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Photosensitizing properties and reactivity of aryl azo naphtol dyes towards singlet oxygen

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Abstract

Quantum yields ϕ_Δ of singlet oxygen ($^1O_2$) formation have been determined for 10 aryl azo naphtol dyes by flash photolysis. The $^1O_2$ NIR luminescence signals at 1275 nm sensitized by the dyes were compared with the signal obtained with the reference sensitizer, phenalenone. All aryl azo naphtols photosensitize the generation of $^1O_2$, but with very low quantum yields $4 \times 10^{-4} \leq \phi_\Delta \leq 5 \times 10^{-2}$. Overall rate constants of $^1O_2$ quenching could be determined for six of these dyes by flash photolysis. A linear correlation between the logarithms of these rate constants and the oxidation potentials of the quenchers could be established, thus indicating that quenching probably involves a charge-transfer mechanism. The roles of $^1O_2$ on the photofading of azo dyes and on the photodegradation of consumer products are discussed.

Keywords: Aryl azo naphtol dyes; Singlet oxygen; Photosensitizer; Photofading; Photodegradation

1. Introduction

Aromatic azo compounds are omnipresent colorants in pharmaceutical, agrochemical, textile and printing industries. Aryl azo naphtol dyes are the most commonly used although their stability is limited by photochemical degradation [1–7]. Several authors reported studies on the fading of these compounds by oxidants such as hydrogen peroxide, hypochlorite, peracids and peroxides [8–13]. Since singlet oxygen ($^1O_2$, $^1\Delta_g$), the lowest excited state of O_2, is a very reactive and metastable species, which induces natural photodegradation processes [14], it can also contribute to the photofading of the aryl azo naphtol dyes [15–18]. Although numerous studies have been conducted in order to improve their stability, either by changing the nature of the substituents or introducing singlet oxygen quenching groups [19], the photofading still remains a major concern. As shown in previous work, the photodegradation of aryl azo naphtols by exposition to sunlight is a complex phenomenon. One of the main processes of degradation is the photo-oxygenation involving singlet oxygen. Griffiths and Hawkins [20] demonstrated that the hydrazone form is responsible for the formation of singlet oxygen. The mechanism by which $^1O_2$ reacts with those dyes depends upon their molecular structure. With 4-aryl azo-1-naphtols, an ene-reaction takes place (Scheme 1) whereas with 1-arylazo-2-naphtols, a two steps reaction occurs (Scheme 2): the first step consisting of the hydrogen abstraction of the NH group by singlet oxygen to give the hydroperoxide radical, that in turn combines itself with the resulting hydrazyl radical.

To determine whether self-sensitized photooxygenation is the main degradation pathway for aryl azo naphtol dyes, it is necessary to quantify their photosensitizing and their quenching properties towards $^1O_2$. For dyes with very small quantum yields ϕ_Δ of $^1O_2$ formation, self-sensitized photooxygenation is presumably only a secondary pathway for photofading. This is particularly true when the overall rate constants of $^1O_2$ quenching by the dyes are small. In the latter case, significant photofading should result from another mechanism. According to the literature [18,21] the quantum yields ϕ_Δ of azo dyes are very low (below 10^{-2}). However, it is still important to estimate their values so to explain the slow photodegradation of coloured consumer products (beverages and fragrances) exposed to visible light. The photodegradation by $^1O_2$, even if considered as a minor process, is certainly responsible for the formation of small amounts of hydroperoxydes that act in turn as radical initia-

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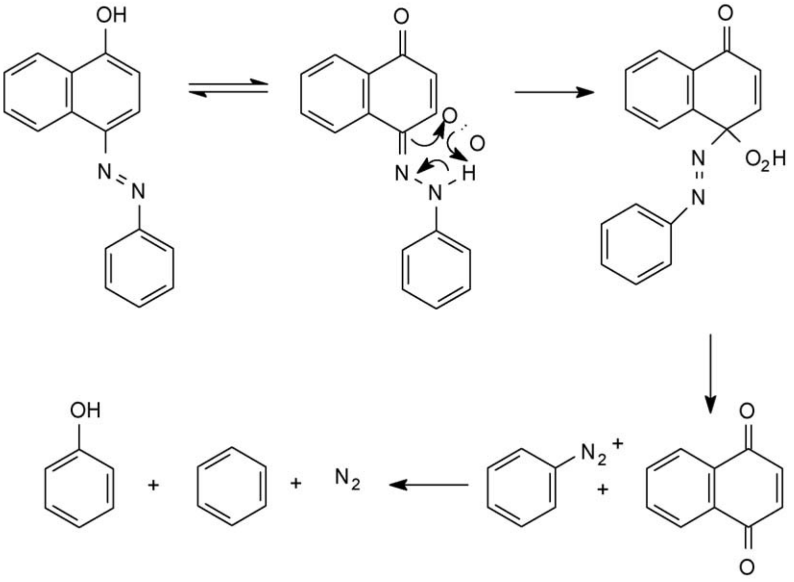


Scheme 1. Reaction mechanism of singlet oxygen with 4-aryl azo-1-naphtol [20].

tors for the subsequent thermal degradation by $^3O_2$. Hence, we determined in the present study quantum yields ϕ_Δ of $^1O_2$ sensitization and overall rate constants $(k_r + k_q)$ of $^1O_2$ quenching by 10 aryl azo naphtol dyes.

These parameters can be obtained under stationary irradiation by chemical methods measuring either the total O_2 consumption [21–23] or the disappearance of a singlet oxygen trap [18], or by monitoring time resolved the $^1O_2$ emission decay at 1275 nm after laser pulse excitation [24]. We used the latter method for the measurement of $(k_r + k_q)$ and ϕ_Δ in CD_3OD using the universal reference sensitizer phenalenone [25].

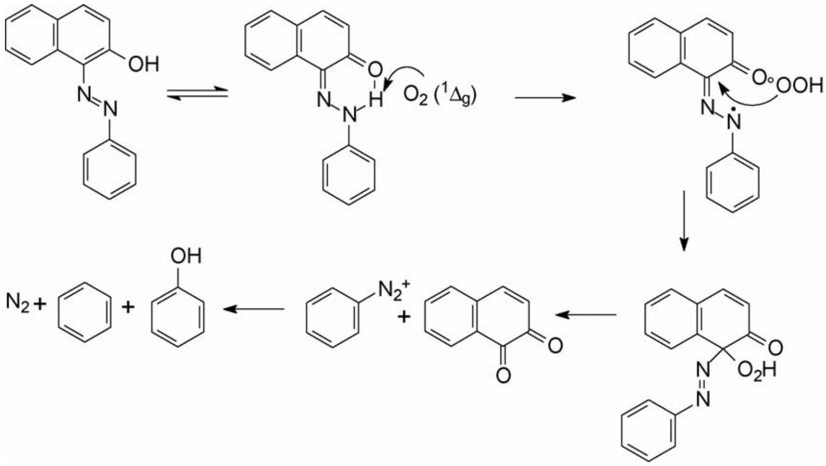
2. Experimental

2.1. Materials

The chemical structures of the investigated compounds are shown in Table 1. Acid orange 10 (AO10), sunset yellow ffc (SYFFC), acid orange 8 (AO8) and acid alizarin violet N (AAVN) were from Aldrich. Acid red 4 (R4) and acid red 33 (R33) from LCW were used as received. Crocein orange G (COG), acid orange 7 (AO7), para red and 4-nitro-phenyl azo-1-naphtol (4NPA1N; Fluka) were recrystallized from dimethylformamide and washed with diethylether and hexane before use. The singlet oxygen sensitizer phenalenone (PHE; Aldrich, 97%) was purified by column chromatography (CH_2Cl_2/silica gel). Deuterated methanol (99.97%) was purchased from Eurisotop. Tetrabutyl ammonium tetrafluoroborate (TBATFB) (≥99%) was obtained from Fluka. Dimethyl sulfoxide (99.7%) was purchased from Acros.

2.2. Cyclic voltammetry

Oxidation potentials of aryl azo naphtol dyes were measured in argon-saturated dimethylsulfoxide solutions by cyclic voltammetry. The apparatus was a potentiostat of radiometer analytical.



Scheme 2. Reaction mechanism of singlet oxygen with 1-aryl azo-2-naphtol [20].

Table 1
Structure of the investigated aryl azo naphtol dyes

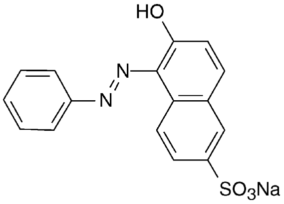
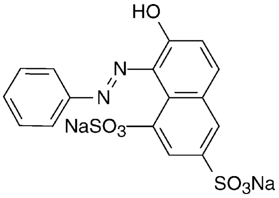
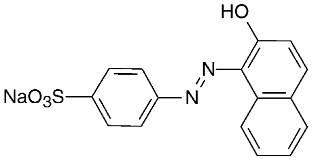
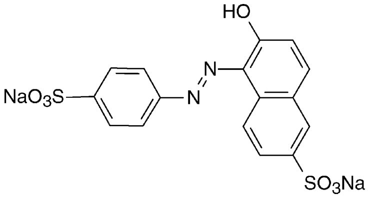
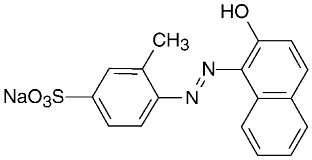
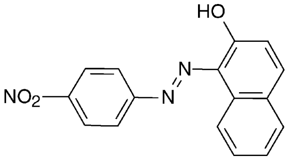
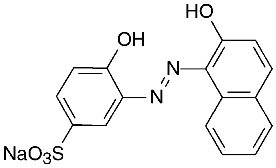
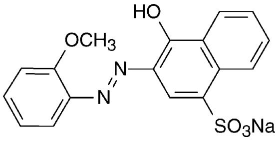
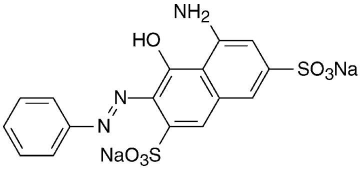
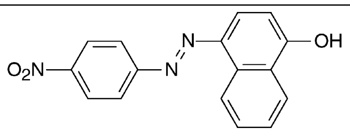
Dye	Name	Formula	ϕ_Δ (%)	E_{ox}[b] (V)	$k_r + k_q$ ($M^{-1}\,s^{-1}$)	ΔG_{CET} ($kJ\,mol^{-1}$)
COG	Crocein orange G		0.4 ± 0.1	1.065	1.6×10^5	83.3
AO10	Acid orange 10		0.22 ± 0.2 0.37 ± 0.02[a]	1.02	3.0×10^6 1.3×10^8[a]	78.9
AO7	Acid orange 7		0.12 ± 0.1 0.52 ± 0.02[a]	1.125	3.5×10^5 1.3×10^8[a]	89.1
SYFFC	Sunset yellow ffc		0.04 ± 0.01	1.13	4.2×10^5	89.5
AO8	Acid orange 8		1.0 ± 0.5	1.10	1.1×10^7	87
PR	Para red		0.17 ± 0.1	1.10	–[d]	–
AAVN	Acid alizarin violet N		1.4 ± 0.7	0.88	1.4×10^7	65.4
R4	Acid red 4		1.0 ± 0.5	0.83	1.5×10^7	60.7
R33	Acid red 33		3.1 ± 1.0	0.82	1.6×10^7	59.8

Table 1 (*Continued*)

Dye	Name	Formula	ϕ_{Δ} (%)	E_{ox}[b] (V)	$k_r + k_q$ ($M^{-1}\,s^{-1}$)	ΔG_{CET} ($kJ\,mol^{-1}$)
4NPA1N	4-Nitro-phenyl azo-1-naphtol		5.0 ± 2.0	1.30	–[c]	–

[a] From ref. [21].

[b] Oxidation potential vs. SCE in DMSO.

[c] The quenching rate constant is very low (<$10^4\,M^{-1}\,s^{-1}$) and cannot be measured under our experimental conditions.

[d] This compound was not soluble enough in deuterated methanol in order to measure its global quenching constant.

A 0.1 M tetrabutyl ammonium tetrafluoroborate solution (Fluka electrochemical grade) was used as the supporting electrolyte. The dyes were used in concentration of 5 mM. Work and auxiliary electrodes were in platinum. The reference electrode was a saturated calomel one (SCE). The scale of potential explored was −1.9 to +1.9 V/SCE with the sweep rate of 100 mV s^{-1}.

2.3. Singlet oxygen measurements

The set-up for the time resolved measurements of the $^1O_2$ emission has been described previously [24,26,27]. For the present work, some changes have been made. Particular care has been taken to improve the emission light collection efficiency by means of aspherical condensor lenses (focal length = 42 mm, diameter = 48 mm, Spindler und Hoyer). A Nd:YAG laser (Brilliant) from Quantel with frequency tripling (4 ns, 355 nm) was used as excitation source. The emissions were recorded in right-angle arrangement. The detector was either a fast liquid-N_2 cooled Ge-diode (North Coast EO 817P (response time defined as half band width (hbw) of the detector signal to a delta pulse is 300 ns)) or a slower but much more sensitive liquid-N_2 cooled Ge-diode (North Coast EO 817S (hbw = 10 µs)). The sample emissions have been filtered by two 1275 nm interference filters (hbw = 40 nm) in order to better reduce the perturbing signal caused by the fast dye fluorescence. The diode signals were intermediately stored with a transient digitizer (Gould 4072) and transferred to a PC for averaging (up to 128 times) and evaluation. The emission experiments have been done with air-saturated solutions in CD_3OD at 23 °C varying the excitation pulse energy by means of attenuation filters. The absorbances of the solutions with the dye and the reference phenalenone (PHE) were optically matched and amounted to about 1 per cm at 355 nm.

3. Results

3.1. Measurements of singlet oxygen quantum yields

If the signals recorded with the fast diode were large enough, the initial $^1O_2$ emission intensities I_{Δ}^{0} at the time of the laser pulse ignition could easily be separated from the fast decaying residual dye fluorescence, since the $^1O_2$ lifetimes τ_{Δ} in CD_3OD amounted to about 300 µs. Results for optically matched solutions of PHE and azo dye are shown in Fig. 1. The values of τ_{Δ} have been evaluated from the slopes of linear plots of $\ln(I_{\Delta})$ versus time. If the slower but stronger amplifying Ge-diode was used (for weak $^1O_2$ emissions) the separation of the residual fast fluorescence and the slow $^1O_2$ emission had to be done by the fit of a convolution of the apparatus function AF(t) with the function $Y(t)$ given by Eq. (1) to the experimentally recorded signal.

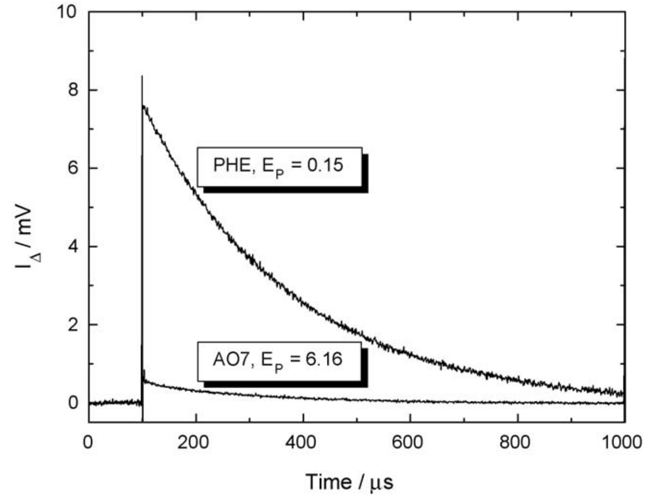


Fig. 1. Singlet oxygen NIR luminescence signal obtained with the fast Ge-diode under irradiation of phenalenone (OD = 1, E_p = 0.15) and AO7 (OD = 1, E_p = 6.16) in CD_3OD at 355 nm. The spike at 100 µs represents the strong residual fluorescence of AO7 penetrating the two 1275 nm interference filters.

$$Y(t) = F_1 \times \exp(-t/\tau_S) + \frac{F_2 \times \{\exp(-t/\tau_{\Delta}) - \exp(-t/\tau_T)\}}{1 - (\tau_T/\tau_{\Delta})} \tag{1}$$

$Y(t)$ is the sum of a fast exponential decay with fixed decay time τ_S = 1 ns mimicking the fast dye fluorescence still penetrating the 1275 nm interference filters and a biexponential rise and decay function of the singlet oxygen emission with time constants τ_{Δ} and τ_T (=sensitizer triplet lifetime), where F_2 is a direct measure for the overall concentration of $^1O_2$ formed. Examples of such convolution fits to the signals of optically matched solutions of PHE and azo dye are shown in Figs. 2 and 3.

The signals of the initial $^1O_2$ emissions recorded for reference PHE and azo dye either with the fast (=I_{Δ}^{0}) or with the slow (=F_2) diode have been measured in dependence of the laser pulse energy E_p. The initial slopes sl_{Δ} of plots of I_{Δ}^{0} or F_2 versus E_p represent energy normalized initial $^1O_2$ emissions which have been used to calculate the quantum yield ϕ_{Δ} of $^1O_2$ sensiti-

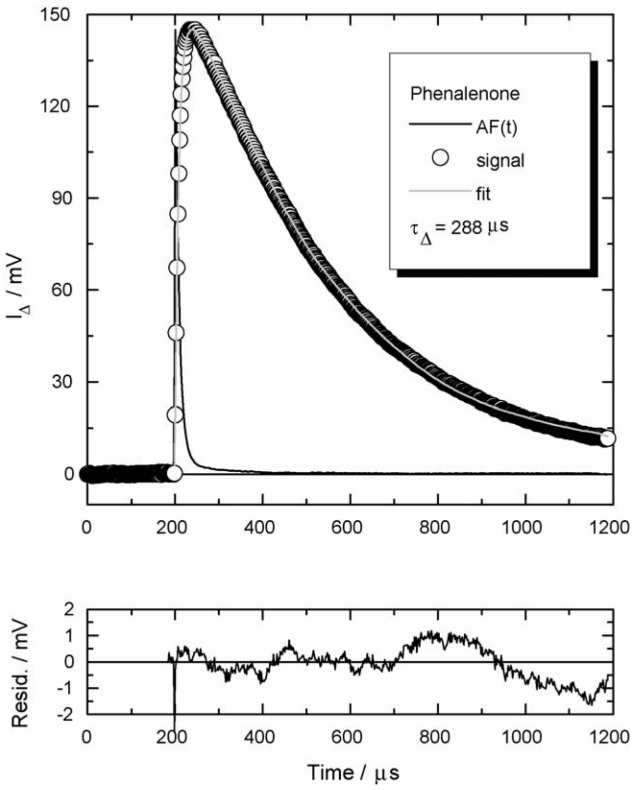


Fig. 2. Overall luminescence signal obtained with the slow Ge-diode at 1275 nm of solutions of phenalenone, CD_3OD (OD = 1, $E_p = 0.64$) (open circles) and its corresponding convolution fit; AF(t) is the scaled apparatus function; the second graphic shows the residual to the fit.

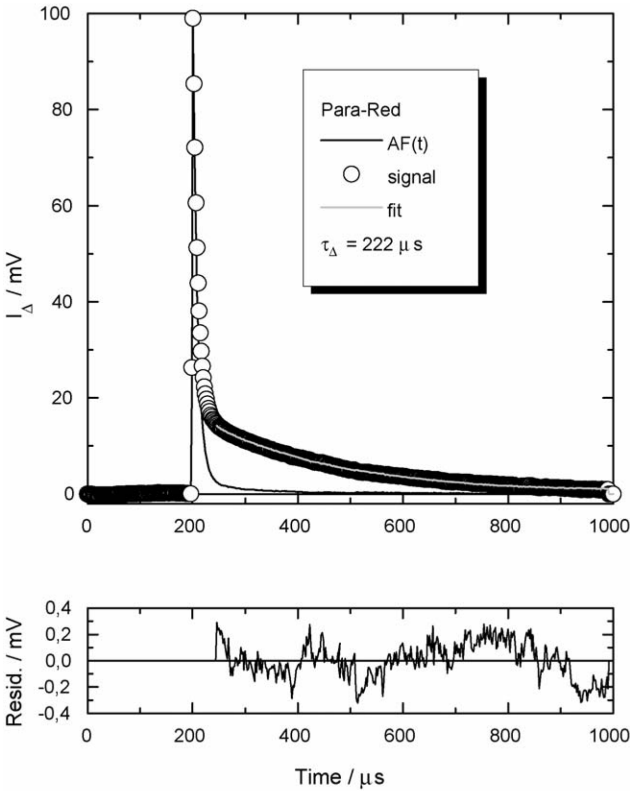


Fig. 3. Overall luminescence signal obtained with the slow Ge-diode at 1275 nm of solutions of para red in CD_3OD (OD = 1, $E_p = 0.64$) (open circles) and its corresponding convolution fit; AF(t) is the scaled apparatus function; the second graphic shows the residual to the fit.

zation via Eq. (2) with the reference value of phenalenone of $\phi_{\Delta,\mathrm{PHE}} = 0.95$ [25].

$$\phi_\Delta = \frac{\mathrm{sl}_\Delta \times \phi_{\Delta,\mathrm{PHE}}}{\mathrm{sl}_{\Delta,\mathrm{PHE}}} \tag{2}$$

3.2. Determination of singlet oxygen overall quenching constant

The different pathways of singlet oxygen decay in solution in presence of a dye (D) are presented in Eqs. (3)–(5) [14].

$$\text{Quenching by solvent} \quad {}^1O_2 + \text{solvent} \xrightarrow{k_d} {}^3O_2 \tag{3}$$

$$\text{Physical quenching} \quad {}^1O_2 + D \xrightarrow{k_q} {}^3O_2 + D \tag{4}$$

$$\text{Chemical reaction} \quad {}^1O_2 + D \xrightarrow{k_r} DO_2 \tag{5}$$

where k_d is the pseudo-first-order rate constant of singlet oxygen decay in the solvent, which proceeds by e–v energy transfer from ${}^1O_2$ to terminal bonds of the solvent molecules [14]. k_q and k_r are the bimolecular rate constants for the physical and the chemical quenching of singlet oxygen by a dye D. Therefore, ${}^1O_2$ decay can be expressed by Eq. (6) [28]:

$$-\frac{d[{}^1O_2]}{dt} = k_{\mathrm{obs}}[{}^1O_2] = \{k_d + (k_r + k_q)[D]\}[{}^1O_2] \tag{6}$$

According to Eq. (6), singlet oxygen decay was fitted with a single-exponential curve. The overall bimolecular rate constant for quenching of ${}^1O_2$ ($k_r + k_q$) was obtained by the Stern–Volmer kinetic analysis in which k_{obs} is plotted versus the dye concentration. The value of ($k_r + k_q$) is the slope of the straight line obtained. ${}^1O_2$ production was performed by using phenalenone as sensitizer. The detector for the ${}^1O_2$ luminescence detection was the fast germanium diode in these experiments.

The values obtained for the quantum yields of singlet oxygen production of the investigated monoazo dyes are very small, $4 \times 10^{-4} \le \phi_\Delta \le 5 \times 10^{-2}$ (Table 1) and cover the results of Merkel and Smith who obtained for two different aryl azo naphtol dyes ($\phi_\Delta = 2.7 \times 10^{-4}$ and 1.6×10^{-3}) using a chemical ${}^1O_2$ trap [18]. They are of same order of magnitude like values of ϕ_Δ determined by Jansen et al. with the method of oxygen consumption (Table 1) [21]. These low quantum yields result from the short lifetime of the triplet state of such azo dyes [29]. The overall reactivity constant values ($k_r + k_q$) are much lower than those obtained by Jansen et al. who also performed time resolved emission experiments. The differences can be explained by the different experimental conditions. Indeed, Jansen et al. used a low sensitivity diode requiring high laser pulse energies. These conditions favour the formation of photochemically produced quenchers of ${}^1O_2$ which increase the apparent overall quenching rate constant. Moreover, the experiments were performed in ordinary methanol in which the lifetime of ${}^1O_2$ is very short (9.5 µs) [30]. Therefore, the discrimination between the signal resulting form the strong residual fluorescence of the aryl azo sensitizer penetrating the 1275 nm interference filter and the actual $^1O_2$ emission becomes very difficult and the measurement of decay rate constants is not very reliable in this solvent. Our method is characterized by lower pulse energy and by the utilization of CD_3OD. In this perdeuterated solvent, the lifetime of $^1O_2$ is much longer (≈260 μs) [28], and as a consequence, it is easier to distinguish the fast initial signal corresponding to the fluorescence and the signal corresponding to $^1O_2$ emission. Thus, we assume the rate constants given in Table 1 much more realistic than those given by Jansen et al.

3.3. *Oxidation potentials of aryl azo naphtol dyes*

Azo dyes that contain a hydroxyl group conjugated with the azo linkage exists as an equilibrium mixture of two tautomeric forms: azo (I) or hydrazone (II) (Scheme 1). The concentration ratio between these two forms depends on the substituents and on the environment [31]. The oxidation potentials reported in Table 1 correspond to the oxidation of the hydrazone form [32]. Indeed, the potential expected for the oxidation of the azo form should be higher. For all compounds, the shape of the cyclic voltammograms indicates an irreversible behaviour probably because of the too low sweep rate. Even by increasing the sweep rate up to $1\ V\ s^{-1}$, the system still remains irreversible. As a consequence, the irreversibility of the voltammograms only allowed measurement of the peak oxidation potentials, E_{ox}.

4. Discussion

Azo dyes are known to quench singlet oxygen mainly through a physical process. In many cases, the contribution of the chemical quenching to the global quenching of singlet oxygen is negligible (about 3 orders of magnitude lower rate constants). Chemical reaction of aryl azo dyes with singlet oxygen is, as far as known, not the main process of $^1O_2$ deactivation. Merkel and Smith determined for two aryl azo naphtol dyes the ratio $k_r/(k_r + k_q)$ of the chemical to the overall rate constant to 0.15 and 0.06 [18]. Taking these results as representative, deactivation of $^1O_2$ by for aryl azo dyes is dominated by physical processes. The quenching cannot be due to electronic energy transfer since the triplet states of the azo dyes are of higher energy than the excitation energy of $^1\Delta_g$ singlet oxygen. Certainly these dyes quench singlet oxygen by the general *e*–*v* energy transfer. However, this process accounts for such molecules only for rate constants $<10^4\ M^{-1}\ s^{-1}$ [14]. Since the experimentally determined rate constants of Table 1 are much larger than this limit an additional deactivation process takes place which could be charge-transfer (CT) induced deactivation of $^1O_2$. Rate constants of CT induced quenching of $^1O_2$ depend generally on the ability of the quencher to be oxidized which can be quantified by the ionization potential IP or the peak oxidation potential E_{ox} of the quencher Q. In fact, Ogryzlo and Tang [33] found a strictly linear increase of $\log(k_q)$ with decreasing IP for the quenching of $^1O_2$ by amines, Thomas and Foote [34] obtained a complementary linear correlation of $\log(k_q)$ with E_{ox} for 2,6-di-*tert*-butylphenols which could be extended by two orders of magnitude in k_q by Tanielian and Wolff [35] including chlorophylls and related compounds as $^1O_2$ quenchers. Thus, exciplexes of quencher and electrophilic $^1O_2$ with partial charge-transfer from Q to $^1O_2$ are formed as intermediates in CT induced quenching of $^1O_2$ [14]. The strength of CT interactions in these exciplexes can be described by the change of the free energy for a complete electron transfer ΔG_{CET} from Q to $^1O_2$. ΔG_{CET} is calculated according to the Rehm–Weller equation (7) [36,37].

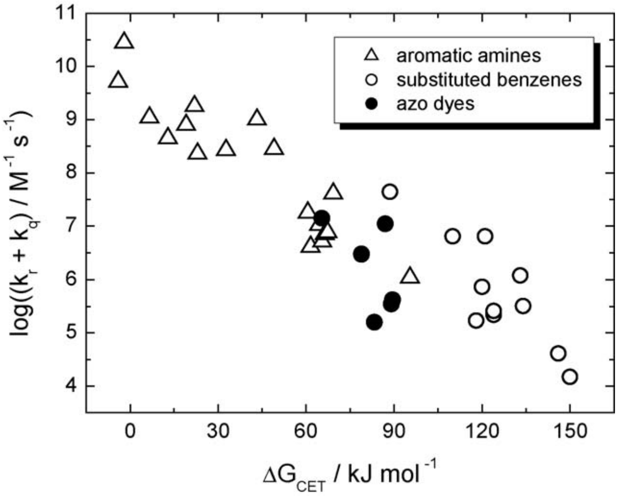


Fig. 4. Dependence of $O_2(^1\Delta_g)$ quenching rate constant on the change of free energy calculated for complete electron transfer.

$$\Delta G_{CET} = F\left[E_{1/2}^{ox}(D/D^+) - E_{1/2}^{red}(A/A^-)\right] - E_\Delta + C \qquad (7)$$

where F and $E_{1/2}^{red}$ represent Faraday's constant and the reduction potential of the electron acceptor (for O_2 −0.78 V/SCE [38]), $E_\Delta = 94\ kJ\ mol^{-1}$ is the excitation energy of O_2 $^1\Delta_g$, and C is the electrostatic interaction energy, which is inversely proportional to the dielectric constant ε and is usually taken as $C = 0$ in highly polar solvents. Values of ΔG_{CET} have been estimated for the compounds under investigation according to Eq. (7) with $C = 0$ and using the peak oxidation potentials E_{ox} instead of $E_{1/2}^{ox}$ (D/D$^+$). The $\log(k_r + k_q)$ of the aryl azo naphtol dyes have been plotted as a function of calculated free energy ΔG_{CET} in Fig. 4. In addition, the corresponding data concerning the quenching of $^1O_2$ by aromatic amines and substituted benzenes of Darmanyan et al. [39] are presented in Fig. 4. The data of the aryl azo naphtol compounds enter well to the general scattered correlation obtained for the aromatic amines and the substituted benzenes. The decrease of $\log(k_r + k_q)$ with increasing ΔG_{CET} in the exergonic range yields a slope of about $-0.04\ mol\ kJ^{-1}$ which is much smaller than the limiting slope $-0.434/RT = -0.175\ mol\ kJ^{-1}$ of corresponding plots for bimolecular electron transfer quenching of singlet excited states [36]. This behaviour is indicative for CT induced quenching of $^1O_2$ [14]. The ratio of the experimentally found slope of such Linear Free Energy Relations (LFERs) to the limiting slope for electron transfer in the exergonic range is sometimes interpreted in a very simplified picture as the fraction δ of charge-transfer in the exciplex [40–42]. Since the aryl azo naphtol data fit to the general correlation of Fig. 4 the fraction δ of charge-transfer in the $^1(O_2{}^{\delta-}\cdots Q^{\delta+})$ exciplexes amounts according to that approximation to about 0.2. However, it should be mentioned that the application of an alternative Marcus type parabolic model for the CT induced quenching of singlet oxygen leads to larger values of δ than LFERs as was shown for two homologues series of naphthalenes and biphenyls as quenchers of $^1O_2$ [43,44].

The quantum yields of the aryl azo naphthol dyes demonstrate that these compounds are poor sensitizers. This is not surprising if the short excited states lifetimes of aromatic azo compounds are considered [45], which allow only for weak and inefficient quenching by O_2. Among these derivatives, many of them show very poor quenching ability towards $^1O_2$, see, for example, Fig. 4. Indeed the rate constants of photofading due to reaction with $^1O_2$ can be considered to be an order of magnitude smaller than the overall quenching rate constants. Thus, the combination of low quantum yields ϕ_Δ, rather small chemical rate constants k_r, short $^1O_2$ lifetimes τ_Δ in water containing environments, and rather low dye concentrations [D] required for colourization lead to very small quantum yields ϕ_{ox} of self-sensitized photooxygenation in possible aryl azo naphthol dye application. Assuming $\phi_\Delta = 10^{-3}$, $k_r = 0.1 \times (k_r + k_q) = 2 \times 10^6\,M^{-1}\,s^{-1}$, $\tau_\Delta = 10^{-5}$ s and $[D] = 5 \times 10^{-5}$ M as representative values results in the very small estimate of $\phi_{ox} = 10^{-6}$, indicating that the final oxidative photodegradation mechanism involves other species as $^1O_2$ namely superoxide anion or radicals. A recent study on the mechanism of decolouration of orange II, the acid form of acid orange 7, reports that $^1O_2$ is not involved in the initial photobleaching stages of orange II. Instead a radical mechanism involving superoxide anion as oxidative species has been put forward [46]. Photodegradation of orange II generates compounds in solution at longer irradiation times, which are responsible for the generation of $^1O_2$ in the medium. This compound has been identified as 4-hydroxybenzenesulfonic acid. The reaction mechanism of aryl azo naphtol dyes with superoxide anion is different from the one involving singlet oxygen but the formed products are the same. So the degradation products of orange II in presence of $O_2{}^{\bullet-}$ are ortho naphtoquinone and phenol derivative, previously quoted. These products are identical to those resulting from the reaction of 1-aryl azo-2-naphtol with $^1O_2$. As a consequence, the identification of the degradation products does not allow determining which species is responsible for the degradation of the dyes.

The whole work carried out hitherto tends to discredit the initial assumption according to which, the oxidation products would result from an ene reaction with singlet oxygen. Indeed Bortolus et al. postulate that the oxidative degradation products result from the CT complex $^1(O_2{}^{\delta-}\cdots Q^{\delta+})$, which can undergo chemical reactions. But the major pathway of $^1(O_2{}^{\delta-}\ldots Q^{\delta+})$ CT induced deactivation is intersystem crossing which lets the dye chemically unchanged. That is the reason why the chemical reactivity of these compounds is of low importance comparing to the physical deactivation process by the CT mechanism.

As a consequence, the photofading of dyes by $^1O_2$ generated by the excited states of the dyes (self-sensitized oxidation) is a minor pathway, vide supra. On the other hand, when azo dyes are used to colour a beverage, a cosmetic or a perfume, submitted to solar light, the low flux of photogenerated $^1O_2$ may be sufficient to oxidize some reactive ingredients such as terpenes, phenols, giving hydroperoxides that would initiate a radical mechanism of oxidation by $^3O_2$. Indeed the main path of food photodegradation consists in the photooxidation of the food materials such as lipids, proteins, carbohydrates and vitamins, which can be responsible for the apparition of off-flavours and also for the colours changing [47].

5. Conclusions

This study aimed at determining the photosensitizing properties of aryl azo naphtol dyes by measuring their singlet oxygen quantum yields by time resolved emission detection. These dyes proved to be very poor sensitizers exhibiting quantum yields mostly much lower than 5%. The linear correlation found between their overall quenching constants and their oxidation potentials shows that the quenching of $^1O_2$ by these compounds mainly occurs via a charge-transfer mechanism. Consequently, the photofading of aryl azo naphtol dyes does not occur through a pure singlet oxygen process. Nevertheless, the small amount of hydroperoxydes generated from the reaction with $^1O_2$ with unsaturated compounds may act as radical initiators for the oxidative degradation of dyes and surrounding molecules by $^3O_2$.

References

[1] T. Hihara, Y. Okada, Z. Morita, Dyes Pigm. 53 (2) (2002) 153–177.
[2] Zs. Csepregi, P. Aranyyosi, J. Rusnak, L. Töke, J. Franki, A. Vig, Dyes Pigm. 37 (1998) 1–14.
[3] Zs. Csepregi, P. Aranyyosi, J. Rusnak, L. Töke, A. Vig, Dyes Pigm. 37 (1998) 15–31.
[4] Zs. Csepregi, P. Aranyyosi, J. Rusnak, L. Töke, A. Vig, Dyes Pigm. 37 (1998) 33–45.
[5] K. Imada, N. Harada, T. Takagihi, J. Soc. Dyers Colourists 110 (1994) 231–234.
[6] Y. Okada, H. Motomura, Z. Morita, Dyes Pigm. 16 (1990) 205–221.
[7] T. Hihara, Y. Okada, Z. Morita, Dyes Pigm. 60 (2004) 23–48.
[8] K. Bredereck, C. Schumacker, Dyes Pigm. 21 (1993) 45–66.
[9] K. Bredereck, C. Schumacker, Dyes Pigm. 23 (1993) 121–133.
[10] P. Gregory, C.V. Stead, J. Soc. Dyers Colourists 94 (1978) 402–407.
[11] D.M. Gould, M. Spiro, W.P. Griffith, J. Mol. Catal. A: Chem. 242 (2005) 176–181.
[12] D.M. Gould, M. Spiro, W.P. Griffith, J. Mol. Catal. A: Chem. 234 (2005) 145–150.
[13] J. Oakes, P. Ratton, J. Chem. Soc. Perkin Trans. 2 (1998) 1857–1864.
[14] C. Schweitzer, R. Schmidt, Chem. Rev. 103 (2003) 1685–1757.
[15] Z. Morita, S. Hada, Dyes Pigm. 23 (1993) 121–133.
[16] J.G. Neevel, H.C.A. van Beek, H.H.I. den Ouden, B. van de Graaf, J. Soc. Dyers Colourists 106 (1990) 176–181.
[17] H.M. Graves, L.G. Johnston, A. Reiser, J. Photochem. Photobiol. A: Chem. 43 (2) (1988) 183–192.
[18] P.B. Merkel, W.F. Smith Jr., J. Phys. Chem. 83 (1979) 2834–2840.
[19] H. Oda, Color. Technol. 120 (2004) 1–5.
[20] J. Griffiths, C. Hawkins, J. Chem. Soc., Perkin Trans. (II) (1977) 747–752.
[21] L.M.G. Jansen, I.P. Wilkes, F. Wilkinson, D.R. Worall, J. Photochem. Photobiol. A: Chem. 125 (1999) 99–106.
[22] K. Gollnick, T. Franken, G. Shade, G. Dörhöfer, Ann. N. Y. Acad. Sci. 171 (1970) 89–107.
[23] C. Tanielian, L. Golder, C. Wolff, J. Photochem. 25 (1984) 117–125.
[24] M. Bodesheim, M. Schütz, R. Schmidt, Chem. Phys. Lett. 221 (1994) 7–14.

[25] R. Schmidt, C. Tanielian, R. Dunsbach, C. Wolff, J. Photochem. Photobiol. A: Chem. 79 (1994) 11–17.

[26] M. Bodesheim, R. Schmidt, J. Phys. Chem. A 101 (1997) 5672–5677.

[27] R. Schmidt, F. Shafii, M. Hild, J. Phys. Chem. A 103 (1999) 2599–2605.

[28] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 24 (1995) 663–1021.

[29] M.W. Rembold, H.E.A. Kramer, J. Soc. Dyers Colourists 94 (1978) 12–17.

[30] R. Schmidt, E. Afshari, Ber. Bunsenges. Phys. Chem. 96 (1992) 788–794.

[31] L. Antonov, S. Stoyanov, T. Stoyanova, Dyes Pigm. 27 (1995) 133–142.

[32] P. Bortolus, S. Monti, A. Albini, E. Fasani, S. Pietra, J. Org. Chem. 54 (1989) 534–540.

[33] E.A. Ogryzlo, C.W. Tang, J. Am. Chem. Soc. 92 (1970) 5034–5036.

[34] M.J. Thomas, C. Foote, Photochem. Photobiol. 27 (1978) 683–689.

[35] C. Tanielian, C. Wolff, Photochem. Photobiol. 48 (1988) 277–280.

[36] D. Rehm, A. Weller, Isr. J. Chem. 8 (1970) 259–271.

[37] A. Weller, Z. Phys. Chem. Neue Folge 133 (1982) 93–98.

[38] S.L. Mattes, S. Farid, in: A. Padwa (Ed.), Organic Photochemistry, vol. 6, Marcel Dekker, New York, 1983, pp. 233–326.

[39] A.P. Darmanyan, W.S. Jenks, P. Jardon, J. Phys. Chem. A 102 (1998) 7420–7426.

[40] P.J. Wagner, R.A. Leavitt, J. Am. Chem. Soc. 95 (1973) 3669–3677.

[41] R.O. Loutfy, S.K. Dogra, R.W. Yip, Can. J. Chem. 57 (1979) 342–347.

[42] J. Mattay, J. Gersdof, K. Buchkremer, Chem. Ber. 120 (1987) 307–318.

[43] C. Schweitzer, Z. Mehrdad, F. Shafii, R. Schmidt, J. Phys. Chem. A 105 (2001) 5309–5316.

[44] C. Schweitzer, Z. Mehrdad, F. Shafii, R. Schmidt, Phys. Chem. Chem. Phys. 3 (2001) 3095–3101.

[45] T. Schultz, J. Quenneville, B. Levine, A. Toniolo, T.J. Martinez, S. Lochbrunner, M. Schmitt, J.P. Shaffer, M.Z. Zgiersky, A. Stolow, J. Am. Chem. Soc. 125 (2003) 8098–8099.

[46] J. Bandara, J. Kiwi, New J. Chem. 23 (1999) 717–724.

[47] A.A. Frimer, Singlet O_2, Volume IV: Polymers and Biomolecules, CRC Press, Boca Raton, FL, 1985.