Photochemical Decomposition of 2,4-Dinitro-4'-dimethylaminoazobenzene in Aerated Solution

Angelo Albini, Elisa Fasani, and Silvio Pietra *
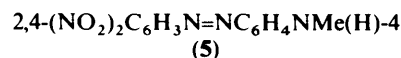*Dip. Chimica Organica, Università di Pavia, 27100 Pavia, Italy*
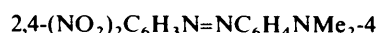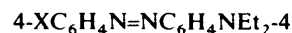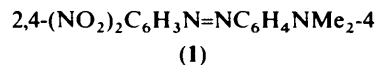
The irradiation of various ketones in the presence of 2,4-dinitro-4'-dimethylaminoazobenzene (1) causes decomposition of the latter. The chemical process actually observed depends on the solvent and on the ketone structure. In benzene the dye (1) undergoes demethylation in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) and benzil. This is due to the reactions of benzoylperoxyl radicals formed from the ketone sensitizers in the presence of oxygen. Benzophenone and anthraquinone cause the same reaction, in this case through direct interaction of the $n\pi^*$ triplet with (1). In alcohols the situation is more varied, as with DMPA, benzil, and benzophenone in methanol, demethylation of (1) *via* the same mechanisms as above is observed, while with anthraquinone and acetone in methanol and with benzophenone in propan-2-ol, 2,4-dinitro-4'-dimethylamino-*NNO*-azoxybenzene, (4), is formed. The latter reaction is initiated by attack of ketyl radicals, formed in the primary photoreaction of the ketone with the solvent, onto (1). The relevance of this model for the fading of azo dyes under applicative conditions is discussed.

In a previous study,[1] it was shown that self-sensitized photo-oxidation is not a significant pathway in the photofading of azo dyes not subject to azo-hydrazone tautomerism† as they are poor oxygen sensitizers and they physically quench, rather than react with, singlet oxygen. This led us to doubt the widely held belief that singlet oxygen plays an important role in the photofading of azo dyes dispersed on textile fibres.‡ Furthermore, it was shown that both in the presence and in the absence of oxygen, degradation of these dyes upon direct excitation in solution is limited to short-wavelength irradiation as it is initiated by inefficient hydrogen abstraction from the solvent by high lying triplets, whereas the only process from lower excited states is thermally reversible *trans–cis* isomerization.[1,3] Therefore, excited states of the dyes are probably not involved in the fading caused by natural light. Another possible explanation of the photofading under practical conditions is that the substrate in which the dye is dispersed, or some additive, absorbs the light, and causes the decomposition of the dye by reaction with some excited state or with radicals formed from them.§

In search of a suitable model for the latter kind of photofading, we began a study of the degradation of azo dyes in aerated solution in the presence of photoexcited carbonyl derivatives. While there is no previous study of similar systems, it is well known that carbonyl derivatives sensitize the photofading of azo dyes in deaerated solution through radical initiation (*e.g.* acetone enhances the quantum yield for the photofading of some simple azo dyes by one to two orders of magnitude)[3] and such a process might also initiate an oxidative degradation (Type I photo-oxidation[2c]). It is also known that ·COOH radicals, formed by photodecomposition of mandelic acid, do cause the fading of certain azo dyes of azo-hydrazone tautomeric structures even in aerated solution.[2d]

The sensitizers currently investigated were carbonyl derivatives with $n\pi^*$ triplets of different energies, lifetimes, and reactivities (acetone, benzophenone, anthraquinone, benzil) as well as 2,2-dimethoxy-2-phenylacetophenone (DMPA), which undergoes efficient Norrish I cleavage to radicals.[5] These were used at a concentration high enough to ensure that they absorbed a large part of the light at the wavelength used.

As we were primarily interested in the initial stages of the photodegradation, we chose to investigate the fading of 2,4-dinitro-4'-dimethylaminoazobenzene as it appeared from preliminary studies to be more resistant to the photocleavage of the azo linkage than the dyes (2) and (3) that we had previously considered. In fact, while the latter dyes are cleaved to aniline ($C_6H_4XNH_2$) and benzene (C_6H_5X) derivatives upon short-wavelength irradiation in aerated alcohols,[1] compound (1) has been reported by Gruen and Schulte-Fröhlinde to give the azoxyderivative (4) on irradiation in aerated propan-2-ol,[6] this being the only instance in which a product conserving the original N=N double bond has been isolated from the irradiation of an azo dye.

$$2,4\text{-}(NO_2)_2C_6H_3N=NC_6H_4NMe_2\text{-}4$$
$$(\mathbf{1})$$

$$4\text{-}XC_6H_4N=NC_6H_4NEt_2\text{-}4$$
$$(\mathbf{2})\ X = H$$
$$(\mathbf{3})\ X = POMe$$

$$2,4\text{-}(NO_2)_2C_6H_3N=NC_6H_4NMe_2\text{-}4$$
$$\downarrow$$
$$NO$$
$$(\mathbf{4})$$

$$2,4\text{-}(NO_2)_2C_6H_3N=NC_6H_4NMe(H)\text{-}4$$
$$(\mathbf{5})$$

The greater part of the experiments was conducted in either benzene or methanol, and the results in these solvents will be separately discussed below, as there are major differences between the two cases. In these sections, the discussion will be limited to small-scale experiments with dye concentrations of 5×10^{-5} to 5×10^{-4}M and analytic chromatographic determination of the products. Larger scale experiments with dye concentrations of 5×10^{-4}M or higher and isolation and identification of the products are reported in the Experimental section, but an overview of the most significant results is given in Table 1.

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† Except where explicitly stated, the present discussion refers to non-tautomeric azo dyes.
‡ For a discussion of the mechanistic hypothesis considered for the photofading of azo dyes, see refs 2a and b.

§ When this work was completed, a paper by Makhviladze *et al.* appeared, that showed that radicals formed by irradiation of polyamide cause fading of azo dyes disperse in it.[4]

Table 1. Preparative results for the decomposition of dye (1) under various conditions[a]

Reagent	Solvent	Conditions of the experiment	Decomposition of (1) ($^\circ_0$)	Products ($^\circ_0$ Yield)
DMPA 2×10^{-3}M	Benzene	hv^b, 5 min	35	(5) (25)
DMPA 2×10^{-3}M	MeOH	hv^c, 15 min	45	(5) (38)
Anthraquinone 2×10^{-3}M	MeOH	hv^c, 30 min	50	(4) (65)
Acetone 1.35M	MeOH	hv^c, 4 h	50	(4) (25)
None	MeOH	hv^b, 10 h	37	d
RB 3×10^{-4}M	MeOH	hv^e, 48 h	40	(5) (33)
(PhCOO)$_2$ 3×10^{-2}M^f	MeOH	reflux, 5 h	90	(5) (50)
Ce(NH$_4$)$_2$(NO$_3$)$_6$ 2×10^{-3}M^g	MeOH	r.t., 5 min	100	(5) (98)

[a] Dye concentration 5×10^{-4}M unless otherwise stated. [b] High-pressure mercury arc, through quartz. [c] Low-pressure mercury arc. [d] Traces of m-dinitrobenzene. [e] High-pressure sodium arc. [f] [(1)] = 10^{-2}M. [g] [(1)] = 10^{-3}M.

Table 2. Quantum yield for the decomposition of dye (1) (5×10^{-4}M)[a]

(a) In benzene

Sensitizer	$I_s^b/^\circ_0$	$\Phi_{-(1)}$	$\Phi_{(5)}$	
DMPA 5×10^{-2}M	64	0.39	0.1	
Benzil 2.3×10^{-2}M	79	0.015	0.004	
Benzophenone 8×10^{-2}M	55	0.029	0.007	
Anthraquinone 3.6×10^{-3}M	79	0.006	0.001	
DMPA 5×10^{-2}M + DMB 1×10^{-3}M	64	0.025	0.01	

(b) In methanol

| Sensitizer	$I_s^b/^\circ_0$	$\Phi_{-(1)}$	$\Phi_{(5)}$	$\Phi_{(4)}$
DMPA 5×10^{-2}M	84	0.16	c	
Benzil 2.3×10^{-2}M	78	0.005	c	
Benzophenone 8×10^{-2}M	79	0.032	c	
Acetone 1.35M	56	0.01		0.003
Anthraquinone^d 2.1×10^{-5}M	82	0.052		0.03

[a] At 313 nm, unless otherwise stated. [b] Fraction of the absorbed light which is absorbed by the sensitizer. [c] Product (8) is formed in 25—30$^\circ_0$ yield. [d] At 254 nm.

Decomposition of the Dye (1) *in Benzene.*—The irradiation of aerated solutions of the dye (1) containing the aforementioned carbonyl sensitizers leads to a single product containing the azo chromophore. This product has been isolated by column chromatography on silica gel and identified as 2,4-dinitro-4'-methylaminoazobenzene (5). In quantum-yield measurements, the formation of this product (5) has been monitored by direct h.p.l.c. determination of the irradiated solution. T.l.c. and h.p.l.c. analysis or column chromatographic separation (silica gel of alumina) of the raw photolysate gave no indication of other coloured products in significant amount. As the yield of (5) is about 25—30% of converted (1) (30—40%), other processes involving more profound decomposition predominate over demethylation to (5). This point was not fully investigated, but we ascertained that m-dinitrobenzene and 2,4-dinitroaniline, *i.e.* the products analogous to those formed from (2) and (3) by direct aerobic decomposition,[1] are not formed from (1) under these conditions.
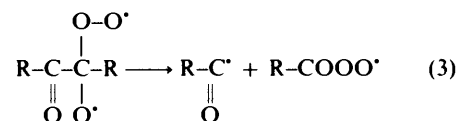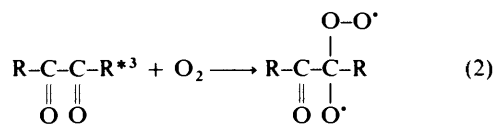
Some indications as to the mechanism of the present decomposition are immediately apparent from the quantum-yield data reported in Table 2. Thus the efficient fading in the presence of DMPA cannot be attributed to a reaction between the short lived triplet of this ketone ($\tau \leqslant 0.1$ ns)[7] and the dye (1) (5×10^{-4} M), and this is the case also for the triplet state of benzil due to its low energy and scarce reactivity,[8] which precludes interaction with (1) both by energy transfer (as low lying triplets of azo dyes undergo only thermally reversible *trans*-*cis* isomerization[3]) and by hydrogen abstraction.

Therefore, it has rather to be assumed that radicals formed by photocleavage of these ketones in the presence of oxygen are the active species. Indeed, it has been shown that benzil and other α-

diketones cleave in the presence of oxygen to yield peroxy radicals according to equation (1).[9]

$$\underset{\substack{|| \ \ ||\\ O \ \ O}}{R-C-C-R} + 2O_2 \longrightarrow 2R-COOO^\bullet \quad (1)$$
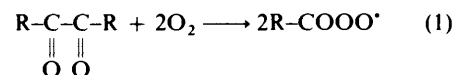
Reaction of the diketone triplet appears to precede cleavage of the carbon–carbon bond [equations (2)—(4)]

$$\underset{\substack{|| \ \ ||\\ O \ \ O}}{R-C-C-R^{*3}} + O_2 \longrightarrow \underset{\substack{|| \ \ |\\ O \ \ O^\bullet}}{R-C-\overset{O-O^\bullet}{\underset{|}{C}}-R} \quad (2)$$

$$\underset{\substack{|| \ \ |\\ O \ \ O^\bullet}}{R-C-\overset{O-O^\bullet}{\underset{|}{C}}-R} \longrightarrow \underset{\substack{||\\ O}}{R-C^\bullet} + R-COOO^\bullet \quad (3)$$

$$RCO^\bullet + O_2 \longrightarrow R-COOO^\bullet \quad (4)$$

Peroxyl radicals are the active intermediates in α-diketone-sensitized photo-oxygenation, *e.g.* epoxidation of alkenes (Bartlett's reaction).[9,12]

$$R-COOO^\bullet + \quad C=C \longrightarrow R-COO^\bullet + \overset{\overline{}}{\underset{| \quad |}{-C-O-C-}} \quad (5)$$
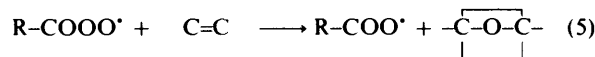
In the above reaction about two molecules of alkene are epoxidized for every molecule of ketone consumed, showing
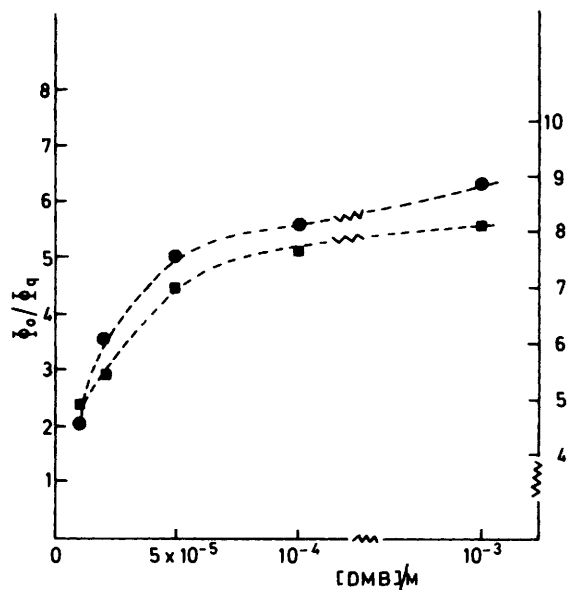
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Figure 1. Quenching of the photofading of dye (1) in benzene by 2,3-dimethylbutene (DMB). Sensitizers are benzil (●) or 2,2-dimethoxy-2-phenylacetophenone (DMPA, ■)

that the decomposition of the sensitizer proceeds essentially according to equation (1).* In our experiment, the quantum yield for the fading of the dye (1) in the presence of benzil is $\Phi_{-1} = 0.015$, which corresponds to 50% of the quantum yield for the decomposition of benzil in aerated benzene (0.03).[9]

Therefore the benzoylperoxyl radical Ph–COOO· is responsible for the fading of dye (1). Indeed, 2,3-dimethylbut-2-ene (DMB) which is oxidized by the same species,[9] efficiently quenches the photodecomposition of (1). Thus, in the presence of 1×10^{-4}M DMB, the rate of the fading is decreased to 20%. However, the ratio of the quantum yield for the unquenched process to that in the presence of the quencher $(\Phi_o : \Phi_q)$ is not linearly dependent on the quencher concentration (Figure 1), thus pointing to the intervention of different quenchable species in the decomposition of (1), at least in the presence of DMB. It appears from Figure 1 that DMB quenches the photofading of (1) in the presence of DMPA in a way similar to that for benzil,† thus substantiating the prediction that the same mechanism will be operative since benzoylperoxyl radicals are formed also from the combination of benzoyl radicals, arising from the cleavage of DMPA, and oxygen [equations (6), (4)].

$$DMPA \longrightarrow Ph-CO· + PhC(OMe)_2·\qquad (6)$$
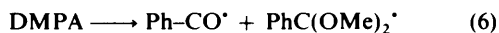
The much more efficient decomposition of DMPA ($\Phi = 0.87$ vs. 0.03 for benzil) accounts for the higher efficiency of the dye fading in this case.

This reaction is well rationalized in terms of electron abstraction by the strong electrophilic benzoylperoxyl radical from the amino group, followed by proton transfer from the α position to yield radical (6), the ultimate fate of which, in analogy with similar cases,[13] is cleavage to the monomethyl derivative (5).

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* However, it must be borne in mind that other potentially reactive radical species are present in the reaction conditions. As an example, when the ketone decomposition is carried out in benzene. ·OOH radicals are also formed.[16]

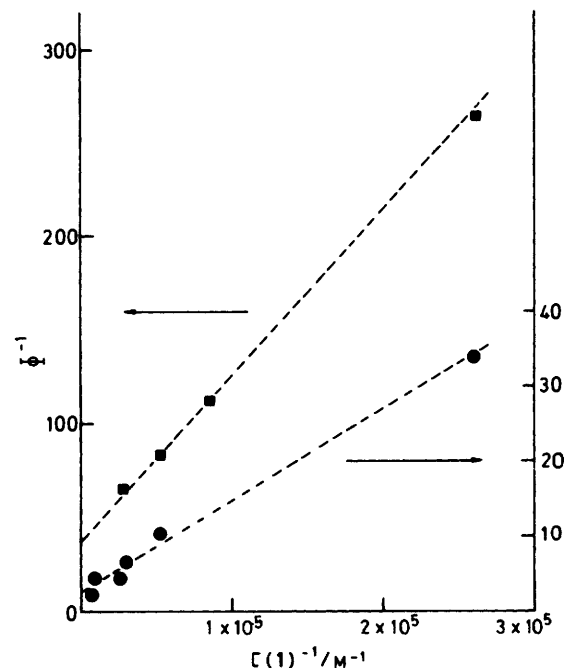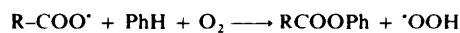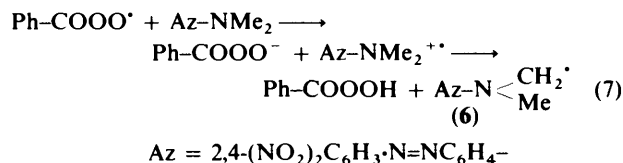$$R-COO· + PhH + O_2 \longrightarrow RCOOPh + ·OOH$$

Figure 2. Double reciprocal plot of the photofading quantum yield in benzene versus the concentration of the dye (1). Sensitizers are DMPA (●) or benzil (■)

$$Ph-COOO· + Az-NMe_2 \longrightarrow$$
$$Ph-COOO^- + Az-NMe_2^{+·} \longrightarrow$$
$$Ph-COOOH + Az-N\overset{CH_2·}{\underset{Me}{<}}\qquad (7)$$
$$(6)$$

$$Az = 2,4-(NO_2)_2C_6H_3·N=NC_6H_4-$$

Quantitative data about the proposed reaction scheme are obtained from the dependence of the quantum yield for the decomposition of the dye on its concentration, as shown in Figure 2. Thus, if η is the efficiency of formation of the active species from the sensitizer and equations (8)—(10) account for the process,

$$Sens \longrightarrow Ph-COOO·\qquad (8)$$

$$Ph-COOO· + (1) \xrightarrow{k_r} Products\qquad (9)$$

$$Ph-COOO· \xrightarrow{k_d} Non\text{-}reactive\ species\qquad (10)$$

then the quantum yield for the decomposition of (1) is shown in (11),

$$\Phi = \eta\frac{k_r[(1)]}{k_r[(1)] + k_d}\qquad (11)$$

or in inverse form (12).

$$\Phi^{-1} = \eta^{-1}\left\{1 + \frac{k_d}{k_r}[(1)]^{-1}\right\}\qquad (12)$$

Thus, the ratio intercept:slope in the plots of Figure 2 affords the value k_r/k_d, viz. 2×10^4M^{-1} for the DMPA-sensitized reaction. With benzil a larger value is obtained, but the

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* It has been established that the chemical process is the same both in the presence and in the absence of DMB (Table 2).
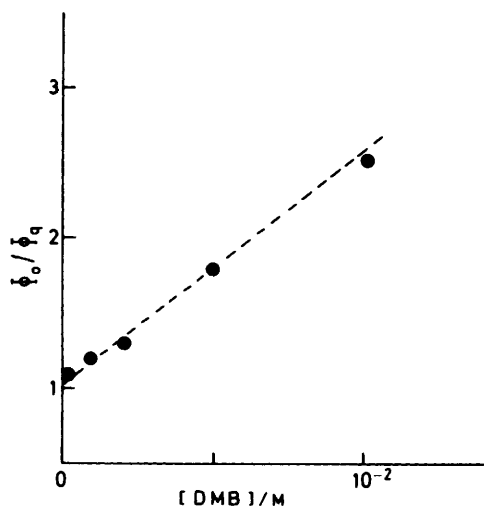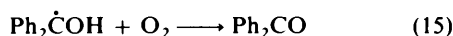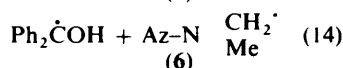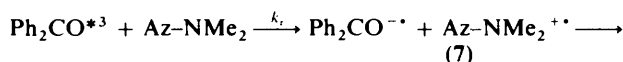
Figure 3. Quenching by DMB of the photofading of the dye (1) in benzene sensitized by benzophenone

Figure 4. Double reciprocal plot of the photofading quantum yield in benzene *versus* the concentration of the dye (1). Sensitizers are benzophenone (●) or anthraquinone (■)

assumption that the mechanism is the same in both cases is confirmed. Taking $k_d = 1.8 \times 10^{-2}$ s^{-1} as determined by Sawaki,[10] the rate constant for the reaction of the benzoyl-peroxyl radical with (1) in benzene solution is *ca.* 1 × 10^6 M^{-1} s^{-1}, a value larger than that observed for aromatic alkenes (1.3—1.8 × 10^5 M^{-1} s^{-1}).[10]

While (as has been mentioned previously) the dye (1) in the presence of benzophenone and anthraquinone is demethylated to (5) just as with DMPA and benzil, the mechanism of the reaction is largely different. The results with benzophenone are discussed first, the situation with anthraquinone being quite similar. DMB is a less effective quencher than in the previous cases, the fading of (1) (5 × 10^{-5}M) being diminished of only 10% in the presence of 1 × 10^{-4}M DMB. The ratio $\Phi_o:\Phi_q$ is linearly dependent on [DMB] (Figure 3). Furthermore, while with DMPA and benzil the rate of decomposition of the ketone is faster than the accompanying fading of (1), with benzophenone the dye is decomposed with an yield by at least an order of magnitude larger that the quantum yield of decomposition of the ketone [$\Phi \ll 2 \times 10^{-3}$ in the absence of (1)] Taking into account the known reactivity with amines of the benzophenone triplet ($\tau = 0.15$ μs in aerated benzene),[14] it can be concluded that in this case the reaction involves direct reaction of the sensitizing triplet with the dye, according to equations 13—15, with formation of the same radical (6) as before. This then reacts to form (5) while benzophenone is regenerated.

$$Ph_2CO^{*3} \xrightarrow{k_d} Ph_2CO \qquad (13)$$

$$Ph_2CO^{*3} + Az-NMe_2 \xrightarrow{k_r} Ph_2CO^{-\cdot} + Az-NMe_2^{+\cdot} \longrightarrow$$
$$\qquad (7)$$

$$Ph_2\dot{C}OH + Az-N\begin{matrix}CH_2^{\cdot}\\Me\end{matrix} \qquad (14)$$
$$\qquad (6)$$

$$Ph_2\dot{C}OH + O_2 \longrightarrow Ph_2CO \qquad (15)$$

As the quantum yield for intersystem crossing of benzophenone is 1, the quantum yield for the dye fading is given by equation (16).

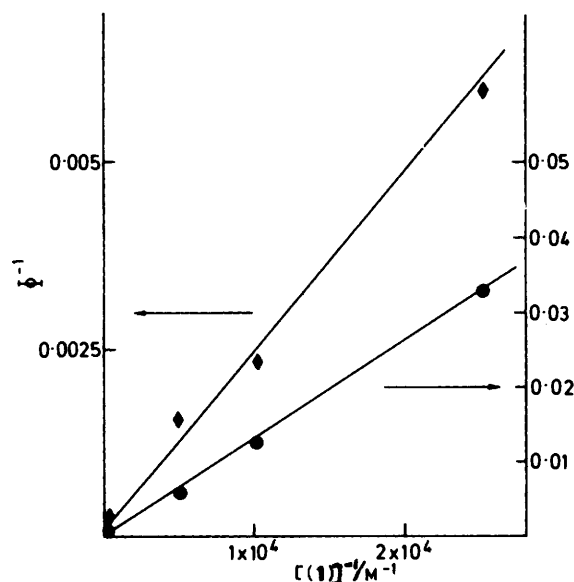$$\Phi = \frac{k_r[(1)]}{k_r[(1)] + k_d} \qquad (16)$$

In the concentration region explored in this study, $k_r[(1)] \ll k_d$ and equation (16) predicts that linear dependence of Φ on [(1)] will be approached. From the plot in Figure 4, $k_r/k_d = 130$ M^{-1} is obtained, and from this $k_r = 8.7 \times 10^8$ M^{-1} s^{-1}, a value similar to that measured for the reaction of Ph$_2$CO^{*3} with aromatic amines.[15]

The DMB quenching involves competition of the alkene for the ketone triplet. Thus the quantum yield in the presence of DMB is as in (17), and the ratio Φ_o/Φ_q is as in (18).

$$\Phi = \frac{k_r[(1)]}{k_d + k_r[(1)] + k_q[DMB]} \qquad (17)$$

$$\frac{\Phi_o}{\Phi_q} = 1 + \frac{k_q}{k_r[(1)] + k_d}[DMB] \simeq 1 + \frac{k_q}{k_d}[DMB] \qquad (18)$$

From the plot in Figure 3, $\dfrac{k_q}{k_d} = 157$ M^{-1} and $k_q = 1.05 \times 10^9$M^{-1} s^{-1} are obtained for the reaction of benzophenone triplet with DMB (lit.,[16] 8.95×10^8M^{-1} s^{-1} in aceto-nitrile).

For the analogous case of the anthraquinone-sensitized reaction, a value of $k_r:k_d = 24$ M^{-1} is obtained. If the lifetime of the triplet state is *ca.* 18 ns,[17] k_r is 0.2 × 10^9 M^{-1} s^{-1} in this case.

Decomposition of the Dye (1) *in Methanol.*—In methanol the photoreaction observed depends on the presence or the absence of carbonyl sensitizers, and on the nature of these. Direct irradiation causes a slow fading and no coloured product is isolated. Irradiation in the presence of DMPA, benzil, and benzophenone is more effective and yields an orange product (8) (u.v. spectrum in Figure 5) which we identified on the basis of its chemical behaviour, as it proved to be too labile for isolation. Thus, the orange product is transformed into the monomethyl derivative (5) when the methanolic solution is either briefly refluxed, or when traces of acid are added, or it is simply kept for several hours. Evaporation in the cold does not destroy the product but attempted chromatography affords only (5) in a yield of *ca.* 30%. Thus the orange substance is the α-aminoether (8).
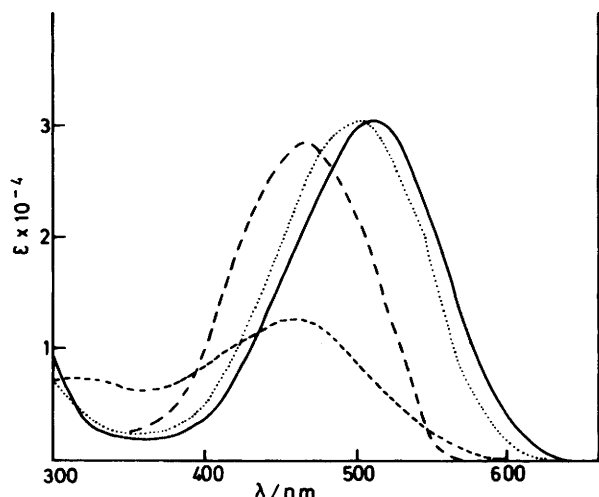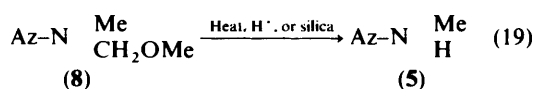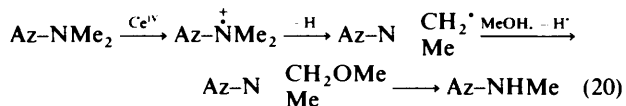
Figure 5. Electronic absorption spectra in methanol of the dye (1) (————) and of its photoproducts, 2,4-dinitro-4'-dimethylamino-NNO-azoxybenzene (4) (– – –), 2,4-dinitro-4'-methylaminoazobenzene (5) (· · · ·), 2,4-dinitro-4'-(N-methyl-N-methoxymethylamino)azobenzene (8) (- - - -)

$$\text{Az-N}\begin{matrix}\text{Me}\\\text{CH}_2\text{OMe}\end{matrix}\xrightarrow{\text{Heat, H}^+\text{. or silica}}\text{Az-N}\begin{matrix}\text{Me}\\\text{H}\end{matrix}\quad(19)$$

$$\quad\quad\quad(8)\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad(5)$$

The initial process is the same as for benzene, *i.e.* hydrogen abstraction (*via* subsequent electron and proton transfer) to yield the α-amino radical (7). DMB quenches the reaction also in this case, the plot of $\Phi_o:\Phi_q$ *versus* DMB reproducing the behaviour observed in benzene, although the effect is smaller (*e.g.* $\Phi_o:\Phi_q = 1.7$ with [DMB] $= 1 \times 10^{-4}$M using both DMPA and benzil as sensitizers). Thus, the reaction can again be attributed to the benzoylperoxyl radical, and the interaction of this species with the solvent accounts for both less efficient decomposition of the dye and less efficient quenching. Likewise, the decomposition sensitized by benzophenone can be rationalized with the same mechanism as in benzene, *via*. reaction of the triplet of the sensitizer with (1) to form radical (7), and both efficiency and DMB quenching ($\Phi_o/\Phi_q = 2.7$ with DMB $= 1 \times 10^{-2}$M) are the same as in benzene.

To support our mechanism for the DMPA- and benzil-sensitized reactions, we carried out some thermal experiments. First, the benzoyloxyl radical, which has a similar, although reduced, reactivity to the benzoylperoxyl radical,[10] causes a similar reaction. Decomposition of benzoyl peroxide in boiling methanol in the presence of (1) causes its demethylation to (5) in 50% yield. Second, other oxidation methods similarly result in demethylation. Thus Ce^{IV} rapidly decomposes the dye in methanol at room temperature. At incomplete conversion (< 1 equiv. Ce^{IV}) the product is predominantly the above mentioned, orange compound (8), whereas at complete conversion (2 equiv. Ce^{IV}), a quantitative conversion into the monomethyl derivative (5) is obtained, probably due to the further oxidation of the intermediate (8). The cerium reaction has analogy in the previously reported demethylation of 4-nitro-N,N-dimethylaniline by this reagent.[18]

$$\text{Az-NMe}_2\xrightarrow{\text{Ce}^{IV}}\text{Az-}\overset{+}{\text{N}}\text{Me}_2\xrightarrow{-\text{H}^+}\text{Az-N}\begin{matrix}\text{CH}_2^{\bullet}\\\text{Me}\end{matrix}\xrightarrow{\text{MeOH. } -\text{H}^{\bullet}}$$

$$\text{Az-N}\begin{matrix}\text{CH}_2\text{OMe}\\\text{Me}\end{matrix}\longrightarrow\text{Az-NHMe}\quad(20)$$

A completely different reaction is observed using either anthraquinone or acetone as the sensitizer in methanol,
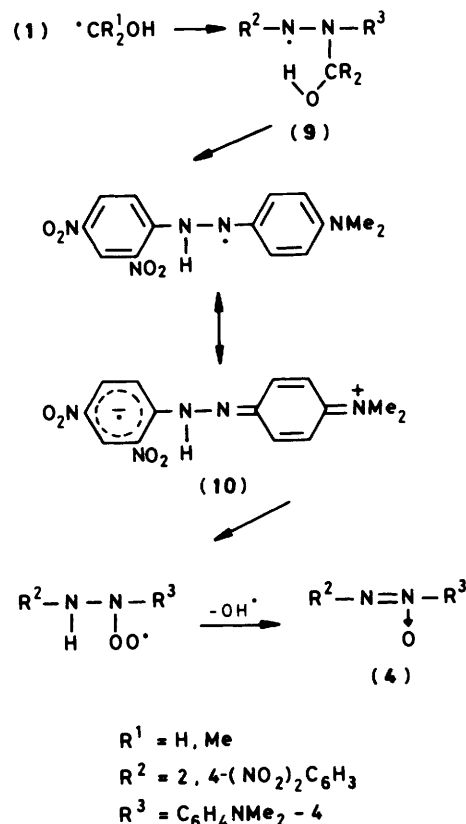
Scheme.

dealkylation to (5) now being a very minor process and the only significant coloured product being 2,4-dinitro-4'-dimethyl-amino-NNO-azoxybenzene (4), the same product obtained by Gruen upon direct photolysis in propan-2-ol, which is isolated in 25—65% yield. Several possibilities were considered in order to explain this reaction, and particularly the solvent dependence of the anthraquinone-sensitized (but not the benzophenone-sensitized) reaction. That the reaction in methanol is due to a peroxydic species or to oxygen activation is discounted as neither hydrogen peroxide nor m-chloroperbenzoic acid reacts significantly with (1) at room temperature or above,* nor do singlet oxygen† or superoxide anion produce any (4). The change in the anthraquinone-sensitized reaction is easily rationalized; in an inert medium (benzene) the triplet state of this ketone reacts with the amino group of (1), whereas in methanol reaction with the hydrogen-donating solvent yields ketyl radicals, which in turn attack the azo dye. This latter process is much more efficient than the reaction of anthraquinone triplet with (1) in benzene (see Table 2).

Therefore the mechanism depicted in the Scheme is proposed. The ketyl radical adds to the N=N double bond selectively forming radical (9), stabilized by the 2,4-dinitrophenyl group. Intramolecular hydrogen shift then leads to the hydrazyl radical (10), and reaction with oxygen yields in the end the azoxy derivative (4), the regiochemistry being determined by the direction of the initial attack of the ketyl radical.

Experimental evidence from other groups leads support to this scheme. Thus, Gruen[6] obtained the azoxy (4) both by direct
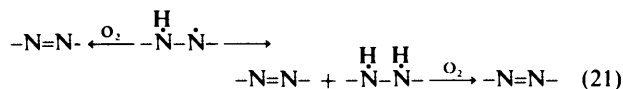
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* At any rate, these reagents are expected to attack the dimethylamino group in preference to the azo group.[19]
† Irradiation in the presence of Rose Bengal causes only very slow demethylation.

irradiation and by radiolysis in propan-2-ol. A species that is formed in both experimental conditions and can react with (1) is in fact the ketyl radical ·CMe₂OH. Furthermore, Flamigni and Monti discovered that ketyl radicals such as ·CH₂OH and ·CMe₂OH add to 4-diethylaminoazobenzene (2), and in the latter case the radical further evolves to a hydrazyl radical.[20]

In order to make sure of this point, we repeated, in propan-2-ol, the benzophenone sensitization which in methanol causes, as previously mentioned, demethylation. In this solvent the azoxy derivative (4) predominates (9:1) over the demethylated derivative (5), showing that a better hydrogen donor such as propan-2-ol successfully competes with dilute (1) for the ketone triplet, forming ketyl radicals which then attack the dye. With anthraquinone and acetone, in contrast, reaction with the solvent predominates over direct reaction with (1) already in methanol.

In the latter part of the Scheme, reaction of the hydrazyl radical (10) with oxygen is indicated. There is evidence that hydrazyl radicals usually are reoxidized in the presence of oxygen, either directly or *via* previous disproportionation to the corresponding azo and hydrazo derivatives and reoxidation of the latter [equation (21)] even though the slow decomposition of azo dyes in the presence of oxygen under short-wavelength irradiation suggests that some different pathway for hydrazyl radicals exists.[1] At any rate, in the present case the strong push-pull effect of nitro and alkylamino substituents substantially changes the structure and reactivity of the hydrazyl radical (10), and this causes its unusual reaction with oxygen to yield an azoxy derivative.*

$$-N{=}N{-} \xleftarrow{\ O_2\ } -\overset{H}{\underset{}{N}}{-}\overset{\cdot}{N}{-} \longrightarrow$$
$$-N{=}N{-} + -\overset{H}{N}{-}\overset{H}{N}{-} \xrightarrow{\ O_2\ } -N{=}N{-} \quad (21)$$

Conclusion.—2,4-Dinitro-4'-dimethylaminoazobenzene (1) is shown in this study to be an efficient and selective radical trap. Strongly electrophilic radicals such as peroxyl radicals are reduced by the amino group and give as the end product the demethylated derivative (5), whereas radicals of opposite character, such as ketyl radicals, preferentially attack the azo chromophore, and in the presence of oxygen give the azoxy (4) as the end product. As these reactions occur in air and equilibrated solvent, and yield coloured products, easily identified by t.l.c. or h.p.l.c., the use of a low concentration of (1) is worth considering for the study of radicals in similar conditions. On the other hand this work shows that efficient fading of azo dyes is caused by species similar to those potentially formed by irradiation of the matrix in which the dye is dispersed or of some additive present. Thus, *e.g.* ketone triplets and radicals at the oxygen attack the amino group while radicals at the carbon attack the azo linkage. Further reaction causing decomposition of the chromophore and fading of the colour accompanies and follows these reactions. Therefore radical processes of this type, rather than singlet oxygen reactions or reactions of the excited states of the dyes, may well be determining for the photofading observed in practical conditions.

Experimental

2,4-Dinitro-4'-dimethylaminoazobenzene was supplied by ACNA, Milan, and was purified by column chromatography on alumina and recrystallization from ethanol. Spectroscopic

grade solvents were used as received. The sensitizers were recrystallized. U.v. spectra were measured on a Cary 19 spectrophotometer, i.r. spectra on a Perkin-Elmer 197 instrument, and n.m.r. spectra on a Brucker 80 Fourier transform spectrometer.

Preparative Irradiation

Photochemical Reaction of (1) *in Benzene in the Presence of* DMPA.—Dye (1) (47 mg) in benzene (300 ml, 5 × 10⁻⁴M solution) containing DMPA (2 × 10⁻³M) was irradiated for 5 min by means of a Philips HPK 125 W high-pressure mercury arc in a quartz apparatus while air was circulated through the solution. It was noticed that the mixture obtained by evaporation of the irradiated solution underwent further thermal decomposition, apparently due to the formation of some reactive species in the photolysis, so that non-reproducible, and often very low, amounts of isolable products were obtained by the following separation. Reproducible results were obtained by adding 2—3 g of silica gel (70—230 Mesh ASTM) to the irradiated solution, so that the product mixture was adsorbed on silica gel during evaporation of the solvent. Chromatographic separation afforded the starting material (30.7 mg, 65%) and 2,4-dinitro-4'-methylaminoazobenzene (5) [3.9 mg, 25% calculated on reacted (1)], obtained as red crystals from ethanol, m.p. 185 °C (Found: C, 51.2; H, 3.7; N, 23.0. Calc. for C₁₃H₁₁N₅O₄: C, 51.8; H, 3.7; N, 23.3%); ν_max. 3 400 cm⁻¹; δ(CDCl₃) 3.50 (s, 6 H), 6.9 (dd, 2 H), 7.9—8.3 (m, 3 H), 8.9 (dd, 1 H), and 8.9, (dd, 1 H).

No other coloured material could be detected in significant amount by silica gel or alumina chromatography.

Irradiation in the same conditions in the presence of benzil (2 × 10⁻³M), anthraquinone (2 × 10⁻³M), or benzophenone (2 × 10⁻³M) for 10 min gave similar results.

Photochemical Reaction of (1) *in the Presence of DMPA in* Methanol.—Dye (1) (47 mg) in methanol (300 ml, 5 × 10⁻⁴M solution) containing DMPA (2 × 10⁻³ M) was irradiated for 15 min by means of a Hanau TN 30 W low-pressure mercury arc in a quartz apparatus while air was circulated through the solution. Work-up as before yielded starting material (25.9 mg, 55%) and (5) [7.7 mg, 38% on reacted (1)]. Similar results were obtained with benzil as sensitizer.

In both cases the product (5) was not present in the initial irradiation mixture, the only significant coloured product being an orange material clearly different from (5) in t.l.c. and h.p.l.c. This was transformed into (5) when the solution was left overnight. Similarly, conversion into (5) was observed on refluxing the solution for 10 min or on adding a drop of aqueous hydrochloric acid. In contrast, the orange product was unaffected by adding triphenylphosphine or sodium borohydride, thus discounting the hypothesis that this compound is a hydroperoxide.

Photochemical Reaction of (1) *in Methanol in the Presence of* Anthraquinone.—300 ml of a solution containing (1) (5 × 10⁻⁴ M) and anthraquinone (2 × 10⁻³M) was irradiated for 20 min and worked up as before, yielding unreacted (1) (23.5 mg, 50%) and 2,4-dinitro-4'-dimethylamino-*NNO*-azoxybenzene (4) [16.1 mg, 65% on converted (1)] obtained as red crystals, m.p. 192 °C, (lit.,[6] 188—189 °C), in all spectroscopic characteristics identical with the material described by Gruen.[6] Similar results were obtained by irradiation in the presence of 1.35M acetone.

Direct Irradiation of (1) *in Methanol.*—A solution of (1) (5 × 10⁻⁴M) was irradiated for 10 h as before. No significant amount of coloured products was revealed by t.l.c.

Detection of Volatile Products.—Solutions irradiated as

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* The formation of the azoxy derivative (4) by direct irradiation of (1) in isopropanol[6] may be due to hydrogen abstraction from the solvent by excited (1) followed by reaction of the radicals thus formed or, more likely, is a reaction sensitized by acetone formed under this condition.

before were concentrated by distillation through a Dufton column to a volume of 10 ml. The concentrate was examined for the presence of either 2,4-dinitroaniline or m-dinitrobenzene by means of a Hewlett-Packard 5700 A chromatograph (OV 17 3% 100—120 on Gas-Chrom Q and SP 2100 3% 80—20 on Supelcoport columns respectively). Only by direct irradiation was a small amount of the latter compound detected.

Quantum Yield Measurements.—These were done on an optical bench fitted with an high-pressure mercury arc (Osram 200 W) collimated by quartz lenses and monochromatized at 313 ± 5 nm by means of an interference filter. When a simple measure of the dye consumption was required, this was obtained from the residual absorption at 600 nm where the products do not significantly absorb, or when appropriate, at the absorption maximum of the dye. Analysis of both disappearance of (1) and of product formation was performed on a Waters h.p.l.c. chromatograph equipped with a μ-Bondapack C_{18} column, eluting with methanol–water (8:2). Light intensity was monitored by ferrioxalate actinometry, and was found to be 6.4×10^{-8} einstein min^{-1} cm^{-2}. In the case of the anthraquinone-sensitized reaction in methanol the irradiation was effected at 254 nm in order to ensure sufficient absorbance by the sensitizer, in this case using a low-pressure mercury arc (flux 1×10^{-7} einstein min^{-1} cm^{-2}).

Thermal Reactions: Decomposition of (1).—(*a*) *In the presence of benzoyl peroxide.* Dye (1) (15.7 mg) in methanol (5 ml, 1 × 10^{-2}M solution) containing 77.5% benzoyl peroxide (50 mg, 3 mol equiv.) was refluxed for 5 h. Work-up as before yielded unreacted (1) (1.6 mg, 10%) and product (5) (6.7 mg, 50%).

(*b*) *In the presence of* Ce^{IV}. To the dye (1) (94.5 mg) in methanol (300 ml, 1 × 10^{-3}M solution) at room temperature $Ce(NH_4)_2(NO_3)_6$ (329 mg, 2 mol equiv.) was added over 5 min. Work-up as above showed complete reaction of (1) and yielded product (5) (88 mg, 95%). A similar reaction conducted with 1 mol equiv. of $Ce(NH_4)_2(NO_3)_6$ gave as the main product the above mentioned orange compound which on silica gel chromatography is transformed into compound (5).

Other Thermal Reactions.—The dye (1) showed no appreciable reaction under the following conditions: treatment of a 10^{-3}M methanolic solution with 2.5% hydrogen peroxide for 30 h at room temperature, or 10 h at reflux; similar treatment with 5 mol equiv. potassium superoxide for 30 h at room temperature; treatment of a 10^{-3}M chloroformic solution with 2 mol equiv. of m-chloroperbenzoic acid for 20 h at room temperature, or 5 h at reflux.

Acknowledgements

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