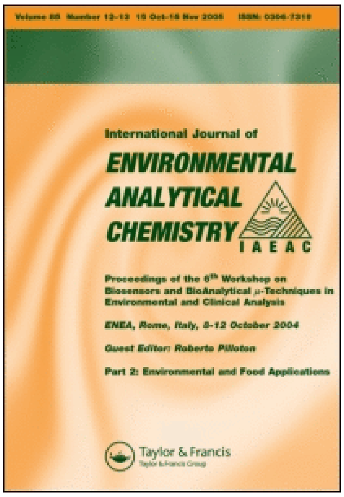

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Singlet Oxygen Analysis in Irradiated Surface Waters

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Singlet Oxygen Analysis in Irradiated Surface Waters†

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A quantitative analysis of singlet oxygen is described, permitting, in combination with actinometry, the determination of quantum yields of photooxydation as well as of singlet oxygen production. The procedure is applied to humic materials dissolved in water which have been shown to be singlet oxygen sensitizers. The quenching of corresponding triplet states by either oxygen or transition metal ions is observed in laser photolysis experiments.

KEY WORDS: Singlet oxygen, photooxydation, humic materials, singlet oxygen sensitizers, surface waters.

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INTRODUCTION

There has been a growing interest in the quantitative analysis of photochemically produced oxidants in natural surface waters because of their importance in the redox reactions of organic and inorganic compounds. These oxidants may include singlet oxygen $^1O_2$,[1,2] superoxide ion $O_2^{-\cdot}$,[3,4] hydrogen peroxide H_2O_2,[4-7] organic peroxides and hydroperoxides ROOR, ROOH,[8,9] and hydroxyl radicals $HO^{\cdot}$.[9-11] In this paper, quantitative singlet oxygen analysis is described as well as the application of this method for the determination of quantum yields of photooxydation and singlet oxygen production, respectively.

Consequently, the importance of the photosensitized production of singlet oxygen by humic materials can be evaluated, but its impact on subsequent, thermal oxydation reactions and on water purification procedures has yet to be quantified.

The photosensitized production of singlet oxygen can be represented by the following scheme of reactions:

$$S + h\nu \longrightarrow {}^1S \tag{1}$$

$$^1S \longrightarrow S + h\nu' \tag{2}$$

$$^1S \longrightarrow S \tag{3}$$

$$^1S \xrightarrow{k_4} {}^3S \tag{4}$$

$$^3S \longrightarrow S + h\nu'' \tag{5}$$

$$^3S \longrightarrow S \tag{6}$$

$$^3S + O_2 \xrightarrow{k_7} S + {}^1O_2 \tag{7}$$

A sensitizer S absorbing the incident light $h\nu$ is electronically excited (1) and may transfer energy to ground state oxygen (7). This energy transfer is usually diffusion controlled and reaches maximum efficiency when it starts from the relatively long-living triplet state

^3S. Good singlet oxygen sensitizers are molecules absorbing in the visible spectral range, exhibiting high intersystem crossing (4) efficiency, relatively long-living triplet states and chemical inertness towards singlet oxygen (or direct photolysis). The above scheme emphasizes the fact that both, intersystem crossing (4) and energy transfer (7) are in competition with other decay modes (e.g. fluorescence (2), radiationless decay from ^1S (3) and from ^3S (6)).

The exothermic energy transfer from ^3S to ground state oxygen (7) is schematically shown in Figure 1. Depending on the energy of ^3S, energy transfer to both, the $^1\Sigma_g^+$ and the $^1\Delta_g$ state of O_2 is possible. The first, however, is thought to be not of importance for subsequent chemical reactions, as its decay to the $^1\Delta_g$ state (spin allowed) and its deactivation to the ground state by solvent interaction reduce its lifetime to some nanoseconds.

$^1\Delta_g$ singlet oxygen is an intermediate of rather specific chemical reactivity. The electronic configuration in its $\pi^*_{p(x,y)}$ orbital explains its electrophilicity, i.e. its reactivity with olefins (2+2 and 2+4 cycloaddition, ene-reaction) as well as with organic sulfides (Figure 2). Electron transfer reactions and, consequently, the formation of superoxide ion,[12] are of secondary importance as far as the topic of this paper is concerned.

In exploiting the specific chemical reactivity of singlet oxygen for analytical purposes, we have, however, also to consider other decay modes of the electronically excited intermediate. Essentially, there are

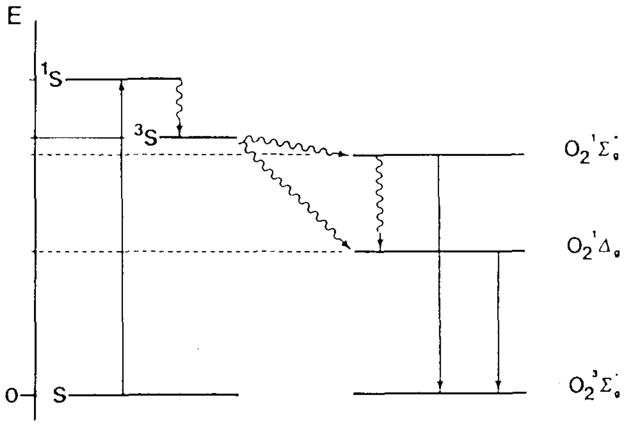


FIGURE 1 Jablonsky diagram for an energy transfer between ^3S and ground state O_2.

three distinct reactions of singlet oxygen in a solution containing substrate A: chemical reaction (trapping) with substrate A (8), physical deactivation in interaction with substrate A (9) and physical deactivation in interaction with the solvent (10). A specific and efficient singlet oxygen trap A should therefore exhibit a high rate constant k_8 and a low rate constant k_9. Given the fact that k_{10} of water is the highest of all usual solvents ($2.3 \times 10^5\ s^{-1}$),

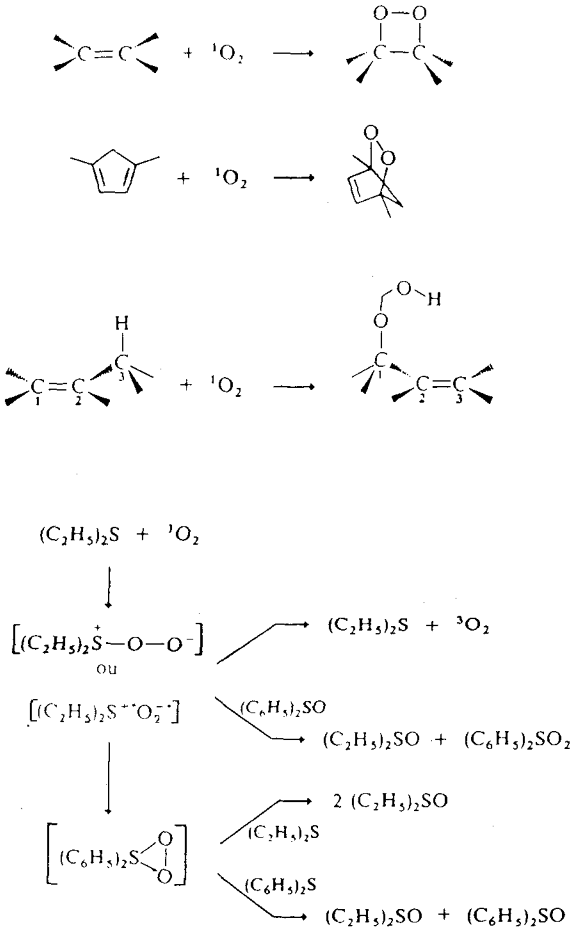


FIGURE 2 Singlet oxygen reactions with olefins and organic sulfides.

$$^1O_2 + A \xrightarrow{k_8} AO_2 \tag{8}$$

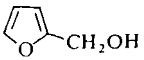
$$^1O_2 + A \xrightarrow{k_9} O_2 + A \tag{9}$$

$$^1O_2 + \text{solvent} \xrightarrow{k_{10}} O_2 + \text{solvent} \tag{10}$$

the pseudo first-order rate constant of the chemical reaction of singlet oxygen with A must be at least a factor of 100 higher, in order to achieve quantitative trapping.

In contrast to Zepp *et al.*[1] who used 2,5-dimethylfuran (A_1) as a trapping agent, we have developed an indirect singlet oxygen analysis exploiting its reaction with furfuryl alcohol (A_2).[13, 14] This acceptor is highly soluble in water and less volatile than the hydrocarbon previously used. Furfuryl alcohol is oxydised by singlet oxygen in a 2+4 cyclo-addition, the intermediate endoperoxide reacting thermally to different products depending on the solvent used (Figure 3).[15]

A_1



A_2

SINGLET OXYGEN ANALYSIS AND QUANTUM YIELD DETERMINATION

The quantum yield of furfuryl alcohol oxydation can be written as the product of the efficiencies of intersystem crossing (4), energy transfer (7) and chemical reaction (8):

$$\Phi_{AO_2} = \frac{k_4}{k_2 + k_3 + k_4} \times \frac{k_7[O_2]}{k_5 + k_6 + k_7[O_2]} \times \frac{k_g[A]}{k_8[A] + k_9[A] + k_{10}} \tag{11}$$

$$= \Phi_4 \times \varphi_7 \times \varphi_8 \tag{12}$$

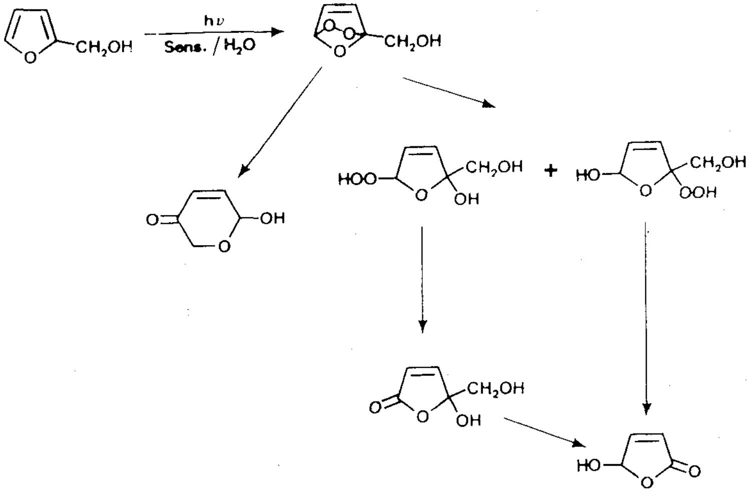


FIGURE 3 The chemical reaction of singlet oxygen with furfuryl alcohol in aqueous solution.

The quantum yield of singlet oxygen production can be calculated from

$$\Phi_{AO_2}^{-1} = \frac{k_8 + k_9}{\alpha \times \Phi_{1_{O_2}} \times k_8} + \frac{\beta \times (k_8 + k_9)}{\alpha \times \Phi_{1_{O_2}} \times k_8} \times \frac{1}{[A]} \qquad (13)$$

derived from (12), where α is an experimental factor linked to the equipment in use, $\Phi_{1_{O_2}}$ is the quantum yield of singlet oxygen production and β an acceptor specific reactivity parameter:

$$\beta = \frac{k_{10}}{k_8 + k_9}. \qquad (14)$$

Having determined α and under conditions where $k_8 \gg k_9$, the intercept of $\Phi_{AO_2}^{-1} = f([A]^{-1})$ (13) yields $\Phi_{1_{O_2}}^{-1}$.

Furfuryl alcohol has a k_8 of 1.2×10^8 $M^{-1} s^{-1}$ and a k_9 of less than 10^5 $M^{-1} s^{-1}$.[16] Experimentally, the rate of oxygen consumption in a closed system is measured by means of an oxygen electrode placed on an irradiated cell. Simultaneously, the flux of absorbed photons is determined by an integrating actinometer (Figure 4).[17]

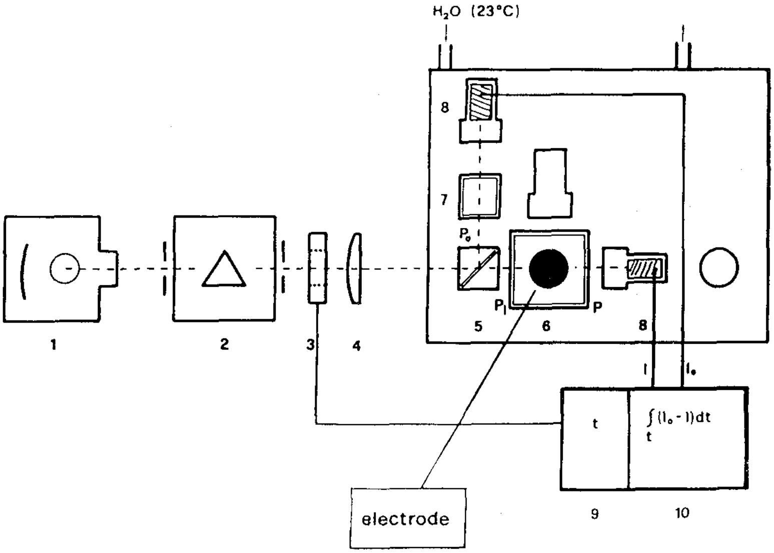


FIGURE 4 Experimental determination of quantum yields of photooxydation using an oxygen electrode and an integrating actinometer.

The ratio of the two parameters is by definition equal to the quantum yield of photooxydation Φ_{AO_2}.

RESULTS AND DISCUSSION

Applying this method of analysis to the determination of the sensitizing efficiency of humic materials, the results shown in Table I have been obtained.

For the first three samples, wavelength dependence of $\Phi_{^1O_2}$ has been investigated,[18] and the decrease of the efficiency of singlet oxygen production with increasing wavelength is similar to the trend reported by Zepp *et al.*[21] A possible explanation of these findings (Figure 5) is that because humic acids are complex polychromophoric molecules, they exhibit intramolecular energy transfer to excited states exhibiting higher transfer efficiency to oxygen.

Figure 6 shows the absorption spectra of the corresponding samples; multiplying the above data with the mass-based absorption coefficients the solar spectrum and the appropriate conversion

TABLE I

Summary of experimental conditions and results of $\Phi_{1_{O_2}}$ determinations ($\lambda = 366$ nm)

Humic materials	HUM ($mg\,l^{-1}$)	pH	$\Phi_{1_{O_2}} \times 10^3$	Ref.
Fluka Humic acid	100–200	8.0	4.9 ± 1.4	18
Black Lake (U.S.A.)	100	7.2	10 ± 4	18
Baldegger See (CH)	280	7.3	26	18
Bansee (F.R.G.)	144	7.0	15	19
Brunnensee (F.R.G.)	100	8.0	16	19
Zillhamer See (F.R.G.)	100	7.0	17	19
Suwannee River (U.S.A.)	130	7.0	10	20

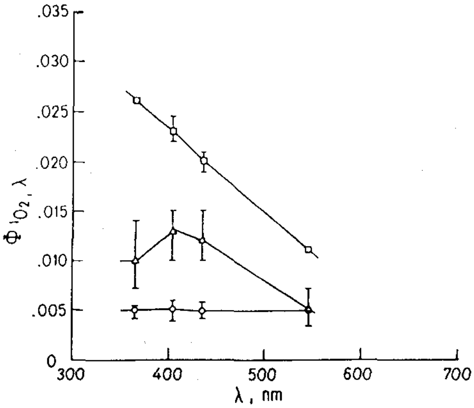


FIGURE 5 $\Phi_{1_{O_2},\lambda}$ for the first three samples (Table I) of humic materials.[18] □, Baldegger See concentrate; △, Black Lake humic acid; ○, Fluka humic acid.

factors yields the singlet oxygen production rates (15) as shown in Figure 7.

$$+\left(\frac{d[^1O_2]}{dt}\right)_{\lambda} = I_{a,\lambda} \times \Phi_{1_{O_2},\lambda}. \tag{15}$$

Figure 7 shows that isolated humic materials exhibit a maximum of singlet oxygen production at about 420 nm, whereas the total dissolved organic material of the Baldegger See has its peak effici-

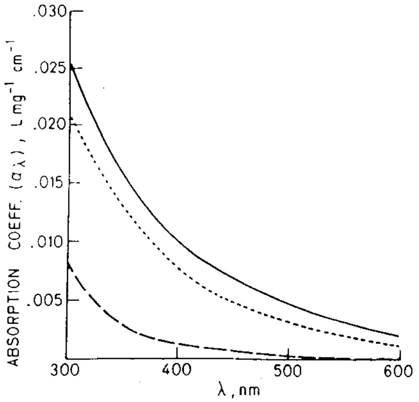


FIGURE 6 Absorption spectra of the samples discussed above.[18] ——, Black Lake humic acid; -----, Fluka humic acid; — —, Baldegger See concentrate.

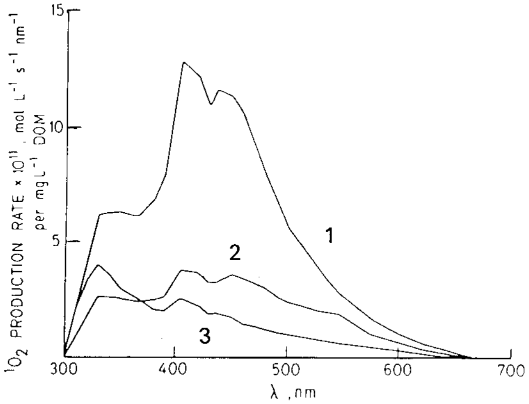


FIGURE 7 Singlet oxygen production rates for samples discussed above, in water, calculated for midday, summer, 40°N sunlight.[18] 1, Black Lake humic acid; 2, Fluka humic acid; 3, Baldegger See concentrate.

ency in the ultraviolet. Zepp *et al.*[22] suggest that humic acids are not representative of natural waters in their photosensitizing properties. Our results with fulvic acid concentrates (samples from the FRG) exhibiting a higher quantum yield of singlet oxygen production than the corresponding humic acid concentrates (Black Lake) confirm this hypothesis.

We are aware of the fact that the quantum yields determined by the method discussed can only comprise the singlet oxygen escaping the cage of macromolecular sensitizer and solvent. The quantification of singlet oxygen produced (7) and immediately trapped (8) or physically quenched (9) is a topic of our current investigations.

Laser photolysis of the Bansee concentrate shows light absorbing transients in a shorter (7×10^{-6} s) and in a longer (6×10^{-5} s) lifetime domain (Figure 8(a)).[19] Both transients are affected in their initial intensity by the presence of oxygen (Figure 8(b)). But whereas the rate of oxygen quenching of the short-lived transient is smaller than its decay in argon, and, hence, its decay is unaffected by the presence of oxygen up to 2.5×10^{-4} M; the longer living transient is completely quenched under those conditions (Figure 8(b)). This

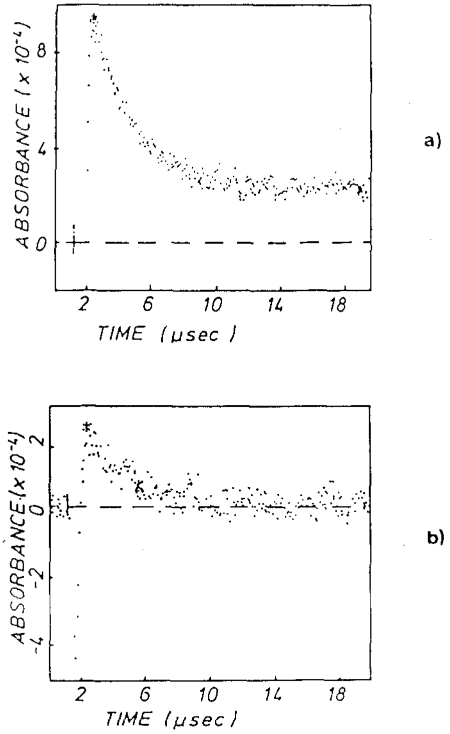


FIGURE 8 Transient adsorption kinetics under exclusion (a) and in the presence of oxygen (2.5×10^{-4} M) (b).

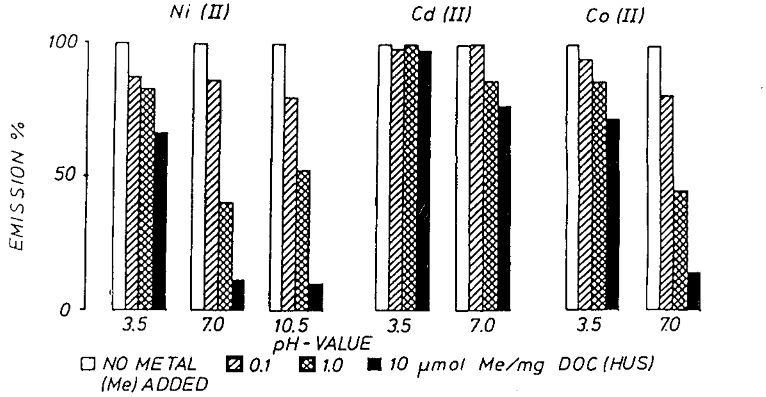


FIGURE 9 Quenching effect of Ni^{2+}, Co^{2+} and Cd^{2+} on a laser excited sample of Bansee, $\lambda_{exc} = 532$ nm, $\lambda_{em} = 700$ nm.

apparent differentiation of the two transients may be expected in view of their lifetime, the pseudo-first order quenching kinetics of the latter and assuming a rate constant close to that of the diffusion.

Finally, paramagnetic metal ions have been found to be good quenchers of transients of humic materials.[23] Our more quantitative investigations on the reaction of the excited Bansee sample with Ni^{2+}, Co^{2+} and Cd^{2+} revealed an interesting variation of the intensity of the emission of the humic materials in function of the ion, its concentration and the pH-value chosen (Figure 9). At pH 3.5 there is a significant quenching effect for Ni^{2+} and Co^{2+} but none for Cd^{2+}. The relatively high decrease of the emission in case of the paramagnetic ions at a concentration of 10^{-7} mol per mg HUM can be explained by the limited availability of metal complexing functional groups in HUM at low pH values. This hypothesis is supported by the non-linear Stern–Volmer analysis indicating static quenching caused by co-ordinative bonds between metal ion and HUM[24] (Figure 10).

An increase of the relative complexation for a total metal ion concentration of 10^{-6} and 10^{-5} mol per mg HUM, respectively, appears at pH 7 and is overcompensated at higher pH values by the competitive formation of hydroxo compounds as shown for Ni^{2+} at pH 10.5.

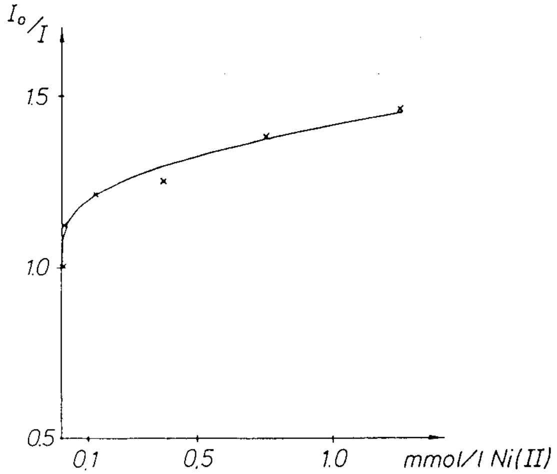


FIGURE 10 Stern–Volmer analysis of the quenching of the HUM emission Bansee sample at pH 3.5, emission quenching by Ni^{2+}. $\lambda_{exc} = 532\,nm$, $\lambda_{em} = 700\,nm$.

Fe^{2+} and Fe^{3+} ions which occur together in HUM in most fresh waters are currently under investigation using the same techniques.

Acknowledgements

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