reactor with RPR 3000 Å lamps; during irradiation the temperature inside the chamber did not exceed 20 °C. The sample tubes were irradiated for 6–8 min to cause ca. 15% conversions of NBS.

To the photolysate (1 mL) was added a measured amount of internal standard (3,3-dimethylglutarimide): the residue after evaporation was taken up in $CDCl_3$ (1.5 mL) saturated with water for 400-MHz NMR analysis. The pulsing sequence of the NMR analysis is the same as before,[9] and the intensities of the following signals were utilized to calculate the yields of the products with reference to the internal standard: β-bromopropionamide (BPA), the triplet at 3.65 ppm for $BrCH_2$ protons; succinimide, the singlet at 2.76 ppm for the methylene protons; *N*-phenylsuccinimide, the singlet at 2.91 ppm for the methylene protons; *N*-(tribromocyclohexenyl)succinimide, the singlet at 2.86 ppm for the methylene protons; 3,3-dimethylglutarimide, the singlet at 2.45 ppm for the methylene protons. The control experiments using known concentrations of these products against the standard show that error margins were ±5% when the correct pulsing sequence was used as reported by others.[1,6]

In series I (Table I), experiments with benzene concentrations lower than 0.027 showed nonreproducible results, probably owing to rapidly changing concentrations of benzene.

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Physical Quenching and Chemical Reaction of Singlet Molecular Oxygen with Azo Dyes[†]

Pietro Bortolus and Sandra Monti*

Istituto di Fotochimica e Radiazioni d'Alta Energia del Consiglio Nazionale delle Ricerche, Via de' Castagnoli 1, 40126 Bologna, Italy

Angelo Albini, Elisa Fasani, and Silvio Pietra*

Dipartimento di Chimica Organica dell'Università di Pavia, Viale Taramelli 10, 27100 Pavia, Italy

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The quenching rate constants of singlet oxygen lifetime by dialkylamino azo dyes **1** and tautomeric azo dyes **2** and **5** (as well as azo- and hydrazone-model methylated derivatives **3** and **4**) were determined by measuring the 1.27-μm $^1O_2$ emission lifetime, and the values obtained are in the range 10^6–10^8 M^{-1} s^{-1}. The quenching involves a charge-transfer interaction, and different correlations with the oxidation potentials of the two classes of azo dyes are observed. Chemical reactions take place with a rate in the range 10^3–10^4 M^{-1} s^{-1} and are rationalized as a secondary pathway for the charge-transfer complex between $^1O_2$ and the azo dye. Products include dealkylated amino azo dyes **6** from **1**; compounds arising from the fragmentation of the aryl–azo bond, viz., benzenes **7** and phenols **8** from **1** and **2**; and 1,4-naphthoquinone **10** as well as the dimer **9** and the oxidized cyclic derivative **11** from **2**. The methoxy derivative **3** yields an endoperoxide, which rearranges to a 1,2-naphthoquinone derivative **14**. The results are discussed in comparison with the currently accepted mechanism for the reaction of $^1O_2$ with azo dyes.

Introduction

Aromatic azo dyes are presently among the most important dyestuffs for different kinds of applications due to a combination of favorable properties. However, as far as light fastness is concerned, they usually do not rate very high, despite the extremely fast nonradiative deactivation processes characterizing their excited states.[1–4]

The photofading mechanism has been the subject of several investigations. In most cases, a photooxidative fading is observed except for some azo dyes which undergo a reductive photofading[5] when applied onto some textile fibers. The intervention of singlet oxygen, $^1O_2$ ($^1\Delta_g$) has been considered. Thus, bromo-substituted 4-(dialkylamino)-4′-nitroazobenzenes[6] and tautomeric (arylazo)naphthols have been shown to be able to sensitize the formation of singlet oxygen. The fading of (arylazo)naphthols due to their reaction with singlet oxygen is believed to be significant,[7] after an important paper by Griffiths.[8] The hydrazone tautomer is thought to be responsible for both singlet oxygen generation and the reaction with singlet oxygen via a diaza analogue of the "ene"[8] reaction. As for azo dyes not subjected to azo–hydrazone tautomerism, their fading is greatly increased in air-equilibrated solutions in the presence of carbonylic compounds.[9,10] The first act of the bleaching process is an electron transfer from the azo dye to the excited ketone or to the radicals formed in the photolysis, depending on

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[†] Work presented, in part, at the Italian–Swiss Conference on Photochemistry, Como, Sept 14–16, 1987.

(1) Kramer, H. E. A. *Chimia* **1986**, *40*, 160 and references therein.
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(9) (a) van Beek, H. C. A.; Heertjes, P. M.; Schaafsma, K. *J. Soc. Dyers Colour.* **1971**, *87*, 342. (b) van Beek, H. C. A.; Heertjes, P. M.; Schaafsma, K. *Recl. Trav. Chim. Pays-Bas* **1973**, *92*, 1189.
(10) (a) Albini, A.; Fasani, E.; Pietra, S. *J. Chem. Soc., Perkin Trans. 2* **1986**, 681. (b) The bleaching can be initiated also by the reductive attack of ketyl radicals. See: Flamigni, L.; Monti, S. *J. Phys. Chem.* **1985**, *89*, 3702. Monti, S.; Flamigni, L. *J. Phys. Chem.* **1986**, *90*, 1179.

0022-3263/89/1954-0534$01.50/0

Table I. Overall Quenching and Chemical Reaction Rate Constants in Methylene Chloride of Singlet Molecular Oxygen with Aromatic Azo Dyes

dye	$E_{1/2}$,[c] V	$10^{-7}k_q$,[d] M^{-1} s^{-1}	$10^{-4}k_r$,[b] M^{-1} s^{-1}
1a	0.84	0.65[a]	1.1
1b	0.97	0.2[a,b]	2.9
1c	0.78	1.0[a]	1.3
1d	0.79	0.9[a]	1.3
1e	0.925	0.2[a]	2.7
1f	0.985	0.3[a,b]	–
1g	0.935	0.4[b]	1.7
1h	1.30	0.1[b]	–
azobenzene	>1.5	<0.01[a,b]	–
4-nitroazobenzene	>1.5	<0.01[a,b]	–
2a	1.12	2.1 (4.2)[b]	2.2
2b	1.06	1.3 (2.6)[b]	8.1
3	1.40	0.15[a]	1.4
4	1.02	8.9[b]	0.2
5a	1.20	0.2 (0.25)[b]	2.0
5b	1.20	0.3 (0.4)[b]	–
5c	1.11	0.35 (0.45)[b]	–

[a] Sensitizer TPP. [b] Sensitizer MB. [c] Half-wave oxidation potential vs SCE in CH_3CN. [d] Reproducibility within 30%. Values in parentheses are normalized to 100% hydrazone form taking K_{eq} azo–hydrazone $\simeq$ 1 for 4-(arylazo)-1-naphthol and 1.4 for 1-(arylazo)-2-naphthol (Buraway, W. A.; Thompson, A. R. *J. Chem. Soc.* **1952**, 4793; **1953**, 1443. Hempel, R.; Visle, H.; Morgenstein, J.; Meyer, R. *J. Prakt. Chem.* **1976**, *318*, 983).

the nature of the carbonylic compound.[10] For these azo dyes, the oxidation involving singlet oxygen generated by the excited states of the azo dye itself (self-sensitized oxidation) is a negligible process.

In a previous work,[11] it was reported that 4-(diethylamino)azobenzene quenches singlet oxygen quite efficiently, but a physical deactivation is largely predominant over the chemical reaction. It is difficult to assess the general importance of singlet oxygen in the fading of different classes of azo dyes and more so under applicative conditions. In order to give a contribution toward this end, it appeared desirable to have a general mechanistic picture of the reaction between azo dyes and singlet oxygen in solution. This requires the knowledge of the rate constants of both physical and chemical quenching and the determination of the final products of the photooxidative fading for the main classes of azo dyes. This work provides such information for a series of nontautomeric 4-(diethylamino)azobenzenes and a series of tautomeric (arylazo)naphthols. A correlation between the singlet oxygen quenching rate constants and the oxidation potentials of the dyes was obtained, and a unified mechanism is proposed for the chemical consequences of the quenching process which is quite at variance with currently accepted hypotheses.

Experimental Section

Materials. The formulas of the compounds studied are collected in Table I. The azo dyes **1**, **2**, and **5** were commercial products (ACNA, Milano) or were prepared by conventional coupling reactions and purified by alumina chromatography and recrystallization. Model compounds **3** and **4** were synthesized according to the literature[7f] and purified as before. Methylene blue, MB (Baker), and 5,10,15,20-tetraphenyl-21*H*-porphine, TPP (Aldrich), were used as sensitizers without further purification. Methanol, RPE grade, and methylene chloride (fluorimetric grade, stabilized by 0.5% ethanol) were Carlo Erba products and were used as received.

Determination of Quenching Rate Constants. Quenching rate constants for the interaction of singlet oxygen with the dyes were obtained from the shortening of $^1O_2$ lifetime in the presence of known amounts of the dye. Singlet oxygen was generated by energy transfer from the sensitizer ^{3}MB or ^{3}TPP, populated by a laser pulse of 10–15 ns either at 532 nm from a Nd-YAG Q-switched laser with KDP harmonic generator or at 694 nm from a ruby laser (JK Lasers). The excitation wavelength was chosen depending on the absorption spectrum of the azo dye studied. Absorbance of the sensitizer was around 0.5 for 532-nm excitation (sensitizer TPP) and around 0.2 for 694-nm excitation (sensitizer MB). In each experimental run, the concentration of the sensitizer was kept constant because the sensitizer itself can act as a quencher of singlet oxygen.

The near-IR luminescence resulting from the forbidden transition $^3\Sigma_g^- \leftarrow {}^1\Delta_g$ of molecular oxygen was observed at 90° geometry through a 5 mm thick AR coated silicon metal filter (II-VI Inc.) with wavelength pass >1100 nm by using a Judson J16-5 germanium photodiode closely coupled to the cuvette and operating at 0 V bias.[12] The photodiode output current was fed into a Tektronix R7912 transient digitizer or a 7834 storage oscilloscope both employing a 7A22 vertical differential amplifier operating with a 0.3-MHz bandwidth and input resistance of 240 ohm. The time resolution of the system was of the order of 1 μs. The lifetime of singlet molecular oxygen was obtained by a single exponential analysis of the emission decay profile with the exclusion of the initial fast signal due to scattered excitation light and sensitizer fluorescence. The values measured in the absence of substrates were 77–83 μs in CH_2Cl_2 depending on the experimental conditions used.[13]

The pseudo-first-order rate constant, *k*, for the decay of singlet oxygen was found to depend on the concentration of the azo dye according to the equation

$$k = k_0 + k_q[\text{azo dye}] \qquad (1)$$

where k_q is the bimolecular rate constant for the interaction of singlet oxygen with the dye molecule. Values of k_q were obtained from the plots of *k* vs [azo dye]. For some azo dyes, both MB and TPP were used as singlet oxygen generators: the k_q values observed with the two sensitizers were the same within the experimental uncertainty.

Photofading Kinetics. The rate of photofading of the dyes was determined by comparison with the rate of disappearance of 9,10-dimethylanthracene (DMA), whose k_r value was taken from literature.[14] Air-saturated solutions (0.3 mL) of the dye (or DMA) and of the sensitizer (3.75×10^{-4} M) were irradiated in a spectrophotometric cell (0.1-cm thick) with a low-pressure Na arc (λ_{em} = 589 nm). The solutions were examined by vapor-phase chromatography and, after filtration on silica gel to eliminate the sensitizer, by absorption spectrophotometry and high-pressure liquid chromatography. The irradiations were carried out up to a conversion not exceeding 10%. Concentrations of the dyes and DMA were such that a reduction <10% of the singlet oxygen lifetime was observed. In these conditions, the irradiation times needed to obtain a 10% conversion of the dye and DMA are directly proportional to the k_r of the two compounds.

Preparative Photochemical Reactions. Solutions (300 mL) of the dye and sensitizer ($c = 6 \times 10^{-4}$ M and 5×10^{-4} M, respectively) were irradiated in an immersion well apparatus with a high-pressure Na arc (or a medium-pressure Hg arc) whose emission was filtered by a cutoff filter at 500 nm. The solutions were flushed with air and kept at 17 °C. When a sufficient conversion was reached, a sample of the solutions was examined by vapor-phase chromatography for the volatile products. The remainders of the solutions were evaporated and the residues chromatographed on silica gel eluting with cyclohexane/ethyl acetate mixtures. Products **7**, **8**, and **10** were identified by comparison with authentic samples. Likewise, samples of the products **12**–**14** were synthesized, for comparison, by literature procedures.[15,16] Product **9** has been previously described by Itoho.[17]

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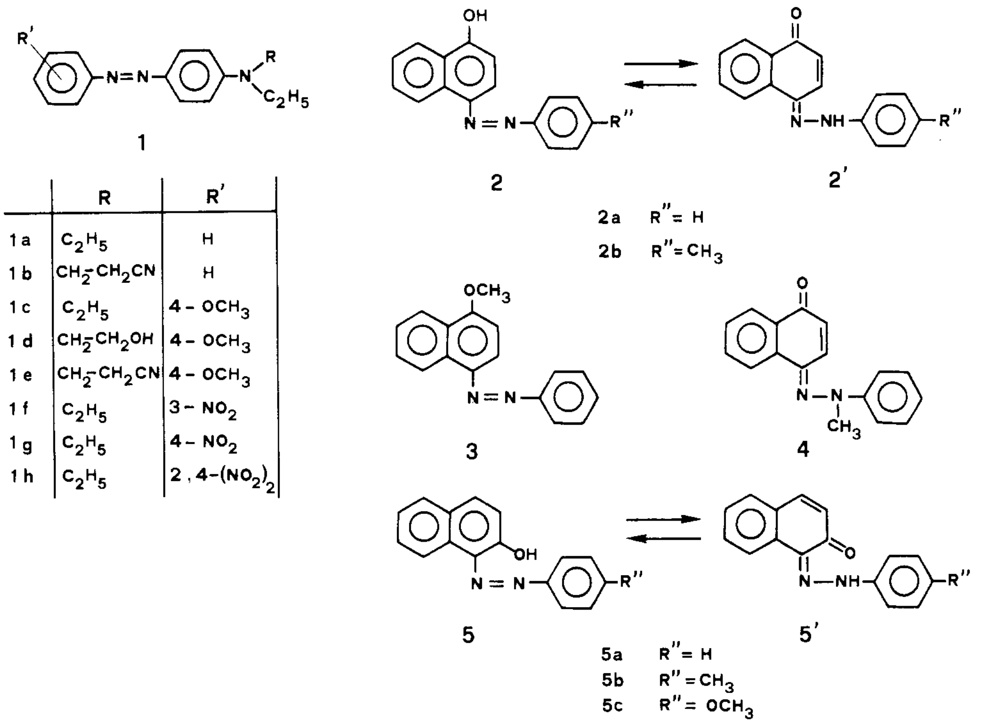
(11) Albini, A.; Fasani, E.; Pietra, S.; Sulpizio, A. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1689.

(12) The detection system was set up with the kind help of Dr. M. A. J. Rodgers, whom we gratefully acknowledge.

(13) For the dependence of the singlet oxygen lifetime on the excitation light intensity, see: Schmidt, R.; Brauer, H. D. *J. Am. Chem. Soc.* **1987**, *109*, 6976.

(14) Stevens, B.; Perez, S. R.; Ors, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 6846.

Scheme I



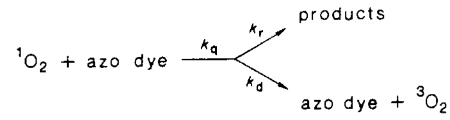
	R	R'
1a	C_2H_5	H
1b	CH_2-CH_2CN	H
1c	C_2H_5	4-OCH_3
1d	CH_2-CH_2OH	4-OCH_3
1e	CH_2-CH_2CN	4-OCH_3
1f	C_2H_5	3-NO_2
1g	C_2H_5	4-NO_2
1h	C_2H_5	2,4-$(NO_2)_2$

Product **11**, yellow crystals with melting point 286–8 °C, analyzed for $C_{26}H_{16}N_2O_3$; spectroscopic characteristics: NMR ($CDCl_3$) δ 8.59 (s), other aromatic signals at 9.02 (1 H), 8.62 (1 H), 8.3 (2 H), 8.12 (2 H), 7.8–7.9 (4 H), 7.5–7.7 (3 H), in agreement with the proposed structure; IR (KBr) 1680 cm^{-1}; mass spectrum, m/z 402 (M^+), 297 (base peak, $M^+ - PhN_2$).

Results

The structures of the dyes examined are reported in Scheme I. The quenching rate constants (k_q) for the interaction of the dyes with singlet oxygen in dichloromethane solution were directly obtained from the shortening of $^1O_2$ ($^1\Delta_g$) lifetime in the presence of the azo dyes, as determined from the decay of the near-IR luminescence. Rate constants for irreversible chemical reactions (k_r) were determined in steady-state experiments by comparison between 9,10-dimethylanthracene and the azo dyes.

The interaction of singlet oxygen with azo dyes can be summarized as follows:



The first process, with rate constant k_r, is the chemical reaction leading to fading products; the second one, with rate constant k_d, represents the physical deactivation.

The overall quenching rate constants $k_q = k_r + k_d$ for the examined azo dyes are collected in Table I together with the corresponding values of k_r and half-wave oxidation potentials ($E_{1/2}$). As it is well-known, 2- and 4-(arylazo)-naphthols exist in solution as an equilibrium mixture of azo and hydrazone[18] forms: the equilibrium composition depends on the nature of the solvent and on the substituents.[19] The half-wave potentials reported in Table I are determined by conventional cyclic voltammetry and correspond to the oxidation potentials of the hydrazone form. In no case was a reversible wave corresponding to the oxidation of the azo form observed: this should occur at higher potential, as it may be inferred from the $E_{1/2}$ of compound **3**, the blocked *O*-methyl-substituted analogue of 4-(arylazo)-1-naphthol. This is not surprising, because the rate of interconversion of the two tautomers is high[20] with respect to the rate of scanning of the potentials. The k_q values of Table I refer to the equilibrium mixture present in CH_2Cl_2.

Table II. Product Distribution from the Chemical Reaction of Singlet Oxygen with Azo Dyes

dye	solvent	product (% yield)[a]
1a	CH_2Cl_2	**6a** (80)
	CH_3OH	**7a** (30), **8a** (48)
1c	CH_2Cl_2	**6c** (78)
	CH_3OH	**7c** (35), **8c** (24)
1g	CH_2Cl_2	**6g** (93)
	CH_3OH	**7g** (17), **8g** (30)
2a	CH_2Cl_2	**9** (64), **10** (15), **11** (14), **12** (5), **7a** (3), **8a** (27)[d]
	CH_3OH	**10** (34), **12** (2), **7a** (10), **8a** (20)
3	CH_2Cl_2	**10** (14), **13** (8), **14** (27), **7a** (15), **8a** (39)
	CH_3OH	**10** (14), **7a** (15), **8a** (40)
4	CH_2Cl_2	**2a** (100)
	CH_3OH	no reaction
2a	CH_2Cl_2[b]	**9** (40), **11** (32), **12** (8)
	CH_2Cl_2[c]	**9** (61), **11** (8), **12** (6), **10** (10), **7a** (5), **8a** (4)

[a] Yield calculated by taking into account that **9–11** are "dimers". [b] 1,4-Naphthoquinone (0.01 M) added. [c] Direct irradiation with a medium-pressure Hg arc and Pyrex filter. [d] Chlorobenzene (1%) also found.

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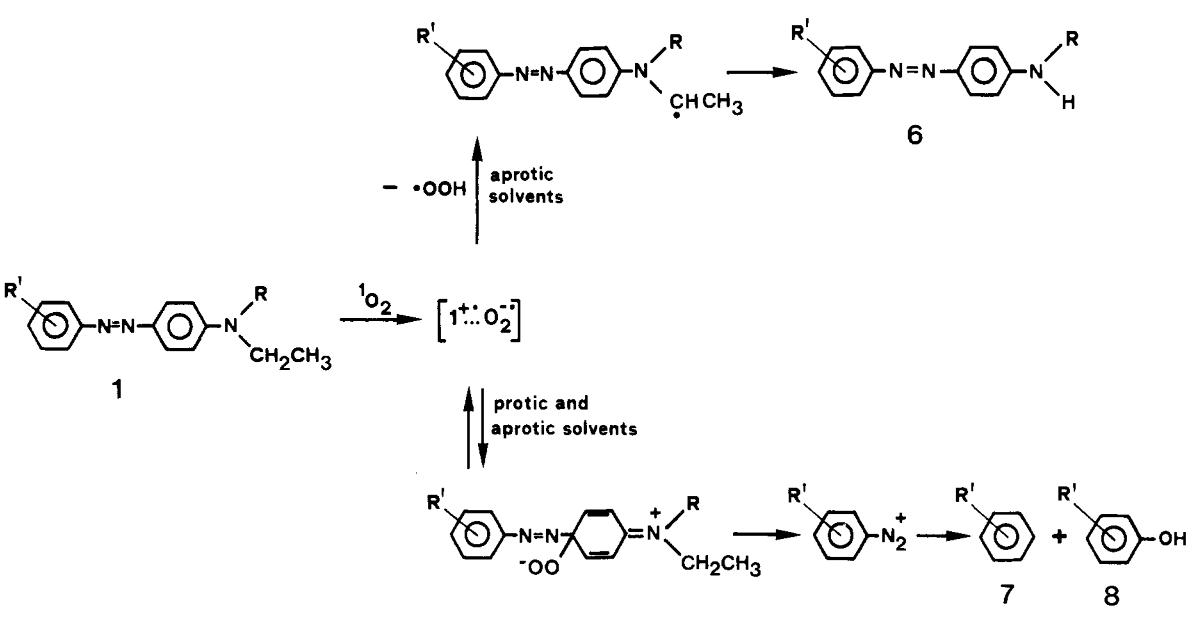
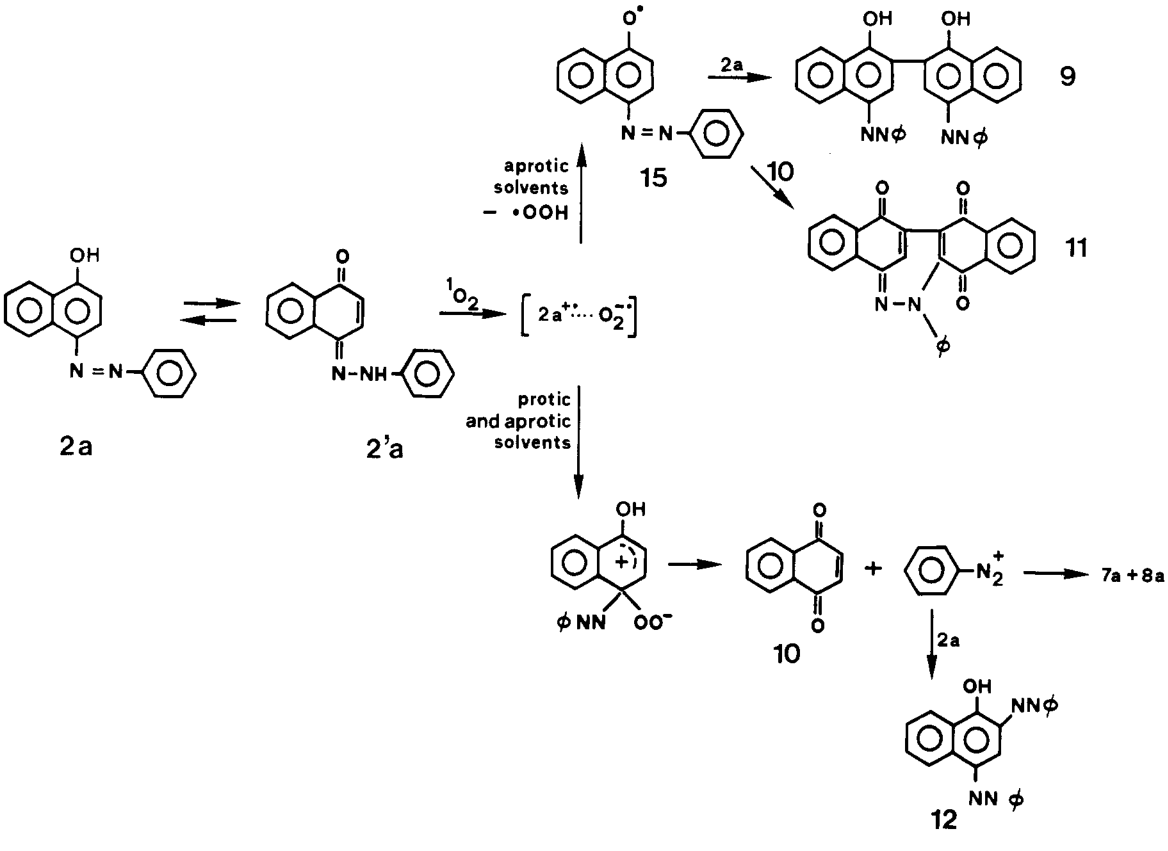
(19) Korewa, R.; Urbanka, H. *Rocz. Chem.* **1972**, *46*, 2007.

(20) Jacques, P.; Payerne, A. *EPA Newsletter* **1986**, *28*, 33.

Scheme II



Scheme III



The products obtained from the sensitized photooxygenation of some of the dyes shown in Scheme I are reported in Table II, and the results can be summarized as follows.

(Dialkylamino)azobenzenes **1** undergo N-dealkylation to yield monoalkyl derivatives **6** in dichloromethane, as well as in other aprotic solvents. In methanol, the main process involves cleavage of the bond between the aryl and the azo groups to yield aromatic radicals, which are trapped by the solvent and oxygen to give benzenes **7** and phenols **8** (see Scheme II).

The tautomeric dye 4-(phenylazo)-1-naphthol (**2a**) yields benzene and phenol, the dimer **9**, 1,4-naphthoquinone (**10**), the oxidized cyclic derivative **11**, the bis azo dye **12** (see Experimental Section for structure identification). Product **9** is largely predominant in aprotic solvents, whereas only compounds **10** and **12** are obtained in alcohols (see Scheme III). Product **9** is itself labile under the reaction conditions and, in part, yields back **2a**.[21] Our results

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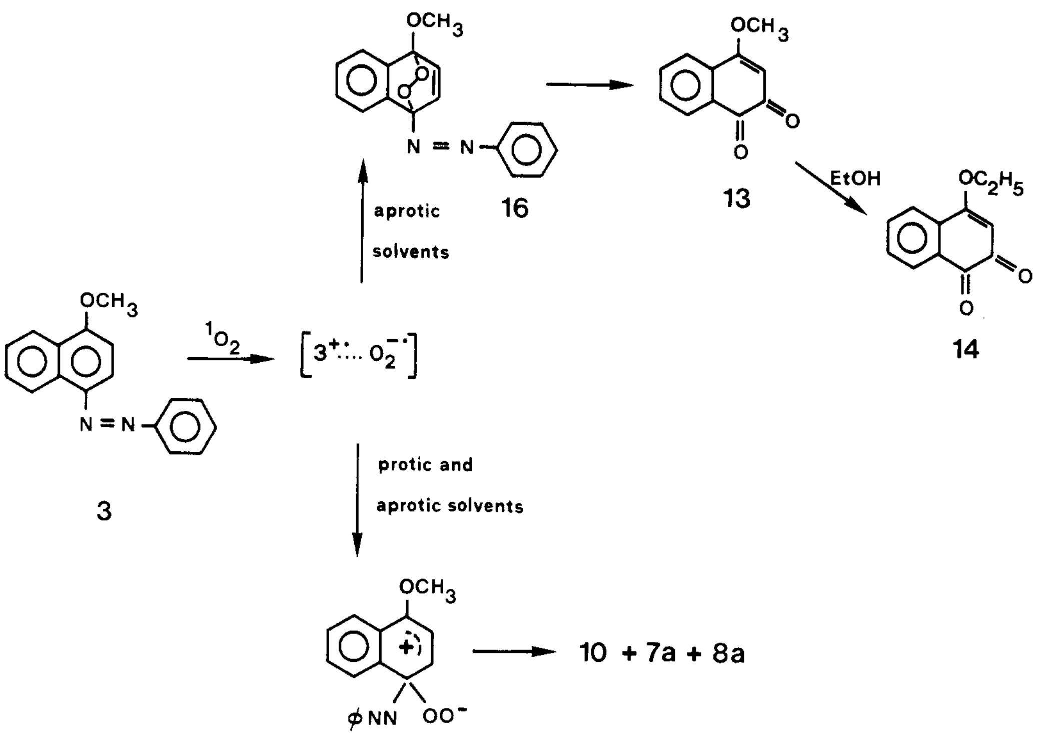
[21] Due to the photoreactivity of compound **9**, its yield in preparative experiments depends on irradiation time and starting concentration, as well as on its very scarce solubility in most solvents. A previous attempt to correlate the yield of this product with the percentage of the hydrazone tautomer present in a given solvent (ref 17) appears, therefore, unfounded. We also checked that product **11** is a primary product and that it does not arise from further oxidation of product **9**.

Scheme IV



complete and, in part, confirm previous reported findings[8b,17] (see also the results of direct irradiation, e.g., last entry in Table II).

The *O*-methyl derivative **3**, reported as unreactive,[8b] yields 1,4-naphthoquinone and, only in dichloromethane, a mixture of 4-methoxy-1,2-naphthoquinone (**13**) and 4-ethoxy-1,2-naphthoquinone (**14**), in which **14** predominates (see Scheme IV). The ethyl derivative **14** arises from the solvolysis of **13** in the presence of the ethanol contained in the solvent as a stabilizer. The *N*-methylhydrazone **4** undergoes only a very slow N-demethylation to yield compound **2a** in dichloromethane and is virtually unreactive in methanol.

Before proceeding to the discussion of the data in Table I, some preliminary observations are in order. Most of the k_q and k_r values of Table I have been obtained by using MB as sensitizer for the generation of $^1O_2$. This choice was dictated by two factors: (i) The favorable absorption spectrum of this sensitizer (λ_{max} = 652 nm in CH_2Cl_2) allowing its selective excitation in the presence of the azo dyes. These compounds have absorption spectra extending beyond 500 nm with high molar coefficients and must be used at relatively high concentrations (up to 10^{-2} M) to observe appreciable quenching in transient experiments. (ii) Its low triplet energy (E_T = 34 kcal/mol) which minimizes the energy transfer process to the low-lying triplet state[22] of the azo dyes.

However, methylene blue has some drawbacks. In fact, MB does interact with some azo dyes, viz., the easily oxidizable diethylamino azo derivatives, as we evidenced by the quenching of the sensitizer fluorescence. Also the singlet oxygen emission intensity is strongly lowered at dye concentrations that do not significantly affect the singlet oxygen lifetime ([azo] < 10^{-3} M). The short lifetime of ^{1}MB (τ_f < 1 ns)[23] implies that the fluorescence quenching process is due to a preformed ground-state complex, even if the absorption spectrum of the mixture azo dye + MB is fully additive with respect to the spectra of the components. MB aggregates are likely involved in the process. However, this interaction does not affect the queching rates since we obtained the same k_q values both when MB and when TPP was used as sensitizer.

As for the chemical reaction, literature evidence[24] suggests the interaction of MB with the substrate to form radicals which subsequently react with oxygen to give products. However, in fluid solution the above-mentioned mechanism is competitive at substrate concentrations such that energy transfer from the excited sensitizer to the substrate prevails on energy transfer to oxygen.[25] This does not apply in the present case; as a matter of fact, no photochemical reaction sensitized by MB was observed in the absence of oxygen, and in all the cases in which both MB and TPP were used as sensitizers, a very similar distribution of dye fading products was observed. Thus, we are confident that the photoreaction products isolated come from the direct attack of singlet oxygen on the azo dye so that the k_r collected in Table I are truly indicative of the reactivity of the azo dyes with singlet oxygen.

Discussion

Inspection of the data reported in Table I shows that azo dyes are quite efficient quenchers of singlet oxygen and that the reaction rate constants, k_r, are in most cases about 3 orders of magnitude lower than k_q, the overall $^1O_2$ quenching rate constant. Therefore the quenching is essentially physical in nature. This conclusion has been previously reached for some azo dyes from their retarding effect on known photooxygenation reactions.[6a,11] Such a method is not fully satisfactory for quantitative determinations since the observed effect can, in part, arise from other sources, e.g., quenching of the sensitizer excited state.

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[22] Monti, S.; Dellonte, S.; Bortolus, P. *J. Photochem.* **1983**, *23*, 249.

[23] Merkel, H.; Hartman, S. R.; Mar, T.; Singhal, G. S.; Govindjee, G. *Science* **1969**, *164*, 3877.

[24] See, e.g.: Foote, C. S. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. 2, pp 85–135.

[25] See, e.g.: Kramer, H. E. A.; Maute, A. *Photochem. Photobiol.* **1973**, *17*, 413 and references therein.

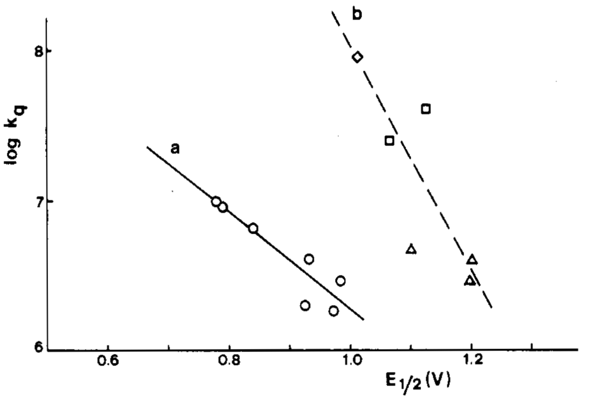

Figure 1. Plot of log k_q vs $E_{1/2}$ for azo dyes. Line a: (diethylamino)azobenzenes. Line b: ◇, hydrazone model **4**; □, hydrazone form of 4-(arylazo)-1-naphthols; △, hydrazone form of 1-(arylazo)-2-naphthols (see Table I).

The method adopted in the present work does not suffer from these restrictions.

Since energy transfer from $^1O_2$ to the azo dyes is a highly endothermic process,[22] reversible electron transfer from azo dyes to $^1O_2$ seems to be the only deactivation process practicable to the electronically excited oxygen. In such a case, one should observe a linear correlation between log k_q and the oxidation potential of the quencher, as already observed for the singlet oxygen quenching by phenols,[26] methoxybenzenes,[27] aliphatic amines,[28-30] aromatic amines, in particular substituted *N,N*-dimethylanilines,[29] and piperidines.[31] Indeed, by plotting log k_q values vs the oxidation potential of the dyes, a fairly good linear correlation is obtained for (diethylamino)azobenzenes (see Figure 1, line a). The slope of this line, $\simeq -3$ V^{-1}, is quite similar to that found in the quenching of singlet oxygen by methoxybenzenes, phenols, and alkylamines.[26] The formation of a transition state characterized by only partial electron transfer is believed to be responsible for the low slope of the correlation line,[26,32] but a recent paper by Jacques[33] suggests that the slope of the correlation line is linked to the nature, n or π, of the electron involved in the charge-transfer process. The free-energy change associated with complete electron transfer from the examined azo dyes to $^1O_2$ (calculated by taking $E(^3O_2/O_2^{\bullet-}) = -0.8$ V and 0.98 eV as $E_{0-0}(^3\Sigma_g^- \rightarrow {}^1\Delta_g)$ and neglecting Coulombic and solvation terms) is positive. The ΔG values obtained range between 0.5 and 0.8 eV for alkylamino azo dyes and between 0.85 and 1 eV for (arylazo)naphthols. Thus, for the latter class of dyes, a higher free-energy change is associated with a higher $^1O_2$ quenching rate constant. The strong sensitivity of the electron-transfer process to the molecular structure is apparent. Such effects have been rationalized in terms of entropic factors brought about by nuclear and solvent rearrangements in intermediate and final stages of the process.[32] Similar arguments could explain also the poor correlation observed in the case of 1-(arylazo)-2-naphthol and 4-(arylazo)-1-naphthol k_q values (see Figure 1, dotted line). In 1-(arylazo)-2-naphthols, the intramolecular H bond[34] reduces the degrees of freedom of these molecules, and possibly increases planarity, with respect to 4-(arylazo)-1-naphthols.

The rate of chemical reaction, low in comparison with physical quenching, makes unambiguous characterization of the mechanism less straightforward. However, the observed chemical reactions are reasonably accounted as a minor path from the same charge-transfer complex involved in the physical deactivation. Schemes II–IV illustrate the hypothesized reaction mechanism. In every case, two main pathways are observed depending on the nature of the solvent.

N-Dealkylation (Scheme II) is a known process for the radical cations of dialkylanilines generated by photochemical, electrochemical, or thermal methods.[35] Dealkylation of *N,N*-dialkylamino azo dyes was actually observed under oxidative conditions.[36] The reaction is initiated by a proton transfer to $O_2^{\bullet-}$ from the carbon α to the amino group.[37] When the photooxidation is carried out in alcoholic solvents, $O_2^{\bullet-}$ is protonated and proton transfer within the radical ion pair is inhibited. The reaction pathway then involves cleavage of the aryl–azo bond, as discussed below together with the related processes for the dyes **2a** and **3**.

The formation of the compounds **9** and **11** by photosensitized oxidation in aprotic solvents of 4-(phenylazo)-1-naphthol (**2a**) involves the intermediate formation of the naphthoxy radical **15** (Scheme III). This radical results from the transfer of an electron and a proton from the azo dye to singlet oxygen[38] (related reactions occur in the photosensitized oxidation of phenols[39]). The origin of the proton, whether from the OH group of the azo form or from the NH group of the hydrazone, remains merely speculative. The naphthoxy radical is then trapped by the starting material to yield compound **9** or by naphthoquinone to give product **11**. Indeed, in dichloromethane, the sensitized oxidation of **2a** in the presence of **10** occurs with an increased yield of product **11** and a decreased yield of the "dimer" **9** (see Table II); for related "dimerization" reactions via naphthoxy radical, see ref 27 and 40.

The other reaction pathway from **2a** involves detachment of the diazonium cation and leads to naphthoquinone, benzene, and phenol as well as to the bis azo dye **12**, resulting from the trapping of the phenyldiazonium cation by the starting azo dye. This process has been previously rationalized as an "ene" reaction between $^1O_2$ and the hydrazone tautomer **2′a**.[8b] However, products of the same type are formed by photooxidation of the dialkylamino azo dyes **1** and of 4-(phenylazo)-1-methoxynaphthalene (**3**) (see Schemes II and IV, lower part) which are not subjected to azo–hydrazone tautomerism.[41] Moreover, the importance of this process increases on going from aprotic solvents to methanol and to methanol/water mixtures. A 20-fold increase in the yield of the products **7a** and **8a** was observed on going from CH_3OH to a CH_3OH/H_2O 1/1 mixture[11] despite the fact that in these media the tautomeric equilibrium is shifted toward the azo form and the $^1O_2$ lifetime is strongly decreased.[42]

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[41] We observed the formation of 1,4-naphthoquinone by cathodic oxidation of **2a**. The reaction, in this case, results from the attack of ground-state molecular oxygen on the radical cation of **2a**.

These results seem to discard the previously proposed reaction mechanism, i.e., the "ene" reaction between $^1O_2$ and the hydrazone tautomer.[8] In Schemes II–IV, the process is formulated as involving the electrophilic attack of singlet oxygen onto the position para to the dialkylamino, hydroxy, or methoxy group for azo dyes **1**, **2a**, and **3**, respectively. This is simply an indication that from the initial charge-transfer state a more tightly bound, but still reversible, complex might result and evolve to the final products (possibly with the intervention of the solvent, e.g., by protonation of a zwitterion).

For the methoxy derivative **3**, easy proton transfer is not possible and reaction with $^1O_2$ leads to the endoperoxide **16**, which, in turn, is converted to the 1,2-naphthoquinone **13**. This cycloaddition is similar to the reaction of the parent 1-methoxynaphthalene[43] but occurs at a lower rate, given the higher oxidation potential of **3** with respect to the parent compound. This process also arises from an initial radical ion pair, as shown by the quenching of the process in methanol where, again, cleavage of the aryl–azo bond takes place, leading to the same product as for **2a** (except the bis azo derivatives, since coupling of **3** with PhN_2 is slower). Formation of 1,4-naphthoquinone is less efficient since it requires the cleavage of an $O-CH_3$ bond. Finally, the only possible process for *N*-methylhydrazone **4**, in aprotic solvents, is N-dealkylation via a mechanism similar to that reported for compound **1**.

Conclusions

Azo dyes are efficient physical quenchers of singlet oxygen as, indeed, it might have been expected since they are good electron donors. Back electron transfer remains by far predominant over chemical reaction, as often observed in photochemical electron transfer reactions,[44] and only a tiny fraction of the charge-transfer complex evolves toward products ($k_r < 10^{-3}k_q$). The rate-determining step of the chemical reaction is a heterolytic cleavage, viz., either proton transfer from the NCH_2, OH, or NH groups or cleavage of the aryl–azo bond. As for the tautomeric dyes, the role of hydrazone tautomers is important both in the generation of singlet oxygen and in its physical quenching, owing to the relatively low E_{ox} of this tautomeric form. Apparently, there is no need to envisage the formation of 1,4-naphthoquinone from these compounds as an "ene" process despite much speculation on this idea.[7b,d,f,8] A concerted process is observed only when there is no acidic proton, viz., in the case of the methoxy derivative **3**, and is a cycloaddition onto the aromatic ring.

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Penning Ionization Electron Spectroscopy of Diphenyl Chalcogenides: PhOPh, PhSPh, and PhSePh

Warō Nakanishi,* Shigeru Masuda,† Toshimasa Ishida,† Koichi Ohno,† and Yoshiya Harada*,†

Department of Chemistry, Faculty of Education, Wakayama University, Sakaedani, Wakayama 640, Japan, and Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, Japan

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Penning ionization electron spectra (PIES) and ultraviolet photoelectron spectra of PhOPh (**1**), PhSPh (**2**), and PhSePh (**3**) have been measured to explain their reactions with electrophiles such as halogens that produce either trigonal-bipyramidal adducts or molecular complexes. The spectral bands were assigned on the basis of ab initio MO calculations using 4-31G basis sets. The intensities of n and π bands were larger than those of σ bands in PIES. This shows that n and π orbitals in these compounds extend far beyond the repulsive surfaces of these molecules. Especially, the exterior electron distributions of the n orbitals in **2** and **3** were found to be very large. Although the ionization potentials (IP) of the pure π bands show little change among **1**–**3**, the IP's for the HOMO's having π and n(p_z) characters were found to decrease from 8.30 (**1**) to 7.90 (**2**) and 7.85 (**3**) eV. The IP values of the n(p_z) orbitals were also observed in the order IP(**1**) $\gg$ IP(**2**) > IP(**3**). These results explain the experimental fact that the electron-transfer reaction proceeds much easier in **2** and **3** than in **1**.

Introduction

Photoelectron spectroscopy has recently been extensively applied to organic molecules, since this method can supply basic information required to understand their chemical behaviors.[1] Studies along these lines involve organic molecules containing VIB elements. For example, ethers,[2–6] sulfides,[3–8] selenides,[4–6,8] tellurides,[4–6] their complexes with Lewis acids,[9] and the tri-[10] and tetravalent

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† The University of Tokyo.

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