Is Self-sensitized Photo-oxidation a Significant Pathway in the Photofading of Azo Dyes?

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The photofading in aerated solution of 4-diethylaminoazobenzene (**1**) and of the corresponding 4'-methoxy (**2**) and 4'-nitro derivatives (**3**) under various conditions has been examined and compared with naphthol derivatives which are subject to azo–hydrazone tautomerism. Dyes (**1**)—(**3**) are efficient physical quenchers of singlet oxygen but show very little chemical reactivity with oxygen. Their ability to sensitize oxygen is low. More efficient photo-oxidative fading is observed upon short-wavelength irradiation, which results from the reaction of oxygen with hydrazyl radicals, formed by initial hydrogen abstraction from the solvent.

Among the different processes of potential significance in the photofading of azo dyes, self-sensitized oxidation *via* singlet oxygen has been considered particularly. Griffiths and Hawkins[1] unambigously showed that some arylazonaphthols are oxidized to naphthoquinone in a reaction with singlet oxygen probably involving the corresponding hydrazone tautomer. It was also shown[1] that arylazonaphthols photosensitize oxygen, and thus the slow fading of these dyes in the absence of added sensitizers can be attributed to self-sensitized photo-oxidation.

Most azo dyes, however, and particularly most commercially significant ones, are not subject to azo–hydrazone tautomerism, and no attempt has been made up to now to elucidate the role of self-sensitized photo-oxidation in the more general case, nor indeed has it been ascertained whether an oxidative pathway is important, except by indirect indications, such as a Hammet $\rho\sigma$ correlation. In order to contribute to the solution of this problem, the photofading of 4-diethylaminoazobenzene (**1**), and of the corresponding 4'-methoxy (**2**) and 4'-nitro derivatives (**3**), chosen as the simplest reasonable models of commercial monoazo dyes, was examined in aerated solution in order to test the involvement of singlet oxygen and the possibility of self-sensitization. While this work was in progress, it was reported[2] that some heavily substituted derivatives of the dye (**3**) do sensitize oxygen, although with low efficiency, thus encouraging the present research.

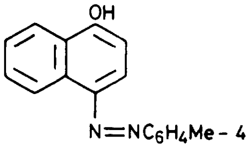
Results and Discussion

(1) *Reaction of Azo Dyes with Singlet Oxygen*.—The azo derivatives (**1**)—(**3**) show only slight reactivity with singlet oxygen. Practically no reaction is observed when singlet oxygen is generated by thermal decomposition of 9,10-dimethylanthracene endoperoxide and only slow fading takes place by irradiation in the presence of oxygen sensitizers, such as Rose Bengal (RB) or Methylene Blue (MB).

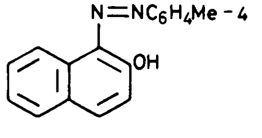
In order to obtain a consistent picture of this reaction, the MB-sensitized photo-oxidation of the monoazo dyes (**1**)—(**3**) was compared with the reactivity under the same conditions of two of the tautomeric dyes studied by Griffiths, *viz.* 4-*p*-tolylazo-1-naphthol (**4**) and 1-*p*-tolylazo-2-naphthol (**5**). Table 1 gathers the results obtained in a set of standard conditions, showing that the non-tautomeric dyes (**1**)—(**3**) fade slower than dyes (**4**) and (**5**). A parallelism can be recognized between the variation in the reactivity of the dyes (**1**) and (**2**) on one hand, and (**4**) and (**5**) on the other under different conditions. Thus, with both classes of dyes the rate of fading strongly increases in deuteriated solvents, as well as in going from methanol to methanol–water mixtures, while the reaction is quenched by diazabicyclo[2.2.2]octane (DABCO) and by nickel salts.

$4\text{-}XC_6H_4N{=}NC_6H_4NEt_2\text{-}4$

(**1**) X = H
(**2**) X = OMe
(**3**) X = NO_2



(**4**)



(**5**)

Table 1. Relative rates of MB-sensitized fading for dyes (**1**)—(**5**)[a]

Solvent	Additive	Dyes (**1**)	(**2**)	(**4**)	(**5**)
MeOH		1	1	26	6
MeOH–H_2O (4:1)		7	6	50	16
MeOH–H_2O (1:1)		24	22	160	42
CD_3OD		11	14	250	270
CD_3–D_2O (4:1)		44	74	530	350
MeOH	DABCO (5×10^{-3}M)	0.5	0.5	80 (8[b])	2
MeOH–H_2O	$Ni(OAc)_2$ (3×10^{-2}M)	4	4	32	1

[a] Taking as unity the rate for the dye (**1**) in methanol. MB, 20 mg per 100 ml. Under these conditions the value for the dye (**3**) in methanol is 0.5. For comparison, the rate for 9,10-dimethylanthracene is 720. [b] Value at [DABCO] 0.1M.

This parallelism also holds for the chemistry of the process. Thus, as previously mentioned, Griffiths showed that 1,4- and 1,2-naphthoquinone are formed in MB-photosensitized oxidation of compounds (**4**) and (**5**), respectively. We now find that toluene is also obtained from both compounds under this condition.† The photo-oxidation of compounds (**2**) and (**3**) gives anisole and nitrobenzene respectively in good yield, and

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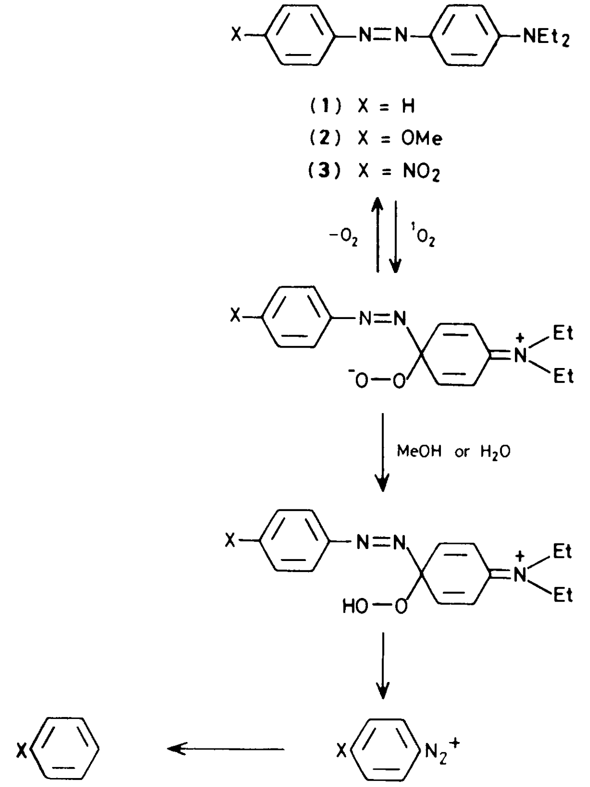
† Note that analogously nitrobenzene has been reported as one of the products obtained by direct irradiation of aerated solutions of 1-(4-nitrophenylazo)-2-naphthol.[3]



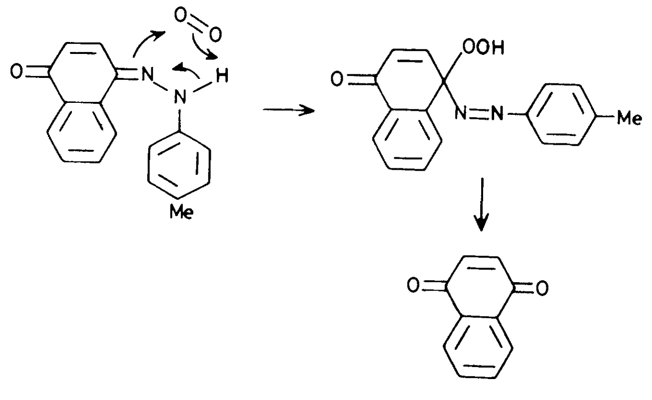
Scheme 1.

likewise benzene is obtained from dye (**1**), although in low yield. Thus equation (1) accounts for the photochemistry of both

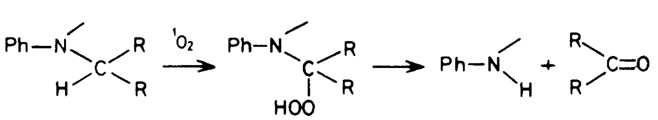
$$\mathrm{Ar{-}N{=}N{-}Ar'} \xrightarrow[\mathrm{MB,O_2}]{h\nu} \mathrm{Ar'H'} \qquad (1)$$

classes of dyes and the same mechanism appears to operate on the basis of the parallelism mentioned above. The involvment of singlet oxygen in the oxidation of dyes (**1**)—(**3**) can be shown by the same kind of reasoning previously presented for dyes (**4**) and (**5**). For both classes of dye, an increase of roughly an order of magnitude is observed in going from methanol to methanol–water mixtures, as expected in view of the corresponding increase in the singlet oxygen lifetime, while known singlet oxygen quenchers such as DABCO or nickel salts quench the reaction.* However, another feature of Table 1 requires different comment. In every case fading is faster in methanol–water mixtures than in pure methanol. This is unexpected in view of the shorter lifetime of singlet oxygen under these conditions. This effect is probably due to the increased protonation by water of an initially formed intermediate, which favours the irreversible reaction of the latter to give the end-products at the expenses of the decay to the starting dye, as illustrated in Scheme 1.

As for the product distribution, it can be observed that small amounts of anilines arising from reduction of the azo dyes are also observed in the MB-sensitized reaction. These are the main products in the direct irradiation in degassed methanol (see Table 2). As MB in alcohols is known to initiate the photoreduction of similar substrates, formation of anilines can be expected from a side-process triggered by triplet MB and different from the main process involving singlet oxygen. At any rate this is a very minor reaction. The scheme proposed here has some similarity with that proposed by Griffiths (Scheme 2) but it differs in that we rationalize the reaction as an electrophilic attack by singlet oxygen on the aromatic ring at the position *para* to the diethylamino group, whereas in Scheme 2 the hydrazone tautomer is invoked and an intramolecular rather than an intermolecular hydrogen source is utilized.



Scheme 2.



Scheme 3.

Still another process can be discussed in this connection, *viz.* the oxidative dealkylation proposed by Griffiths[4] as an important process in the photofading of non-tautomeric azo dyes containing dialkylamino groups, on the basis of an analogy with similar processes which have been found in the case of aliphatic amines (Scheme 3). In fact, only a small amount (*ca.* 2%) of the corresponding monoethylamino derivatives is obtained from both dyes (**1**) and (**2**). This low yield is not due to fast decomposition of the secondary amines under our conditions, as we established by separate experiments that monoethylaminoazobenzene is distinctly less reactive than the diethylamino derivative (**1**) towards photo-oxidation. Therefore the main photofading reaction does not involve chemical attack on the amino group.

The measurements in Table 1 were made under conditions in which MB is selectively excited. Therefore, quantum yield measurements and comparison with the rate of reaction in the same conditions of substrates of known reactivity, such as dimethylanthracene and diphenylisobenzofuran allow the determination of the rate of reaction between the azo dyes and singlet oxygen, provided that the fading observed with this condition is attributed exclusively to the singlet oxygen reaction, neglecting the previously mentioned side-reactions which have little quantitative importance.

The values obtained, *viz.* k_r 1—2 × 10^4 l mol $^{-1}$ s $^{-1}$ for the azo dyes (**1**)—(**3**) not subject to azo–hydrazone tautomerism, place these compounds at the lower limit of reactivity with singlet oxygen.

To the low chemical reactivity corresponds a high rate for the physical quenching of singlet oxygen by azo dyes. In fact, flash photolytic measurements[5] of quenching by dye (**1**) of the MB-photosensitized oxidation of 1,3-diphenylisobenzofuran

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* Note however that DABCO quenches the oxidation of the dye (4) only at high concentrations; at low concentrations some other mechanism increases the rate of fading. In ref. 1, the 'protection' of (5) by nickel salts is related to the formation of a complex rather than to quenching of singlet oxygen.

Table 2. Percentage yield of photoproducts from the preparative irradiation of dyes (**1**) and (**2**) and quantum yield measurements

			Products and yield[a]		
Dye	Solvent	Lamp and conditions	Aniline	Benzene	Φ_{dec} at 254 nm[b]
(**1**)	MeOH, degassed	Hg through quartz	95[c]		1.6×10^{-2}[d]
	MeOH, aerated	Hg through quartz	14	22	1×10^{-4}
	MeOH, aerated	Na, MB sensitized	2	18	
	MeOH–H_2O 1:1, aerated	Na, MB sensitized	1	15	
			p-Anisidine	Anisole	
(**2**)	MeOH, degassed	Hg through quartz	33[c]		8×10^{-3}[d]
	MeOH, aerated	Hg through quartz	28	67	2.5×10^{-4}
	MeOH, aerated	Na, MB sensitized	0.1	58	
	MeOH–H_2O 1:1, aerated	Na, MB sensitized	0.1	71	

[a] Calculated on reacted starting material. [b] The quantum yield for the fading by irradiation into the visible band (λ_{exc} 434 nm) is lower than 2×10^{-5} both in degassed and aerated solutions. [c] *NN*-Dimethyl-*p*-phenylenediamine also obtained. [d] From ref. 6.

resulted in a value of k_q of 2×10^8 l mol^{-1} s^{-1}, four orders of magnitude greater than the rate of chemical reaction.

The naphthol derivatives (**4**) and (**5**) react faster with singlet oxygen than (**1**) and (**2**), but even in this case the reactivity remains limited.

(2) *Photosensitization of Oxygen by the Azo Dyes*.—By irradiation of the azo dyes in the presence of singlet oxygen acceptors such as diphenylisobenzofuran and tetraphenylcyclopentadienone,* we attempted to measure whether they could act as oxygen sensitizers. Parallel experiments were conducted using RB as sensitizer. Irradiation in the presence of dyes (**1**)—(**3**) did not give any result within the detection limit of the experiment, *i.e.* the efficiency of oxygen sensitization is $\eta < 2 \times 10^{-3}$, taking as unity the value measured when using RB as sensitizer. The naphthol (**4**) shows a barely detectable effect and the value of η is 2—4 $\times 10^{-3}$ in this case.

As mentioned in the Introduction, the quantum yield for oxygen sensitization has been measured in the viscous solvent di-n-butyl phthalate for some derivatives of (**3**),[2] and found to vary between 0.002 and 0.03 according to the substitution pattern. Much smaller values are found in less viscous solvents.

(3) *Direct Irradiation in Aerated Solution*.—It has been previously shown that the main process in irradiation of degassed solutions of the dyes (**1**)—(**3**) is reductive cleavage of the azo linkage to give the corresponding anilines.[6] This process is quenched by oxygen.

As shown in Table 2, in aerated solutions the quantum yield for fading upon irradiation at 254 nm of dyes (**1**) and (**2**) is more than an order of magnitude lower than in degassed solution. In the case of dye (**3**), the fading becomes too slow to measure. For compounds (**1**) and (**2**), the fading in aerated solutions is not linearly related to the absorbed dose. The reported quantum yields refer to the initial phase of the process, but after a certain conversion (10—20%) is reached, the process accelerates considerably. Analysis of the products shows that together with reduction to anilines, the products previously obtained in the sensitized oxidation, *viz.* benzene and anisole, are obtained under these conditions. It must also be noted that this process is actived only by u.v. light, the fading with visible light being negligible both in degassed and in aerated solutions.

(4) *Conclusions*.—The present report shows that the dialkylaminoazobenzenes (**1**)—(**3**) resemble dialkylanilines in their behaviour with singlet oxygen,[7] acting as efficient physical quenchers but very poor chemical acceptors. If this result is considered together with the poor characteristics of these dyes as oxygen sensitizers, a fact which is related to the excessively short lifetime of their triplet state, it can be concluded that fading due to self-sensitized photo-oxygenation occurs with a quantum efficiency lower than 1×10^{-9},† and thus in the present conditions (dilute alcoholic solution, full mercury arc) is not a significant component of the observed photofading. This is not unexpected in view of the structure of these compounds and of the well known quenching of singlet oxygen by tertiary anilines,[7] and should be valid for the numerous azo dyes containing the dialkylanilino group. In contrast, the introduction of a benzylamino group has been reported to lower the dye fastness, but this is due to a radical process (hydrogen abstraction from the benzylic position) and not to the interventions of singlet oxygen.[4]

The conclusion from this work is that fading of the azo dyes (**1**) and (**2**) is observed under our conditions at a rate that, while low in absolute terms, far exceeds that expected for a singlet oxygen process. The fading is only observed upon irradiation at short wavelengths just as in the photoreduction in degassed medium,[6] but in the present case the yield of aniline is much lower and the main products are those obtained in photo-oxidation. This reaction could hardly involve direct interaction of some excited state of the dyes with oxygen because of the short lifetime of the lowest triplet (10—20 ns at low temperature)[8] or of any other excited state,[9] and has rather to be initiated by the same process considered for photoreduction, *i.e.* hydrogen abstraction from the solvent to give a hydrazyl radical. We have previously shown that high-lying triplet states of dyes (**1**)—(**3**) reached by short-wavelength irradiation and intersystem crossing abstract hydrogen;[6] and hydrazyl radicals formed from azo dyes and good hydrogen donors, such as mandelic acids, have been well characterized.[10] In the absence of oxygen, the radicals disproportionate to the starting material and a hydrazobenzene derivative, which is further cleaved to the aniline.[6,11] This process can now be completed by admitting that oxygen reacts with the hydrazyl radical at the nitrogen, as shown in Scheme 4, or at a ring carbon, yielding a peroxyl radical which either reverts to the starting azo derivative or undergoes further decomposition to the end-products. The rate of the various phases of the process is determined by the structure, so that with the nitro derivative (**3**) oxygen simply causes reoxidation to the starting material and no net fading is

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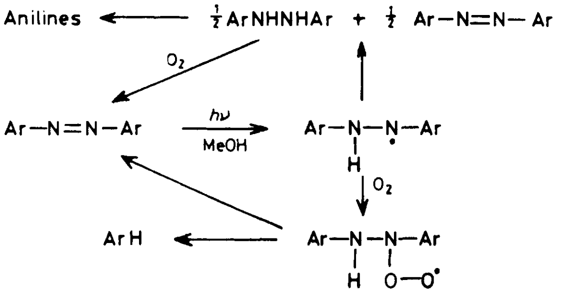
* These highly reactive singlet oxygen acceptors were used at concentration high enough to ensure that quenching of $^1O_2$ by the dye itself (5×10^{-5} M) was negligible.

† At the low azo dye concentration used, the main reaction of singlet oxygen is unimolecular decay (τ in methanol *ca.* 10 μs). Thus, $\Phi_r = \eta\tau k_r[\text{Dye}]$.



Scheme 4.

observed, in the case of the dyes (**1**) and (**2**) some fading takes place with formation of benzene and anisole, respectively. It can be envisaged that this kind of process would produce further radical species (OOH, OH radicals from hydrogen abstraction from the solvent) which could in turn cause further fading.

Although the above conclusions are valid only under our experimental conditions and cannot be automatically extended to the practical conditions for photofading of azo dyes dispersed on textile fibres, the present data show that the generality of the involvent of singlet oxygen in the photofading to azo dyes has been possibly overestimated, while radical pathways could play a more important role than hitherto suspected in oxidative photofading.

Experimental

The azo dyes (**1**)—(**5**) and 4-ethylaminoazobenzene were prepared according to standard methods and purified by chromatography on alumina followed by recrystallization of the central fraction from toluene. Other commercial reagents were purified by repeated chromatography and their purity was checked by t.l.c. Spectroscopic grade solvents were used without further treatement.

Preparative Photochemical Reactions.—Solutions of the dyes (5 × 10^{-4}M) were irradiated in an immersion well apparatus while flushing by air under the conditions specified in Table 2, by means of (1) a low-pressure mercury arc (Hanau TNN 15), (2) a high-pressure mercury arc (Helios 500 W), (3) a high-pressure sodium arc (Helios 250 W). Irradiation was terminated when a 20—30% conversion had been reached as shown by u.v. measurements. The solution was then fractionally distilled and the fractions examined by u.v. and g.l.c. (OV 17 3% on Gaschrom Q, 2 m; SP 2100 2% on Gaschrom Q, 2 m) for volatile compounds, which were identified by comparison with authentic samples. Chromatography of the residue allowed the determination of monoalkylaminoazobenzenes.

Quantitative Measurements.—Solutions of the dyes (5 × 10^{-4}M) in 1 cm optical path cuvettes were irradiated in the conditions specified in Table 1 by means of (1) a low-pressure mercury arc (Helios 20 W), (2) a super-high-pressure mercury arc (Osram 200 W) collimated and filtered through the appropriate interference filters, and (3) a high-pressure sodium arc (Helios 250 W). The light flux was measured by means of chemical actinometers (potassium ferrioxalate or reinekate). Measured light fluxes were 2—10 × 10^{-7} Einstein min^{-1} over a 3 cm^2 area. The fading of the dye was measured by absorption spectrometry (by means of a Cary 219 spectrophotometer). Correction for partial absorption was made when appropriate. In the sensitized experiments, light was practically completely absorbed by the sensitizer. In the determination of the efficiency of dyes (**1**)—(**4**) as oxygen sensitizers, solutions of 1,3-diphenylisobenzofuran (DPIBF) or tetraphenylcyclopentadienone (TPCP) (1—5 × 10^{-3}M) were used. The consumption of the acceptor was determined by absorption spectroscopy at the appropriate wavelength. DPIBF was not consumed in this conditions (λ_{irr} 545 nm) in the absence of the dye, and TPCP only slightly (correction was made for partial absorption and reactivity). Reported values are the average from at least three independent experiments.

Acknowledgements

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