



The role of singlet molecular oxygen in the photodegradation of 1-arylaazo-2-naphthols in methanol and on cotton

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Abstract

The contribution of a type II singlet oxygen mechanism to the photodegradation in the visible region amongst several 1-arylaazo-2-naphthols in methanol was established and shown to be in the range from 10% to 30%. The quantum yield for photodegradation, the quantum yield for the production of singlet oxygen together with the total and reactive quenching constants for reaction with singlet oxygen were measured by steady-state irradiation and time-resolved emission experiments. The values for a type II contribution towards the photodegradation are the first experimentally determined percentages giving quantitative information about different photodegradation pathways of azo compounds. On cotton linters, the dyes were found to quench singlet oxygen and to degrade in the presence of thermally generated singlet oxygen. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Singlet oxygen; Azo dyes; Cotton linters; Photodegradation

1. Introduction

Elucidation of photodegradation mechanisms caused by sunlight of 1-arylaazo-2-naphthols, which are the most frequently commercially used azo dyes, is of considerable interest. Azo dyes may photodegrade either via photo-oxidative or photoreductive pathways, depending to a large extent on the environment [1–3]. Photoreduction mainly occurs in the presence of a suitable electron or hydrogen donor and may be partly or completely reversible [1,4–7]. Photo-oxidation occurs mainly in the presence of oxygen and usually is irreversible. Such photo-oxidations can involve singlet oxygen, free radicals or the superoxide ion [8]. It has been shown that singlet oxygen contributes to photodegradation of well-used colourants like indigo [9], anthraquinones [10], quinophthalone [11] and most importantly to arylazonaphthols [12–18].

Griffiths and Hawkins [12] proposed a type II mechanism for the self-sensitisation and photo-oxidation of 4-arylaazo-1-naphthols and 1-arylaazo-2-naphthols. In both cases, the hydrazone tautomer was proposed to be the most likely sensitizer for the production of singlet oxygen via energy transfer. For 4-arylaazo-1-naphthols, the reaction of the hydrazone tautomer with singlet oxygen was proposed to be a concerted ene reaction resulting in a quicker reaction

than for 1-arylaazo-2-naphthols. The ene reaction is sterically less likely to happen for 1-arylaazo-2-naphthols, where a two-step reaction was proposed as shown in Fig. 1. Singlet oxygen has been formed via energy transfer and abstracts a hydrogen atom from the NH group from the hydrazone tautomer (II). The resulting hydroperoxide radical combines with the resulting hydrazyl radical (III) to give (IV), which decomposes to yield product (V), a 1,2-naphthaquinone and the diazonium ion (VI). It was shown that the photofading of 1-phenylazo-4-naphthol in films of cellulose acetate and cellulose triacetate was due to oxidative attack on the ground-state hydrazone tautomer of the dye by singlet oxygen. The lowest excited triplet state of the hydrazone form was held responsible for sensitising singlet oxygen [15]. The complex kinetics of the self-sensitised photo-oxidation of arylazonaphtholates have been analysed by Merkel and Smith [19] with singlet oxygen as the oxidising species according to a type II mechanism. However, the relative importance of the type II mechanism compared to other fading mechanisms has not been reported yet. The aim of this work is to establish the proportion of the type II mechanism which occurs in the total photodegradation in air equilibrated methanol and adsorbed onto cotton linters of 1-arylaazo-2-naphthols upon excitation in their absorption bands in the visible. The contribution of a type II singlet oxygen mechanism to the total photodegradation in methanol is calculated for the monoazo dyes Acid Orange 7

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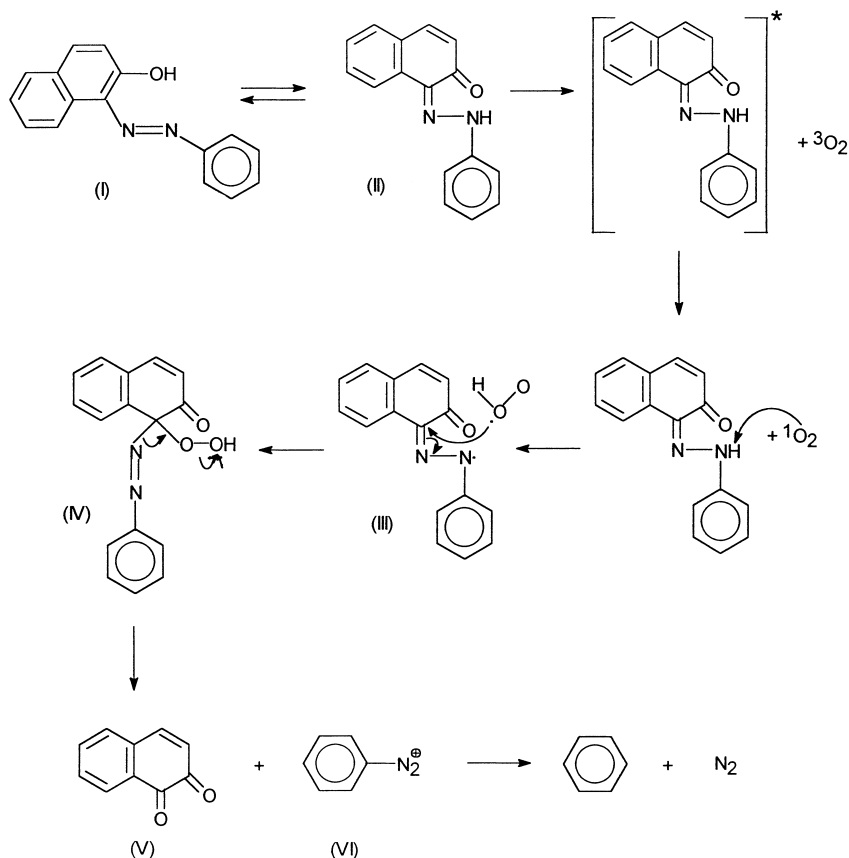


Fig. 1. Self sensitized photo-oxidation of an 1-aryloxy-2-naphthol dye via a singlet oxygen type II mechanism.

(AO7), Acid Orange 10 (AO10), Acid Red 27 (AR27) and Calmagite (CAL) and for the *bis*-azo dye Reactive red 120 (RR120) which structures are given in Fig. 2.

The efficiency of the autophoto-oxidation of a dye via a type II (singlet oxygen) mechanism depends on both, the efficiency of singlet oxygen production, arising from singlet and/or triplet-state quenching by ground-state molecular oxygen, and the efficiency with which singlet oxygen reacts chemically with the dye. The latter can be expressed in terms of the magnitude of the chemical quenching constant relative to that of the physical quenching constant.

The assessment of the role of singlet oxygen in the photodegradation of dyes adsorbed or dyed onto a cellulosic substrate is less straightforward, owing in some degree to the heterogeneous nature of the substrate. In this paper, we present results which demonstrate the degree of involvement of singlet oxygen in the observed photodegradation of dyes in such environments.

2. Experimental

2.1. Materials

AO7, AO10, AR 27, CAL (Aldrich) and RR120 (Hoechst) were recrystallised from dimethylformamide and washed

with diethylether and hexane before use. 2-Acetonaphthone (Aldrich) and aluminium phthalocyanine chloride (Aldrich) were recrystallised from ethanol before use. Rhodamine 123 (Aldrich) was used as supplied. 9,10-Diphenylanthracene peroxide was synthesised according to the method published by Wasserman et al. [20]. The procedure was modified slightly, the 9,10-diphenylanthracene peroxide was formed upon irradiation of 9,10-diphenylanthracene in a solution of chloroform bubbled continuously with oxygen with an immersed mercury lamp as light source for 24 h. The reaction was followed by TLC until no starting material could be observed. The product was analysed with ^{13}C and ^1H -NMR and showed no other compound than 9,10-diphenylanthracene peroxide. Singlet oxygen was produced from 9,10-diphenylanthracene peroxide by heating the compound at a temperature of 120°C . All solvents used were obtained from Aldrich and were of spectrophotometric grade. The dyes were adsorbed onto cotton linters from methanol as described earlier [21].

2.2. Determination of quantum yields of singlet oxygen production

The quantum yields for the production of singlet oxygen by the dyes have been determined by the method of oxygen consumption measurements. Tanielian and Wolff [22] have

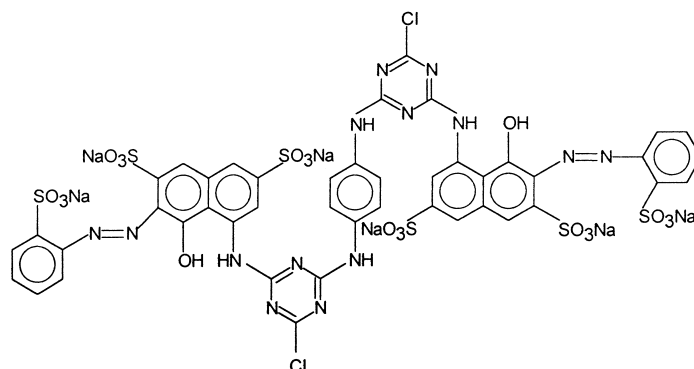
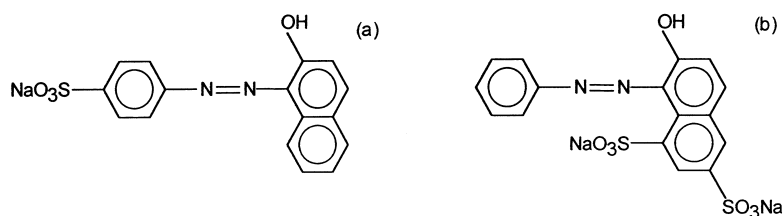
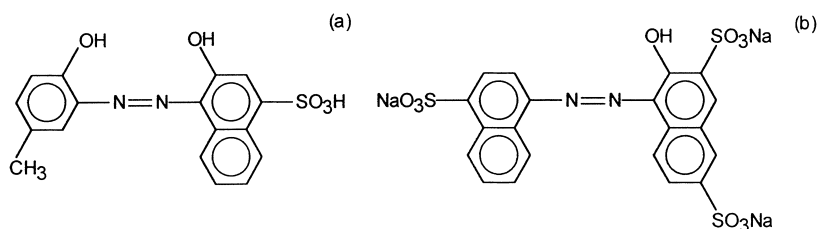
C.I. reactive red 120. (RR120)*C.I. acid orange 7 (AO7) (a) and C.I. acid orange 10 (AO10) (b)**Calmagite (CAL) (a) and C.I. acid red 27 (AR27/ amaranth) (b)*

Fig. 2. Structures of the investigated dyes.

made measurements using both, the steady-state and pulsed-laser excitations with detection of singlet oxygen by photo-oxygenation reactions or time-resolved emission detection, respectively. Good correlation between the experimental techniques used to measure values for ϕ_{Δ} was found by these workers. They reported that lower values for ϕ_{Δ} could be determined with greater accuracy using the method based on comparing oxygen consumption rates, which was employed to measure the ϕ_{Δ} of the arylazonaphthols. The experimental setup is described elsewhere [22]. The light source used was a continuous Argon laser with an output of 4 W at 514 nm. The oxygen consumption rates by the solutions of dyes in methanol and the standard solutions were measured. Energy transfer from the excited triplet states of the dye to ground-state molecular oxygen takes place resulting in the production of singlet oxygen. The

singlet oxygen goes on to react with a singlet oxygen acceptor to form a product, which results in the consumption of oxygen. The acceptor used is furfuryl alcohol at a concentration of 0.1 mol dm^{-3} and, hence, is present in large excess, thereby ensuring that all singlet oxygen produced reacts with the acceptor. The dye concentrations were chosen to have an absorbance of 2 at the excitation wavelength (514 nm) in order to absorb practically all the light (99%). When all the light is absorbed by the sensitizer the rate for oxygen consumption is constant.

The expression for the rate of oxygen consumption, VO_2 is given in Eq. (1).

$$VO_2 \propto A\phi_{\Delta}\varphi_F \quad (1)$$

with A representing the value of fractional absorption by the sensitizer at the excitation wavelength, ϕ_{Δ} the quantum

yield for the production of singlet oxygen by the sensitizer and φ_F the fraction of the acceptor that reacts with singlet oxygen. The expression for φ_F is given in Eq. (2):

$$\varphi_F = \frac{k_r[F]}{k_r[F] + k_{\text{phys}}[F] + k_d} \quad (2)$$

where k_r and k_{phys} represent the reaction rate constant for the chemical reaction and physical interaction, respectively, of acceptor F with singlet oxygen. The acceptor used was furfuryl alcohol for which $k_r \gg k_{\text{phys}}$ at a concentration of 0.1 M. From Eq. (2) it can be seen that when $k_r[F] \gg k_d$ and $\varphi_F = 1$. For furfuryl alcohol k_r in water is $1.2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and in fully deuterated methanol it is $3 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [23]. Assuming k_r in methanol is of the same magnitude as that in deuterated methanol and using $k_d = 1 \times 10^5 \text{ s}^{-1}$ in methanol [24], φ_F is calculated as >0.97 . Under this condition ($\varphi_F \cong 1$), the rate of oxygen consumption can be assumed to be directly proportional to the quantum yield for the production of singlet oxygen:

$$V_{\text{O}_2} \propto A\phi_{\Delta} \quad (3)$$

Eq. (3) is used to express the rate of oxygen consumption of a compound with an unknown quantum yield for the production of singlet oxygen, i.e. the studied dyes D and the rate for a sensitizer, S, with a known quantum yield for the production of singlet oxygen. Therefore $V_{\text{O}_2}^S \propto A_S \Phi_{\Delta}^S$ and $V_{\text{O}_2}^D \propto A_D \Phi_{\Delta}^D$

When ensuring that A_S equals A_D at the excitation wavelength, the quantum yield for the production of singlet oxygen by the dye is calculated according to Eq. (4).

$$\Phi_{\Delta}^D = \Phi_{\Delta}^S \frac{V_{\text{O}_2}^D}{V_{\text{O}_2}^S} \quad (4)$$

Rhodamine 123 in ethanol was used as the standard compound which has a ϕ_{Δ} of 0.058 [25]. The value for ϕ_{Δ} of Rhodamine 123 in ethanol was verified by comparing its oxygen consumption rate with the oxygen consumption rate of Rose Bengal which has a ϕ_{Δ} value of 0.79 in methanol [26] using a 100-ml burette. The oxygen consumption of the standard solution was measured immediately after measuring the oxygen consumption for a dye solution with no change in experimental conditions.

2.3. Determination of total singlet oxygen quenching constants

When considering the possibilities for the decay of singlet oxygen in solutions in the presence of a dye, a number of different processes take place. The singlet oxygen comes into contact with the dye resulting in dissipation of its energy excess via non-radiative pathways described by its physical quenching constant, k_{phys} . The possibility of singlet oxygen coming into contact with the dye resulting in chemical reaction is described by its reactive quenching constant, k_r , and a unimolecular decay of singlet oxygen is described

by its k_d . These processes contribute to the rate of disappearance of a singlet oxygen as shown in Eq. (5):

$$-\frac{d[{}^1\text{O}_2^*]}{dt} = k_r[\text{Dye}][{}^1\text{O}_2^*] + k_{\text{phys}}[\text{Dye}][{}^1\text{O}_2^*] + k_d[{}^1\text{O}_2^*] \quad (5)$$

or where the total quenching constant k_T as the sum of the physical and reactive quenching constants.

$$-\frac{d[{}^1\text{O}_2^*]}{dt} = k_T[\text{Dye}][{}^1\text{O}_2^*] + k_d[{}^1\text{O}_2^*] \quad (6)$$

The rate constants for total quenching of singlet oxygen by the dyes were measured by determining the first-order observed singlet oxygen phosphorescence decay constant as a function of dye concentration. 2-Acetonaphthone was used as sensitizer for the production of singlet oxygen, which has a value for ϕ_{Δ} of 0.75 in methanol [27]. The singlet oxygen emission was detected with a Judson germanium diode (J16-8SP-RO5M) connected to a Judson PA100 amplifier from solutions placed in 1-cm quartz cells at an angle of 90° with respect to the laser beam, provided by a Q-switched JK2000 Nd:YAG laser. Either a long-pass silicon filter (CVI Laser) or a 1270-nm narrow band pass filter (Melles Griot) was placed in front of the diode. The resulting voltage signal from the amplifier was applied to a digitising oscilloscope (Tektronix TDS420).

To detect singlet oxygen from an opaque sample the detection angle is $\approx 45^\circ$ with respect to the laser beam always using the 1270-nm narrow band-pass filter in front of the diode. The time resolution of the system was $2 \mu\text{s}$ for detection of singlet oxygen in solutions. Solid samples were moistened with carbon tetrachloride in order to give a long singlet oxygen lifetime, allowing measurements on time scales that reduce the level of interference from scattered laser. The magnitude of the scatter from the opaque, highly scattering cellulosic samples was such that, under these circumstances, kinetic analysis of the first $50 \mu\text{s}$ of the singlet oxygen decay is unreliable.

2.4. Determination of reactive quenching constants of singlet oxygen with the dyes

The reactive quenching constants, k_r , for the dyes in methanol have been determined by comparing the fading of the dyes with the fading of a compound for which the quenching is fully reactive. This is a commonly used procedure for the determination of k_r [16]. The sensitizers used were aluminium phthalocyanine chloride (ALP) and methylene blue. These sensitizers were chosen for the positions of their wavelengths of maximum absorption at 675 and 652 nm, respectively, enabling selective excitation of the sensitizers when irradiating solutions of the sensitizers with either a dye or a standard present. A cut-off filter letting light pass with wavelengths $>620 \text{ nm}$ was used. The standard used was diphenylisobenzofuran (DPBF). DPBF quenches singlet oxygen almost exclusively reactively, exhibiting only very weak physical quenching [28]. For

the degradation of DPBF several samples of the solution were taken and irradiated for different amounts of time. The plot of irradiation time vs. DPBF concentration was used to determine the time for the degradation of an equal amount of DPBF to the time for the degradation of a given amount of dye. The experiments were repeated at least thrice and the averages of the resulting values for k_T were determined.

2.5. Determination of quantum yields of photodegradation

The light source used was a 300-W xenon arc lamp from which the samples were placed at a distance of ≈ 30 cm in round quartz cells. A 450-nm band pass filter was placed between the lamp and sample. The lamp photon output was measured using the chemical actinometer potassium ferrioxalate ($K_3Fe(C_2O_4)_3 \cdot 3H_2O$) at concentrations of 10^{-2} M. The quantum yield for the formation of ferrous ions was taken to be 0.97 at 450 nm and the molar absorption coefficient of the iron–phenanthroline complex 1.11×10^4 L mol $^{-1}$ cm $^{-1}$ at 510 nm [29,30]. The quantum yields for photodegradation were determined by monitoring dye loss using absorption values at the maximum absorption wavelengths of the dyes in methanol.

3. Results and discussion

3.1. Production of singlet oxygen by the dyes

No singlet oxygen was observed at 1270 nm after excitation of the dyes in methanol and D $_2$ O, indicating that the quantum yields for the production of singlet oxygen, ϕ_Δ , are below 10^{-2} . The values for ϕ_Δ depend on the triplet state lifetimes of the azo dyes, which have been reported to be short-lived [13], ≈ 10 ns in viscous solvents [31], resulting in low values for ϕ_Δ .

The oxygen consumption resulting from the formation of singlet oxygen by the dyes is plotted as a function of time in Fig. 3. The rates of oxygen consumption of the dyes, under similar conditions, are all in the same order of magnitude indicating that the values of ϕ_Δ for the dyes are of comparable size. The rate of oxygen consumption was determined

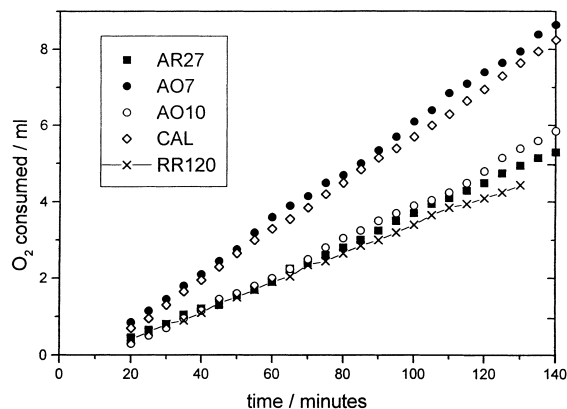


Fig. 3. Determination of the rate of oxygen consumption by the dyes in methanol under continuous irradiation at 514 nm.

to be at least 10 times higher for rhodamine 123 than that for the dyes, indicating that the values for ϕ_Δ of the dyes are at least a factor of 10 lower, at 0.058, under oxygen saturated conditions in methanol. The rates of oxygen consumption for the dyes were calculated from the linear fits to the data shown in Fig. 3. The rate of oxygen consumption for rhodamine 123 was calculated in the same way. The intercepts of the graphs are not positioned exactly in the origin due to pressure instabilities when starting each experiment. For this reason, the first few points on the plots were disregarded when calculating the slopes. Eq. (4) was used to calculate the values for ϕ_Δ of the dyes which are given in Table 1. The values found for the quantum yields of singlet oxygen production of the studied monoazo dyes and RR120 are a similar order of magnitude to the values of ϕ_Δ reported for some substituted arylazo naphthols dissolved in dimethyl formamide [10] and in isopropanol : water at 10 : 1 mixtures [32]. The hydrazone tautomer was proposed to be the most likely sensitizer for the production of singlet oxygen by Griffiths and Hawkins [12]. The variation in the values of ϕ_Δ found for the dyes was relatively small. The findings, that the dyes mainly exist in the hydrazone form in methanol and that the triplet states of the dyes are more than 10 kJ mol $^{-1}$ higher than the first excited singlet state of molecular oxygen, are consistent with the fact that the values for ϕ_Δ of the dyes are similar. For 1-phenylazo-4-naphthol in films

Table 1

Quantum yields for the production of singlet oxygen, ϕ_Δ , by the dyes in methanol; The excitation wavelength is 514 nm

Dye	ϕ_Δ	k_T^a (1 mol $^{-1}$ s $^{-1}$) (MeOH)	k_T^b (1 mol $^{-1}$ s $^{-1}$) (MeOH)	$k_{T,rel}^c$ (1 mol $^{-1}$ s $^{-1}$) (cotton lintens)
AO7	$5.21 \pm 0.2 \times 10^{-3}$	$1.3 \pm 0.1 \times 10^8$	$1.5 \pm 0.2 \times 10^5$	$1.1 \pm 0.2 \times 10^6$
AO10	$3.68 \pm 0.2 \times 10^{-3}$	$1.3 \pm 0.1 \times 10^8$	$1.4 \pm 0.1 \times 10^5$	$1.3 \pm 0.3 \times 10^6$
AR27	$3.29 \pm 0.2 \times 10^{-3}$	$9.2 \pm 1.3 \times 10^7$	$1.3 \pm 0.1 \times 10^5$	$8.3 \pm 1.7 \times 10^6$
CAL	$5.13 \pm 0.2 \times 10^{-3}$	$7.0 \pm 1.0 \times 10^7$	$1.6 \pm 0.2 \times 10^6$	$2.1 \pm 0.4 \times 10^6$
RR120	$3.01 \pm 0.2 \times 10^{-3}$	$8.6 \pm 1.3 \times 10^7$	$2.8 \pm 0.3 \times 10^3$	$4.1 \pm 0.8 \times 10^6$

^a Total quenching constant.

^b Reactive quenching constant.

^c The relative quenching constants for the quenching of singlet oxygen by the dyes in cotton lintens soaked with carbon tetrachloride.

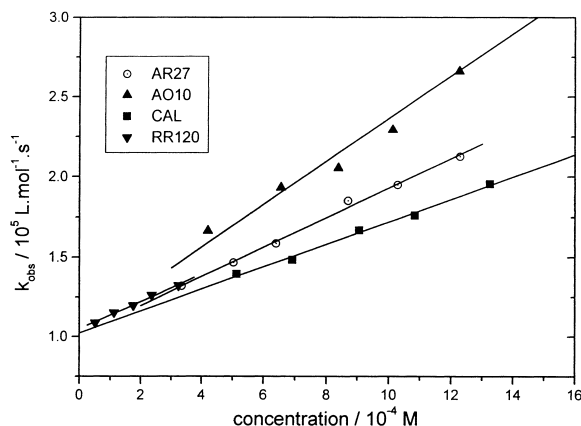


Fig. 4. Determination of the total quenching constants for the quenching of singlet oxygen in methanol. The sensitizer used to produce singlet oxygen is 2-acetonephthone.

of cellulose acetate, it was also proposed that the lowest excited triplet state of the hydrazone tautomer was responsible for sensitising singlet oxygen [16]. It has been reported that irradiation of substituted dialkylamino nitroazobenzenes, which are unable to form hydrazone tautomers also leads to the formation of singlet oxygen. However, the values for ϕ_{Δ} of these dyes measured in di-*n*-butylterephthalate are lower and are $<2 \times 10^{-3}$ [33].

3.2. Quenching of singlet oxygen by 1-arylaazo-2-naphthols

3.2.1. Physical and reactive quenching of singlet oxygen

The total quenching constants for the quenching of singlet oxygen by the investigated dyes in methanol were determined. The solutions were excited at 355 nm.

The plots of the observed rate constants of the decay of singlet oxygen phosphorescence as a function of dye concentration measured in methanol are shown in Fig. 4.

The values for the total quenching constants are listed in Table 1. The errors in the values of k_T are 10% for the orange dyes and 15% for the red dyes. The error is increased for the red dyes, because they show some emission at 1270 nm, thus rendering measurements at higher dye concentrations less reliable.

3.3. Reactive quenching of singlet oxygen

The values, which were obtained for the reactive quenching constants using both, ALP and methylene blue as sensitizers for the production of singlet oxygen, were similar. However, the reproducibility of the values of k_T obtained using ALP was better. This may be due to the fact that methylene blue decomposes during irradiation of the solutions. The values for k_T are presented in Table 1.

The total quenching constants for the quenching of singlet oxygen found for the azo dyes are significantly less than those for diffusion-controlled reactions and they are in the range of quenching constants for charge-transfer quenching

Table 2

Quantum yields for the photodegradation of the azo dyes in methanol, ϕ_{deg} , at 450 nm, k_T/k_T and the calculated percentages of the contribution of a type II mechanism to the photodegradation of the monoazo dyes and RR120 in methanol

Dye	$\phi_{\text{deg},450\text{nm}}$	k_T/k_T	% type II
AO7	$5.3 \pm 0.3 \times 10^{-5}$	1.2×10^{-3}	11
AO10	$1.9 \pm 0.1 \times 10^{-5}$	1.1×10^{-3}	21
AR27	$1.6 \pm 0.1 \times 10^{-5}$	1.4×10^{-3}	29
CAL	$7.2 \pm 0.4 \times 10^{-4}$	2.3×10^{-3}	16
RR120	$4.3 \pm 0.2 \times 10^{-7}$	3.2×10^{-5}	23

mechanisms. The finding that the dyes quench singlet oxygen via a charge-transfer mechanism agrees with the results that the triplet energies of the azo dyes lie relatively far above the energy level of the first excited state of molecular oxygen ensuring that the quenching of singlet oxygen by these compounds does not proceed via an energy-transfer process.

Several researchers have proposed [19,34] that the quenching of singlet oxygen by the dyes proceeds via a charge-transfer pair that has become correlated through an initial encounter and is capable of undergoing physical or chemical processes. The values for k_T/k_T listed in Table 2 imply that only a small fraction of the initially formed complex evolves towards oxidation products. The main pathway for the quenching of singlet oxygen occurs via intersystem crossing of the formed complex which dissociates leaving the dye chemically unchanged.

3.4. Quantum yield of photodegradation of the dyes in methanol

The values obtained for the self-sensitised quantum yields of degradation for the dyes in methanol are listed in Table 2. The reproducibility of the values lies within 5%. The quantum yields of photodegradation are low, especially for the commercially used textile dye RR120. These dyes dissipate excess excitation energy via non-radiative pathways with high efficiency. The values found are consistent with earlier reported values of ϕ_{deg} for azo dyes [35,36].

3.5. Contribution of a type II singlet oxygen mechanism to the photodegradation of the investigated dyes in methanol solution

Eq. (7) was used to calculate the percentage of the contribution of a type II mechanism to the total photodegradation of the 1-arylaazo-2-naphthols, listed in Table 2:

$$\% \text{ type II} = \frac{\Phi_{\Delta} k_T / k_T}{\Phi_{\text{deg}}} \quad (7)$$

The contributions of the auto-sensitised photo-oxidation to the photodegradation of the dyes in methanol imply that this is not the main photodegradation mechanism.

3.6. Role of singlet oxygen in dye fading on cotton

When the dyes were adsorbed on cotton lintens saturated with carbon tetrachloride, no phosphorescence caused by singlet oxygen could be detected upon pulsed excitation of the dyes, either at 355 nm or at 532 nm. This result was expected since the sensitivity of the detection system when using opaque samples is much decreased. Even if the lifetime of the azo dye triplet state increases when adsorbed onto a substrate, compared to the triplet state lifetime in solution, the quantum yield for the production of singlet oxygen would still be too low to allow the observation of phosphorescence caused by singlet oxygen produced by the dye.

The lifetime for the singlet oxygen phosphorescence in cotton was determined as described earlier [37] and was found to decrease with increasing dye concentration. This correlation was taken to be linear and the total quenching constants for the quenching of singlet oxygen by the dyes adsorbed on cotton lintens were determined from the slopes of the plots in Fig. 5. These values for the quenching of singlet oxygen in cotton lintens obtained for the adsorbed dyes must be considered as relative values since the concentrations are calculated in moles per litre cotton lintens which cannot be compared quantitatively to values obtained in solution. The errors in these relative total quenching constants are substantial and are estimated to be at least 20% on the basis of replicate measurements. The large error is mainly due to laser scatter which causes overloading of the detector at the start of the trace, making the determination of the rate constant more difficult at higher dye concentrations. The total relative quenching constants for quenching of singlet oxygen by the adsorbed dyes are listed in Table 1.

The reaction of singlet oxygen with dyes adsorbed onto cotton lintens was studied. To avoid problems of sensitizer decomposition and the occurrence of sensitizer-mediated photochemical side reactions, singlet oxygen was generated

non-photochemically. Singlet oxygen was generated thermally by decomposition of the 9,10-diphenylanthracene at 120°C which was found to react with the singlet-oxygen acceptor DPBF. For the fading of the azo dyes on cotton lintens, the amount of peroxide which was needed to obtain a change in the remission function of 0.1 at the wavelength of maximum absorption was calculated on the basis that the ratio k_r/k_T found for quenching of singlet oxygen in methanol equals the ratio $k_r/k_{T,rel}$ for quenching of singlet oxygen on cotton lintens.

A large excess of 9,10-diphenylanthracene peroxide of $\approx 10^4$ was needed with respect to the azo dyes AO7, AO10 and AR27. Therefore, the peroxide was adsorbed on the cotton lintens in two stages. Firstly, half of the peroxide was adsorbed onto dyed samples, the sample was heated for 3 h and the resulting 9,10-diphenylanthracene was removed by washing with chloroform. Then, the second half of the peroxide was applied to the same sample to undergo the same treatment. Fig. 6 shows the degradation of AO7 as a result of the reaction with singlet oxygen. The values for $\Delta F(R)$ at the maximum wavelengths of absorption for AO7 and AO10 were 0.094 and 0.091, respectively, which is close to the value of 0.1 for $\Delta F(R)$, implying that the ratios of the reactive and physical quenching constants in methanol and on cotton lintens are similar. For AR27, this value was lower, 0.02, indicating that reaction with singlet oxygen is less efficient for this dye adsorbed on cotton lintens. It was concluded that the adsorbed dyes undergo a chemical reaction with singlet oxygen causing degradation of the dyes. The observation that the dyes only exhibit a small degradation in the presence of a large excess of singlet oxygen may indicate that the efficiency of the chemical reaction with singlet oxygen is low, or alternatively may arise from the heterogeneity of the sample matrix which allows some chromophores to be in more reactive environments than others, possibly as a result of differential oxygen accessibility. Thus, the dyes adsorbed on cotton lintens quench

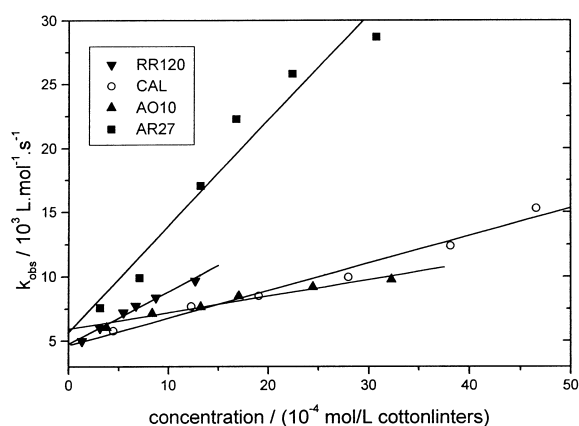


Fig. 5. Determination of the total relative quenching constants for the quenching of singlet oxygen by the dyes adsorbed on cotton lintens. The sensitizer is Rose Bengal and the samples are soaked with carbon tetrachloride.

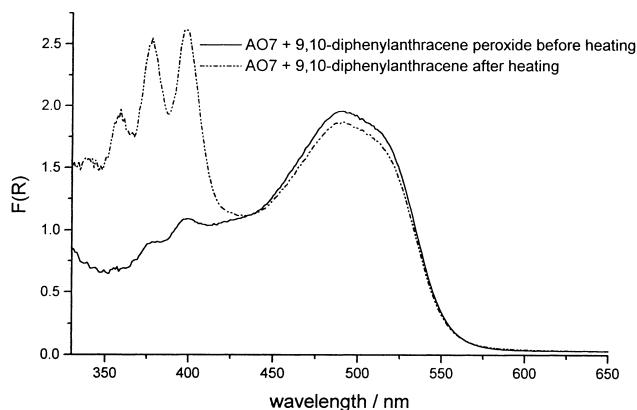


Fig. 6. Ground state absorption spectra of AO7 with 9,10-diphenylanthracene peroxide before, and after, thermal decomposition of the peroxide.

singlet oxygen mainly by a physical mechanism, mirroring their solution phase behaviour.

4. Conclusions

The role of singlet oxygen in the photodegradation of 1-aryazo-2-naphthols was studied in methanol and on cellulosic substrates. Oxygen-consumption measurements were made and the dyes were found to produce singlet oxygen, probably via energy transfer from the hydrazone tautomer upon excitation at 514 nm with relatively low quantum yields. When comparing the reactive and total singlet oxygen quenching constants the dyes are found to quench singlet oxygen mainly via physical quenching and only a small fraction of the initially formed complex, $\approx 10^{-3}$ for the monoazo dyes and 10^{-5} for RR120, evolves towards oxidation products. On cellulosic fibres the dyes were also shown to quench thermally generated singlet oxygen, resulting in their photodegradation.

The contribution of a type II singlet oxygen mechanism to the photodegradation of the 1-aryazo-2-naphthols in methanol was established and shown to be in the range from 10% to 30%. These values are the first experimentally determined percentages and give reliable evidence that the photodegradation of arylazonaphthols does not mainly proceed via a type II singlet oxygen mechanism either in solution or on a cotton surface. These percentages indicate that different photodegradation pathways under oxidative conditions take place which, to a large extent, contribute to the photooxidation of arylazonaphthols other than a type II singlet oxygen mechanism.

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