (1) with $^1O_2$ by a factor of *ca.* 22.

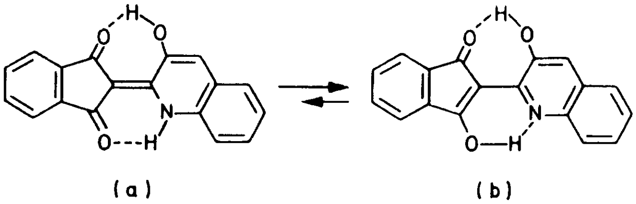
Relevance to Photofading of Quinophthalone Dyes in Commercial Usage.—Quinophthalone derivatives [19,20] are used commerically extensively as dyes and pigments for fibres or resin materials.

Many quinophthalone dyes show greatly improved photochemical stability when a hydroxy group is introduced into the 3'-position [*e.g.* 2-(3-hydroxy-2-quinolyl)-indan-1,3-dione (7), $\lambda_{max.}$ 420 and 440 nm],[6,20] or a halogeno group into the 8'-position [*e.g.* 2-(8-chloro-2-quinolyl)indan-1,3-dione)].[19]

With this in mind the photofading behaviours of (1) and (7) on a silica gel plate have been compared, since this situation is relevant to the practical application of these dyes. When (1) on silica gel plate was exposed to filtered radiation ($\lambda > 300$ nm) and air, it was oxidized to give main products identical with those derived from photo-oxidation in solution, by t.l.c. The fading was accelerated in the presence of Rose Bengal, and could be inhibited by DABCO. Similar fading behaviours for (7) were obtained on prolonged exposure. Compound (7) has better photochemical stability as established empirically. These results indicate that the photo-oxidation of quinophthalone dyes not only in solution but also on silica gel plate takes place predominantly *via* the singlet oxygen mechansim.



Inverse of the rate of decomposition of quinophthalone (1) $\{-\Delta t/\Delta[(1)]\}$ as a function of NMC concentration. Initial concentration of (1) 4.0 × 10^{-4}M in acetone. Sensitiser: Rose Bengal (2.9 × 10^{-5}M). The duration of irradiation ($\lambda > 520$ nm), Δt, was 600 s



(7)

EXPERIMENTAL

Preparations of (1) *and* (7).—Compound (1) was synthesized from phthalic anhydride and 2-methylquinoline according to the procedure described in the literature.[6] Similarly, (7) was prepared from phthalic anhydride and 3-hydroxyquinaldine-4-carboxylic acid.[6]

Self-sensitised Photo-oxidation of (1).—A solution of (1) (27.3 mg) in dichloromethane (200 ml) was prepared, and then placed in a 250 ml quartz flask equipped with a thermometer, condenser, magnetic stirrer, and introduction tube for oxygen. The solution was irradiated at 21—23 °C under oxygen (O_2 gas, 10 ml min^{-1}) with a 500 W high pressure mercury lamp (Ushio Electric Inc. UI-501) from outside the vessel. The vessel was kept at a distance of *ca.* 25 cm from the light source, and a Pyrex glass filter was used for filtered radiation ($\lambda > 300$ nm).

After irradiation for 40 h, most of the solvent was reduced in volume to 3 ml using a rotary evaporator under reduced pressure. The crystals, which were isolated by sublimation from the resulting residue, were identified as phthalic anhydride by comparing its m.p., i.r. spectrum, and R_F value with those of an authentic sample. The yield of phthalic acid was determined by g.l.c. analysis (180 °C; 10% silicon OV-17). Quinoline-2-carboxylic acid was determined using a thin layer chromatoscanner (Shimadzu CS-900). In addition, quinoline-2-carbaldehyde, and unidentified material which seems to be identical to a compound derived from irradiation of quinoline-2-carbaldehyde alone under these conditions was observed by t.l.c.

Rose Bengal-sensitised Oxidation of (1).—A solution containing (1) (27.3 mg) and Rose Bengal (20 mg) in dichloromethane–methanol (200 ml; 9 : 1 v/v) was irradiated with filtered radiation ($520 < \lambda < 800$ nm) through coloured glass filters (Toshiba V-052 and IR-80) in a similar manner as above.

After irradiation for 8 h, the solution of (1) showed 78% conversion. Phthalic acid, dimethyl phthalate, quinoline-2-carboxylic acid, quinoline-2-carbaldehyde, and unidentified material as already described, were analysed by g.l.c. or t.l.c.

Effect of Additives to the Photo-oxidative Fading of (1) *in Solution.*—Solutions (1.0 × 10^{-3}M) of (1) (0.137 g) in methanol (500 ml) with or without the additives Rose Bengal (0.05 g, 1.0 × 10^{-5}M), Methylene Blue (0.19 g, 1.0 × 10^{-3}M), DABCO (0.56 g, 1.0 × 10^{-2}M), or 2,6-di-t-butylphenol (0.515 g, 5.0 × 10^{-3}M), were prepared. These solutions were then placed in an inside-irradiation-type reaction flask equipped with a thermometer, condenser, magnetic stirrer and a tube for introducing oxygen. The solutions were irradiated at 23—25 °C with a 100 W high-pressure mercury lamp (Ushio Electric Inc.) under oxygen (O_2 gas, 10 ml min^{-1}).

The absorption spectra of the solution was measured before and after irradiation, and the conversion (%) was monitored by determining the absorbance at $\lambda_{\text{max.}}$ of the dye. After 20 h the solution without additive showed *ca.* 32% conversion. The solution containing Rose Bengal showed over 95% conversion, whereas that containing DABCO showed *ca.* 5% conversion. A solution containing 2,6-di-t-butylphenol showed nearly the same conversion as that without additive.

Competitive Photo-oxygenation.—A solution of (1) (2.0 × 10^{-3}M) in acetone (200 ml) was prepared and 1 ml was mixed with NMC solution (3 ml) and Rose Bengal solution (1 ml). This solution was sealed in a Pyrex cell and irradiated with filtered radiation ($\lambda > 520$ nm). After irradiation the conversion (%) of (1) was determined spectrophotometrically. The irradiation time was kept constant (10 min) for a given concentration of NMC, and the conversion was kept to < 10%.

Photofading of (1) *and* (7) *on Silica Gel.*—Solutions containing 5.0 × 10^{-6} moles of (1) or (7) in dichloromethane–methanol (10 ml; 1 : 1 v/v) were prepared. The solutions (20 μl) were spotted on silica gel t.l.c. plates using a microcylinder and dried. The plates were exposed to air and light through a Pyrex glass filter from a 100 W mercury lamp *ca.* 5 cm from the plate. The apparatus was kept at 33 ± 2 °C. After irradiation for several hours, plates were developed with benzene–acetone (9 : 1 v/v). The yellow spots of separated dyes were scanned at the $\lambda_{\text{max.}}$ of each dye using a thin layer chromatoscanner. The conversion (%) was calculated from the integration values obtained by scanning.

Similar operations on the dye solutions were carried out with Rose Bengal (97 mg per 10 ml) or DABCO (0.45 g per 10 ml). After irradiation for 10 h, (1) in absence of additive showed 46.4% conversion, and in the presence of Rose Bengal and DABCO showed 84.5 and 28.6% conversion, respectively. Compound (7) in the absence of additive showed 9.5% conversion and in the presence of Rose Bengal or DABCO showed 42.4 and 5.3% conversion after irradiation for 10 h, respectively. It was found that DABCO has a inhibiting effect on the photo-oxidation.

As the photo-decomposition products in case of (1), the spots which seem to be identical to phthalic acid, quinoline-2-carboxylic acid, and quinoline-2-carbaldehyde were observed by t.l.c. comparison with authentic samples.

Reaction of (1) *with Hydrogen Peroxide–Sodium Hypochlorite.*—A solution of (1) (25 mg, 9.2×10^{-5} mol) in methanol (200 ml) was cooled to 0 °C and aqueous hydrogen peroxide (2.8×10^{-4} mol; 0.03 ml of a 30% solution in 1.0 ml water) was added. The solution was stirred and sodium hypochlorite solution (2.3×10^{-4} mole in 20 ml distilled water) was added dropwise over 90 min. The absorption spectra of the dye solution, adjusted in volume, were measured, and the conversion (71.6%) was determined spectrophotometrically.

Most of the mixture was diluted with cold water (200 ml) and extracted with dichloromethane. The dried dichloromethane extract was reduced in volume to 3 ml using a rotary evaporator under reduced pressure. The product distribution closely resembled that from the photo-sensitised oxidation, as shown in Table 1.

When the reaction was repeated in the presence of DABCO (0.24M), the extent of oxidation of (1) was greatly reduced (conversion, 32%).

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