

Photo-oxidation of sodium sulfide by sulfonated phthalocyanines in oxygen-saturated aqueous solutions containing detergents or latexes

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Abstract

The water-soluble zinc and aluminum complexes and the metal-free derivative of tetrasulfophthalocyanine were employed as sensitizers for the photo-oxidation of sodium sulfide under irradiation with visible light in oxygen-saturated aqueous alkaline solutions containing oppositely charged micelles or latex particles. With all photosensitizers the oxidation process was strongly enhanced upon irradiation, and sulfate was the final oxidation product. Autoxidation as well as singlet oxygen and hydrogen peroxide formed during the photoreaction contribute to the complex overall process. The initial step is dominated by energy transfer. In contrast, Co(II)-tetrasulfophthalocyanine exhibits catalytic activity in the dark, and no pronounced additional activity under irradiation, with the formation of thiosulfate as oxidation product. In this case an electron transfer mechanism occurs according to known results.

Detergents strongly increase the photoactivity of sensitizers with high aggregation tendency (e.g. Zn(II)-tetrasulfophthalocyanine) by stabilizing monomeric dispersions and accumulating oxygen and the substrate. Latexes increase the photoactivity and simultaneously the photodegradation of the sensitizer, caused by high local accumulation of the sensitizer and consequently also ¹O₂. Al(III)-tetrasulfophthalocyanine, exhibiting a low aggregation tendency in strongly alkaline solutions, shows high photoactivity and photostability even without detergent.

Keywords: Photo-oxidation; Sodium sulfide; Sulfonated phthalocyanines; Detergents; Latexes

1. Introduction

An increasing fraction of the chemical literature is currently dealing with reactions involving light [1–7]. The concern for the interactions of molecules with photons of visible light is stimulated by the requirement to obtain more detailed knowledge about light-harvesting processes like photosynthesis. Photosynthetic organisms provide paradigms for many of the most basic photochemical and photophysical processes, like antenna systems with translocation of the energy to the reaction center. Very important is the protection of the photosynthetic apparatus against light-generated singlet dioxygen causing damage by triplet–triplet processes. Therefore it is now important to investigate artificially colored compounds for energy conversion, not only with respect to their quantum efficiency but also with consideration of their photostability.

Synthetic compounds of porphyrin-analog structure such as 5,10,15,20-tetraaryl porphyrins, phthalocyanines and naphthalocyanines structurally related to chlorophyll have turned out to exhibit high performances for a variety of photochemical applications, e.g. for photodynamic cancer therapy [8–13] and different reaction systems [14]: photochemistry in solution and organized media [15–36], photoelectrochemical [37–40] and photovoltaic devices [41]. Photochemical oxidations with porphyrin analogs have been carried out on thiols, thioethers, tryptophan, tyrosine and cholesterol [18,22–25,33–35]. In photo-oxidation reactions using porphyrin-type compounds as photocatalysts, either electron transfer occurs (type I) or singlet dioxygen is formed by energy transfer (type II) after excitation which starts oxidation [42]. Additionally the formation of superoxide anion radicals by electron transfer to triplet oxygen is conceivable [26,42]. In the case of the phthalocyanines this process is only possible from the excited singlet state (not triplet or ground state) for thermodynamic reasons [26]. Usually it is

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necessary to add a detergent of opposite charge to the reaction solution to prevent aggregation of the sensitizer, since agglomerates of phthalocyanines are much less photoactive than the respective monomers owing to triplet–triplet annihilation of the excited dye [16,17].

Oxidation reactions under irradiation with visible light generally result in more highly oxidized products than reactions in the dark. Thiols, for example, are catalytically oxidized by cobalt(II)–phthalocyanine complexes to the corresponding disulfides in darkness [43–58] (Eq. (1)), whereas photo-oxidation leads to the corresponding sulfonic acids in the presence of zinc(II)–phthalocyanines [18,19] (Eq. (2)).

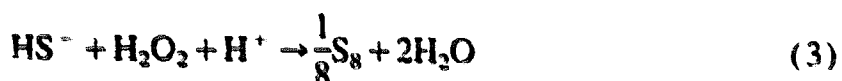


The catalytic oxidations (Eq. (1)) are technically important for the cleaning of gasoline fractions (MEROX process) [58–61].

Another interesting substrate for catalytic and photocatalytic oxidations is hydrogen sulfide. Employing this simple substrate, on the one hand the reaction can be considered as a model reaction using photons of visible light (solar photochemistry). On the other hand, the oxidation and photo-oxidation of hydrogen sulfide is of high technical importance for waste-water cleaning owing to the occurrence as by-product of certain industrial processes (kraft pulping, petroleum refining, tanning, coking, natural gas purification, food processing) and its high environmental and human toxicity [62].

The use of solar light for chemical syntheses or decomposition of toxic compounds is only rarely explored. After an early example — photooxygenation of α -terpinene to ascaradiol [63,64] — activities in the SOTA program (Solares Testzentrum Almeria = solar test center Almeria) concentrate, for example, on the sensitized photooxygenation of furfural by rose bengal and methylene blue [7,65] and photocatalytic water decontamination from halogenated hydrocarbons by TiO_2 as photoexcitable semiconductor [65,66].

The catalytic dark oxidation of sulfide in aqueous alkaline solution was studied employing transition-metal complexes of sulfonated phthalocyanines as catalysts [67–70]. Kotronarou and Hoffmann [69] proposed a mechanism in which an electron transfer from sulfide to oxygen is promoted by the cobalt complex. Elemental sulfur and hydrogen peroxide were postulated as products of the catalytic cycle. The latter is known to react with sulfide ions yielding elemental sulfur (Eq. (3)) and sulfate (Eq. (4)).

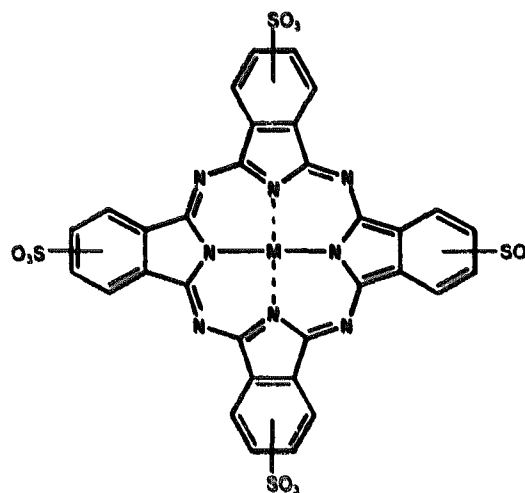


Elemental sulfur can be further oxidized to thiosulfate and sulfate if enough oxygen is present. Recently, Fischer [70] proposed a slightly changed mechanism with the polysulfides and hydrogen peroxide as intermediates of the cobalt(II)–

phthalocyanine-catalyzed reaction step, and further autoxidation to thiosulfate as main product and only small amounts of sulfate. This result is consistent with results from Kundo and Keier [67], who also found some sulfide remaining in the reaction solution at high pH.

Among the catalytic processes described, hydrogen sulfide ions are slowly oxidized in solutions in the presence of molecular oxygen [69–75]. The reaction is influenced by the pH value, the initial concentration of sulfide ions, the ionic strength and the presence of transition-metal ions [74]. Depending on the reaction conditions, elemental sulfur, thiosulfate, sulfite and sulfate are detected as products in different ratios. A free-radical mechanism is proposed involving polysulfides as intermediates [69,70,75].

The photo-oxidation of sodium sulfide was studied using cadmium sulfide as semiconductor [76]. An electron-transfer mechanism was proposed. Reaction products of sulfide were not identified. Recently, we reported first results on the photo-oxidation of 2-mercaptoethanol with water-soluble sulfonated phthalocyanines [18,19]. In this paper we describe the results on the photo-oxidation of sodium sulfide under different reaction conditions employing phthalocyanines 1–4 as photocatalysts. Up to now only some preliminary results have been published by us [20]. The stability of the photocatalysts is studied, and the mechanism of the photoreaction is discussed.



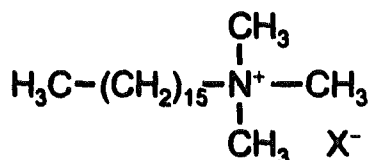
	M
1	Zn(II)
2	Al(III)OH
3	Co(II)
4	2 H

2. Experimental details

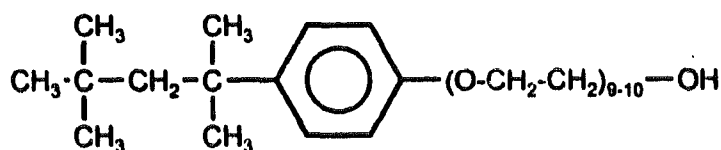
2.1. Chemicals

Commercially available solvents and reagents were of reagent grade (GR) and were employed as supplied. Double-

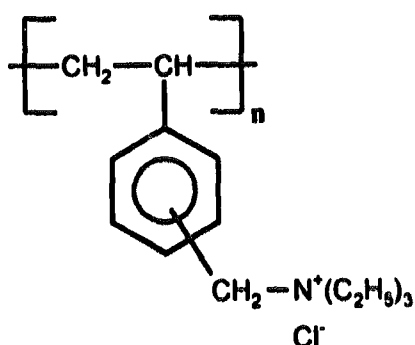
distilled water was used for the photo-oxidation experiments. The syntheses of the zinc(II), aluminum(III), cobalt(II) complexes and the metal-free derivative of 2,9,16,23-tetra-sulfophthalocyanine (1-4) were carried out as described elsewhere [18,77]. The compounds prepared were characterized by elemental analyses, IR and UV-Vis spectroscopy. The detergents cetyltrimethylammonium chloride (5) (CTAC, 25% solution in water), cetyltrimethylammonium bromide (6) (CTAB) and Triton X-100 (7) were purchased and used without further purification. Poly[(vinylbenzyl)-triethylammonium chloride] (8, PVBtAC) was synthesized according to a method of Paliuras [78] with poly-(vinylbenzyl chloride) and triethylamine as starting materials. 2,4-Ionene 9 and 2,10-ionene 10 were prepared as described by Brouwer et al. [49]. Syntheses and properties of the latexes 11 have already been published [79]. The notation of the samples in this paper corresponds to those in Ref. [79] according to the following list: L1N+ (Q5HE) 11a, L15N+ (Q25HE) 11b, L33N+ (Q50HE1) 11c, L54N+ (Q75HE1) 11d and L61N+ (Q75JL) 11e. The number indicates the mol percentage of N⁺ sites in the respective latex. Therefore the hydrophilicity of the samples increases with the number.



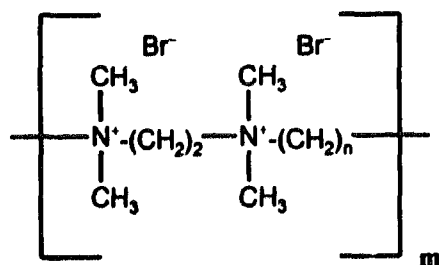
- 5: X = Cl (CTAC)
6: X = Br (CTAB)



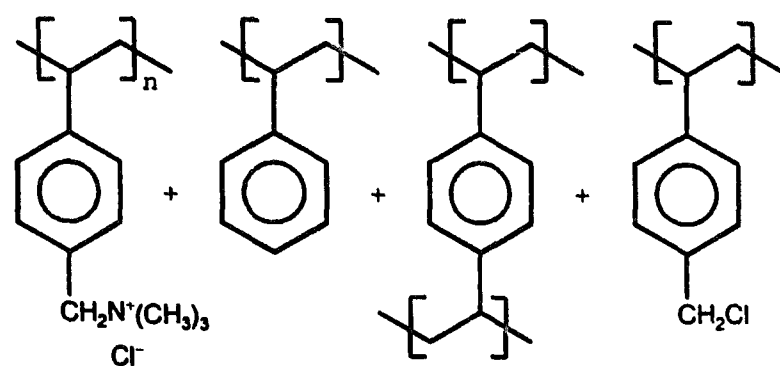
7



8 (PVBtAC)



- 9: n = 4
10: n = 10



- 11a: n = 1 mol %
11b: n = 15 mol %
11c: n = 33 mol %
11d: n = 54 mol %
11e: n = 61 mol %

2.2. Spectra

Infrared spectra were recorded on a Bio-Rad SPC-3200. UV-visible spectra were taken on a Perkin-Elmer Lambda 9 and a HP 8452A diode-array spectrophotometer, respectively. Elemental analyses were carried out by Beller Laboratories (Göttingen, Germany).

2.3. Photo-oxidation experiments

The photo-oxidation experiments under oxygen were carried out by measuring the oxygen consumption over time under stirring and illumination with visible light in equipment described by us [18]. For experiments at pH 9.0, commercially available borate buffers (Kraft, Germany) were used. At pH 7.8, pH 9.8 and pH 11.0 phosphate buffers were employed. Reaction solutions at higher pH value were prepared with NaOH in the corresponding concentration. Sodium sulfide was added as solution, whose concentration was determined as described in Section 2.4. The standard conditions were 0.5 μmol photocatalyst and 0.71 mmol sulfide in 50 ml oxygen-saturated reaction solution of pH 9 (0.1 M CTAC) in a flask at 25 °C and a light intensity of 150 mW cm⁻² (halogen lamp, 250 W). The photocatalytic activity was calculated from the initial slope of the oxygen consumption rate (mmol O₂ min⁻¹). The degradation of the photocatalyst was followed by measuring the UV-Vis absorption intensity at the beginning and after termination of the photo-oxidation.

The experiments for determining the action spectrum of 1 were carried out in the apparatus described under the same conditions, with the exception of the use of interference filters (Oriel, 580-700 nm, 20 nm stepwise, bandwidth at half-peak = 10 nm) which were placed into the light-beam path and constantly cooled by air. The light intensity was measured with a calibrated silicon PIN photodiode (BPX65). Using this value, the number of photons was evaluated for every wavelength. The photoactivity was calculated as mentioned before, normalized to the number of photons, and plotted vs. the wavelength of irradiation.

The quantum yield for the oxygen consumption was determined from the initial rate at 680 nm and calculated according

to $\Phi = d[\text{O}_2]/dt$ per I_{abs}/V (I_{abs} = absorbed photons, V = volume of the solution). The light intensity was 1.06×10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$ and the initial flux was 4.23×10^{-7} mol s^{-1} .

2.4. Determination of the sulfide concentration of the stock solution

Sodium sulfide was dissolved in distilled water and the concentration of the stock solution was determined by titration. A volume of 750 μl of this solution was diluted with deionized water, and 20 ml of a 0.1 M CuCl_2 were added under shaking. The CuS precipitate was separated from the solution by filtration. The amount of remaining Cu^{2+} was analyzed by titration with 0.1 M EDTA after adding some drops of murexide dye till the color had just changed from green to blue. Under standard conditions, 0.71 mmol sodium sulfide (about 375 μl) were employed for the photo-oxidation.

2.5. Photochemical methylviologen test

The photochemical methylviologen test was developed as a model system to simulate and detect photoinduced electron-transfer processes to oxygen. The experiments were carried out as described previously [18,21], dissolving 1.4×10^{-2} M sodium sulfide as donor, 7.5×10^{-4} M of methylviologen dichloride as acceptor, 1.0×10^{-5} M of **1** as sensitizer and 0.1 M CTAC in 3 ml solution.

2.6. Determination of hydrogen peroxide

The experiments were carried out according to a modified method of Egerton et al. [80] using titanil sulfate and determining the UV absorption at 408 nm of the $[\text{Ti}(\text{O}_2) \cdot \text{aq}]^{2+}$ complex formed.

2.7. Dynamic light-scattering experiments

The DLS experiments for determining the size of the latex particles and the polydispersity of the latex solutions were performed as described previously [79].

3. Results

Different sulfonated phthalocyanines were applied for the photo-oxidation of sulfide under different conditions. Some plots are shown in Fig. 1, and results are summarized in Table 1. The highest initial rate was found for **3** under standard conditions. However, the oxygen consumption stopped after a conversion corresponding to slightly more than a complete oxidation of the sulfide to thiosulfate (Eq. (5)). Thiosulfate was analytically found by HPLC.

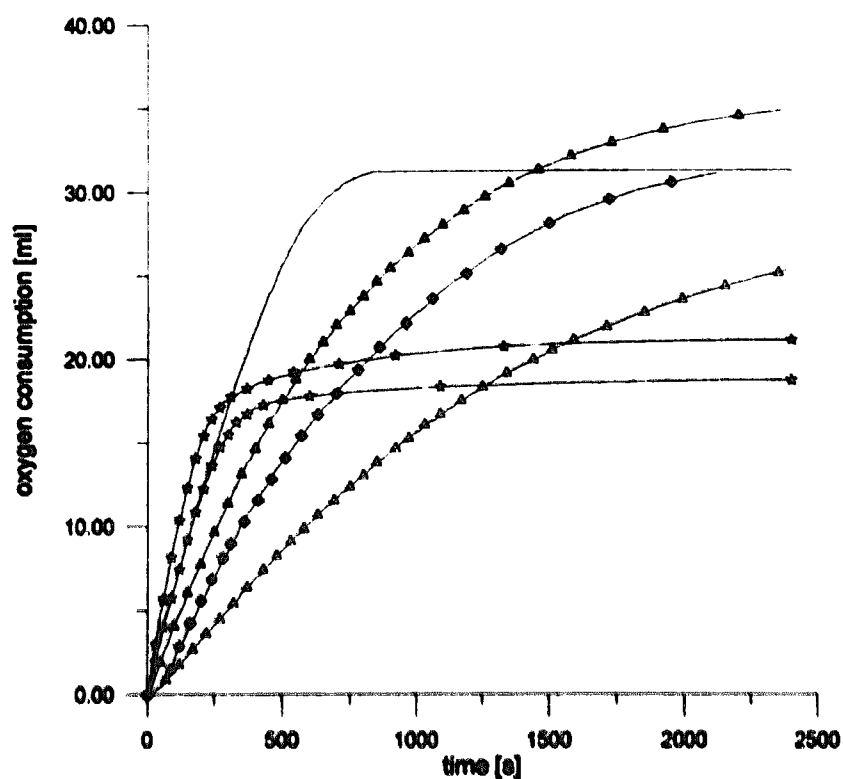
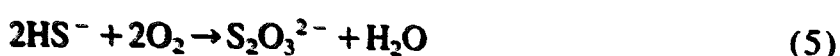
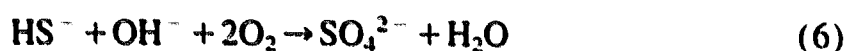


Fig. 1. Photo-oxidation of 0.71 mmol sodium sulfide using 0.5 μmol of different catalysts in solutions containing 0.1 M CTAC at pH 9: no symbol, **1**; \blacktriangle , **2** at pH 13; \blacktriangle , **2** at pH 13 without CTAC; \blacklozenge , **4**; \blackstar , **3**; \blackstar , **3** not irradiated.

In the case of **3**, the activity is not much reduced without irradiation, and the final oxygen consumption is comparable. The same initial reaction rates were obtained in nonmicellar solutions (results not shown). Only the oxygen consumption after 40 min was slightly reduced under these conditions in comparison to the experiments in the presence of 0.1 M CTAC. The degradation of **3** during the catalytic process in the dark was around 40%, increasing to around 90% under irradiation. These results indicate that the oxidation of sulfide in the presence of **3** is predominantly not light-driven.

Concerning final oxygen consumption along with photocatalytic activity, **1** exhibited the most interesting results in the presence of CTAC. Around 20% degradation occurred (Table 1, Fig. 1). In the dark, **1** was stable and the activity measured was due to autoxidation. **1** did not contribute to the oxidative process without irradiation. Using varying amounts of sulfide for the photoreaction under standard conditions, the oxygen consumption corresponded to a complete conversion of the substrate into sulfate in all cases according to the following stoichiometry (Eq. (6)):



Sulfate was also found analytically by IR after precipitation as BaSO_4 . In strongly alkaline solution, **2** is monomeric even in the absence of CTAC [34,81]. The stability of this complex under the photo-oxidation conditions in nonmicellar medium is noteworthy. However, the photocatalytic activity is less than that of **1** in the presence of CTAC. The catalyst **4** exhibited a slower initial reaction rate than **1** under otherwise identical conditions.

The degradation of **1** in the photocatalytic process under standard conditions was studied over time and compared with the oxygen consumption (Fig. 2(a)), revealing a higher ini-

Table 1

Photo- and dark oxidation of 0.71 mmol sodium sulfide using 0.5 μ mol of different catalysts in 50 ml reaction solution

Sample	pH	Detergent (0.1 M)	Total O ₂ consumption after 40 min ^a (mmol)	Initial reaction rate ^a (mmol O ₂ min ⁻¹)	Degradation of catalyst after 40 min ^a (%)
1	9	CTAC	1.30 ^b	0.191	18
1 ^c	9	CTAC	0.57	0.025	~0
1	9	–	0.26	0.008	^d
1	13	CTAC	1.38	0.310	17
1 ^e	9	CTAC	0.80	0.046	24
1 ^f	9	CTAC	0.63	0.091	17
1 ^g	9	CTAC	0.36	0.066	18
2	9	CTAC	1.28 ^b	0.138	54
2	13	CTAC	1.41	0.103	22
2	13	–	1.04	0.046	3
3	9	CTAC	0.86	0.249	87
3 ^c	9	CTAC	0.76	0.168	38
4	9	CTAC	1.30 ^b	0.086	33

^a Mean value of several measurements.^b Part of the sulfide was oxidized by triplet oxygen at pH 9 immediately after injection of the substrate before the apparatus could be closed. This amount could not be detected by the equipment used. Therefore the oxygen consumption measured is less than that expected for complete conversion into sulfate. At pH 13, where the autoxidation by triplet oxygen is drastically reduced, the oxygen consumption determined corresponds exactly to that calculated for complete conversion into sulfate.^c Measurements in the dark.^d Partially precipitated.^e In the presence of 0.01 M NaN₃.^f Using 0.36 mmol Na₂S₂O₃ instead of 0.71 mmol Na₂S as substrate.^g Using 0.71 mmol Na₂SO₃ instead of Na₂S as substrate.

tial decomposition rate followed by a lower constant one. After 40 min, 18% of **1** was destroyed during the photo-oxidation, whereas only 12% was degraded under irradiation of the solution in the absence of sodium sulfide. The situation in the presence of latex **11d** is shown in Fig. 2(b). In this case the degradation rate is much higher than in the presence of CTAC, yielding complete destruction of the sensitizer within less than 30 min.

Fig. 3 shows the dependence of the Q-band absorption of **1** on the CTAC concentration. The aggregation of the phthalocyanine decreases with increasing amount of CTAC. This is indicated by the red shift of the absorption maximum at higher wavelength (around 660–680 nm) and the enhancement of its intensity along with the blue shift of the absorption band at lower wavelength (around 610–630 nm) and the reduction of its intensity. The photo-oxidation of sulfide was affected by the concentration of CTAC. Lowering the concentration of CTAC led to a decrease in the photoactivity of **1**. Also the stability of the sensitizer was drastically reduced (Table 2). In the absence of CTAC, where most of the phthalocyanine is aggregated, only 20% of the oxygen consumption under standard conditions was determined after 40 min of photo-oxidation. In the case of 0.1 M CTAC, complete oxidation was already observed after 15 min.

Thiosulfate and sulfite are potential intermediates of the process examined. If these compounds were exposed to the photo-oxidation under standard conditions using **1** as sensitizer complete or almost complete oxidation to sulfate was observed according to the oxygen consumption measured

(Table 1). The initial rates are comparable with the reaction rate of the sulfide photo-oxidation taking into consideration the different stoichiometries. In the case of sulfide, two oxygen molecules per sulfur atom are needed for complete conversion. In the case of thiosulfate and sulfite, this value is one molecule and a half-molecule of oxygen, respectively. Therefore the expected oxygen consumptions are in a ratio of 1:0.5:0.33 (sulfide:thiosulfate:sulfite) when the same amounts of sulfur are applied for the photocatalytic process. The initial reaction rates determined are approximately in the same ratio, i.e. the kinetics are represented by equivalent reaction rates $\nu_i r$, where r is the reaction rate and ν_i is the stoichiometric coefficient of the consumed oxygen.

Using **1** as sensitizer, the photo-oxidation of sodium sulfide was studied under different conditions. Adding increasing amounts of NaCl to the solution, the photo-oxidation rate slightly decreased with the ionic strength at pH 12 (Table 3). The dark reaction and the photoreaction depend on the pH value, as seen in Table 3. The highest photoactivity was found at pH 12. In these experiments the ionic strength was not kept constant. At the same ionic strength, the initial reaction rate was slightly higher at pH 13 and much higher at pH 14 than at pH 12. The degradation of **1** during the photocatalytic process was not affected by the pH value. After 40 min of irradiation, about 18% of the sensitizer was destroyed.

The dependence of the initial photo-oxidation rate on the amount of photocatalyst **1** at pH 9 is depicted in Fig. 4. As expected, the course of the oxygen consumption without sensitizer under irradiation is the same as with or without sen-

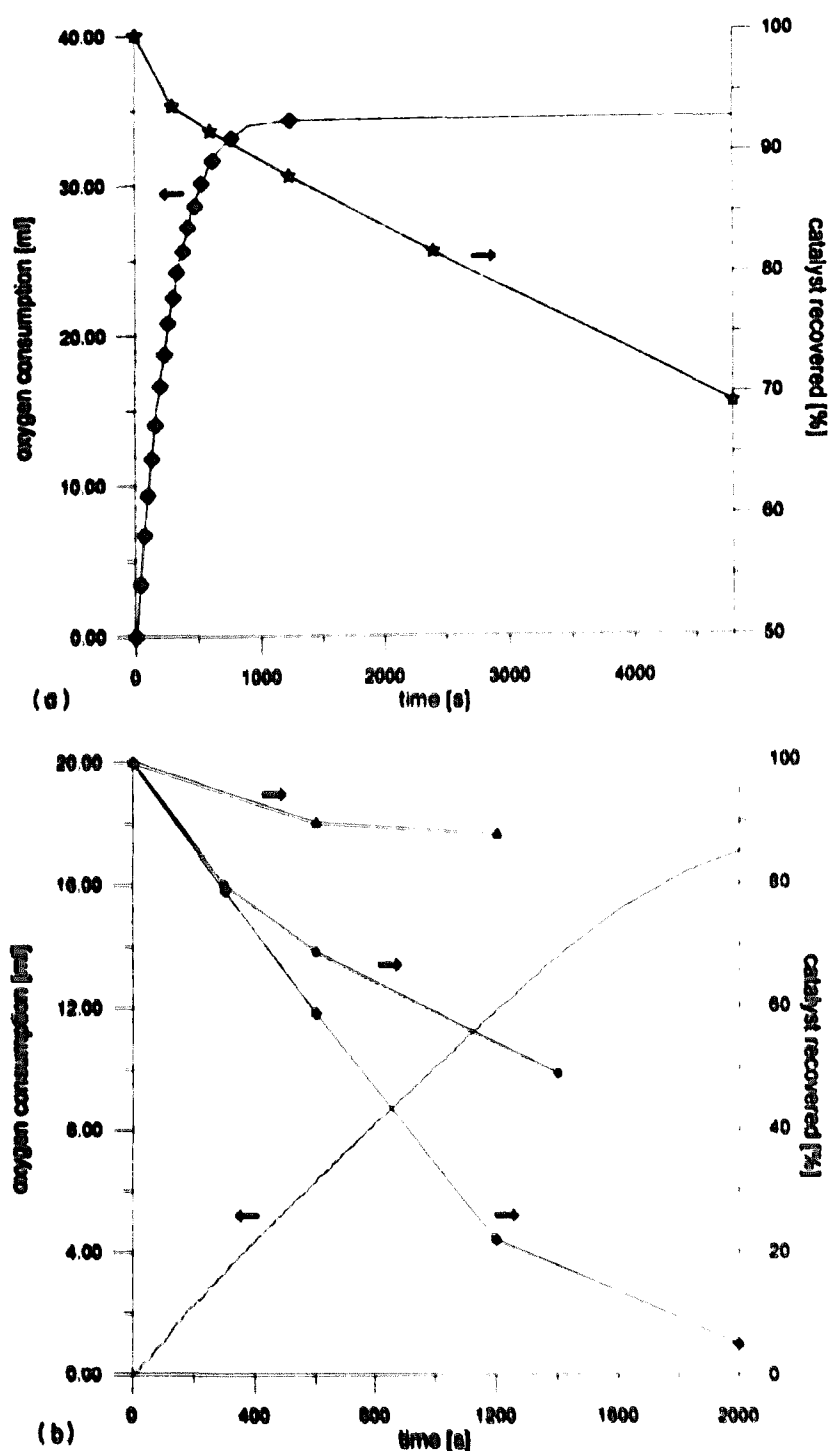


Fig. 2 (a) Degradation (*) of **1** under standard conditions with 0.1 M CTAC (pH 13 instead of pH 9) in comparison to the course of the oxygen consumption (\blacklozenge). (b) Degradation of **1** in a solution containing latex **11d** ($[N^+] = 10^{-4}$ M) in the presence of 14 mM sodium sulfide (\blacklozenge), 10 mM sodium azide (\blacktriangle) and without sodium sulfide or sodium azide (\bullet), respectively, in comparison to the course of the oxygen consumption (no symbol) at pH 12.

sensitizer in the dark. According to the oxygen consumption, after 40 min all sulfide ions were only oxidized to thiosulfate on average under these conditions, whereas under irradiation in the presence of **1** sulfate was obtained, as mentioned before. The degradation of the sensitizer in the photo-oxidation experiments was increased to 20% and 24% in the case of $5.2 \mu\text{M}$ ($0.26 \mu\text{mol}$) and $2 \mu\text{M}$ ($0.1 \mu\text{mol}$), respectively, whereas at the highest concentration examined ($20.4 \mu\text{M}$, $1.02 \mu\text{mol}$) only 16% was destroyed.

Beside CTAC, other detergents or detergent substitutes were applied for the photo-oxidation of sulfide with **1**: Triton X-100 **7**, poly[(vinylbenzyl)triethylammonium chloride] **8**, 2,4-ionene **9**, 2,10-ionene **10** and latexes of different properties **11a-11e**. The results are shown in Figs. 5 and 6.

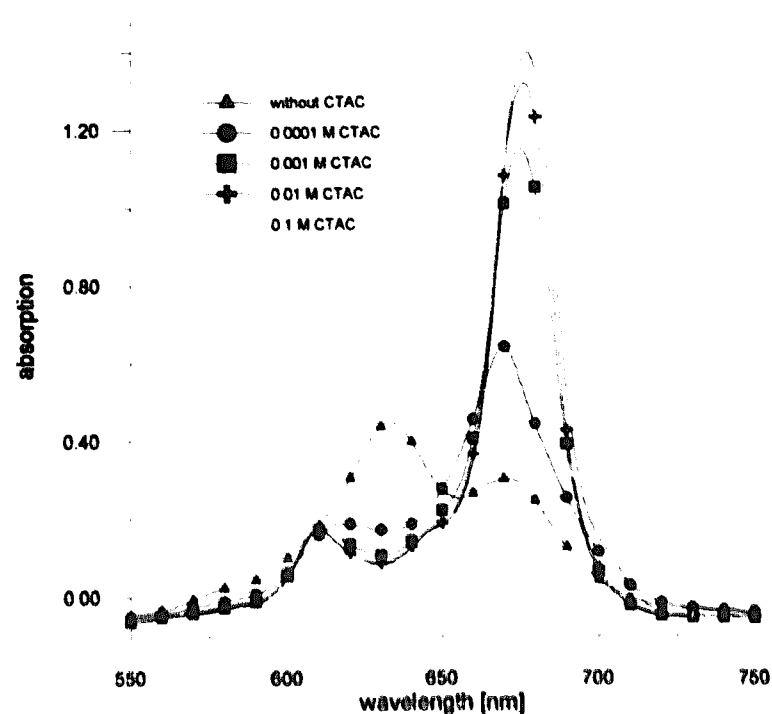


Fig. 3. Dependence of the UV-Vis spectrum of a $10 \mu\text{M}$ aqueous solution of **1** on the CTAC concentration.

Table 2
Dependence of the photooxidation of 0.71 mmol sodium sulfide on the concentration of CTAC using $0.5 \mu\text{mol}$ **1** in 50 ml reaction solution at pH 9

CTAC concentration (mol l^{-1})	Initial oxidation rate under irradiation ($\text{mmol O}_2 \text{ min}^{-1}$)	Degradation of 1 after 40 min of photooxidation (%)
0.0 ^a	0.008	^a
0.0001	0.030	78
0.001	0.110	78
0.01	0.168	47
0.5	0.177	—
0.1	0.191	18

^a Photocatalyst partly precipitated.

^b pH 12.

Although the sensitizer was predominantly monomeric in the cases of **7**, **8**, **10**, **11d** and **11e** as in the case of **5** and the other conditions were kept constant, the initial rate was drastically lower. The highest photoactivity and the highest stability of **1** during the photocatalytic process were found in the presence of 0.1 M CTAC. In the case of **5**, **7**, **8** and **10**, 82%, 52%, 44% and 61% of the originally applied catalyst **1** remained in the reaction solution after 40 min of photo-oxidation, respectively. For **9** as well as in the absence of detergent the accurate degradation cannot be determined by comparing the UV-Vis absorption of the Q band before and after the photocatalysis since the Lambert-Beer law is not valid for aggregated phthalocyanines. However, the intensity of the Q band was reduced to 24% in the case of **9**. In the absence of any detergent or detergent substitute, part of the catalyst precipitated at pH 9.

The aggregation of the photocatalyst was strongly affected by the kind of latex used (Fig. 7). The more hydrophilic the latex, the more monomeric looked the spectrum of **1** at a ratio of $N^+/Zn = 10$. However, the activity of the photocatalyst

Table 3
Effect of the pH value and the ionic strength on the photo- and dark oxidation of 0.71 mmol sodium sulfide using 0.5 μmol **1** in the presence of 0.1 M CTAC in 50 ml reaction solution

pH value	Initial oxidation rate ($\text{mmol O}_2 \text{ min}^{-1}$)	
	Under irradiation ^a	In the dark ^b
7.8 ^c	0.220(0.159)	0.061
9.0 ^c	0.191(0.166)	0.025
9.8 ^c	0.275(0.257)	0.018
11.0 ^c	0.283(0.269)	0.014
12.0	0.332(0.323)	0.009
12.0 ^d	0.325(0.317)	0.008
12.0 ^e	0.289(0.282)	0.007
12.0 ^f	0.235(0.231)	0.004
12.0 ^g	0.212(0.208)	0.004
13.0	0.310(0.304)	0.006
14.0	0.291(0.286)	0.005

^a In brackets: activity without dark oxidation.

^b **1** is not active in the dark. The observed oxygen consumption is due to uncatalyzed oxidation of sulfide in the micellar solution. In none of the dark oxidation experiments was the reaction completed within 40 min. The highest oxygen consumption measured in the dark corresponds to an oxidation to thiosulfate.

^c Buffered solutions.

^d In the presence of 0.01 M NaCl.

^e In the presence of 0.1 M NaCl.

^f In the presence of 0.3 M NaCl.

^g In the presence of 0.5 M NaCl.

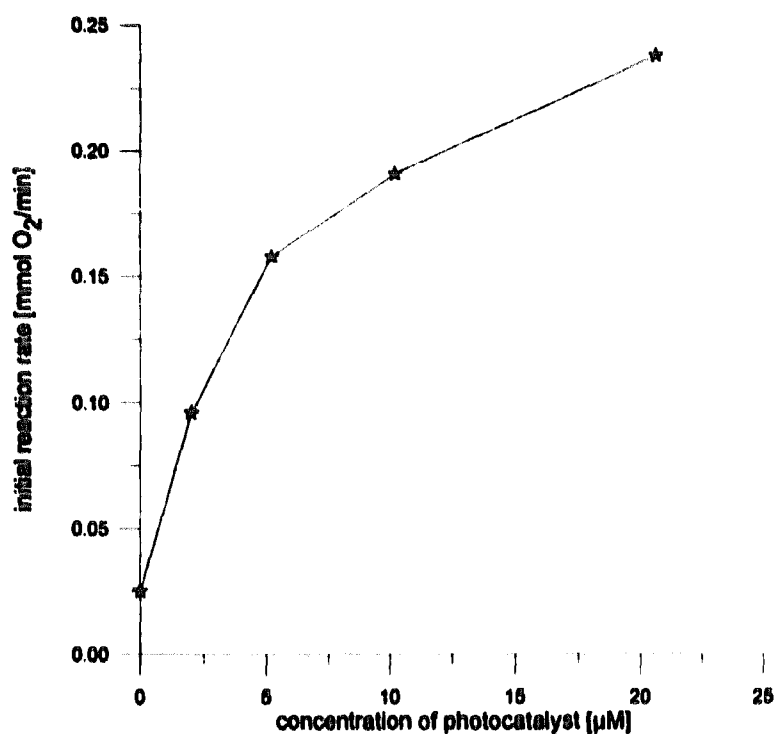


Fig. 4. Dependence of the initial photo-oxidation rate for 0.71 mmol sodium sulfide on the amount of **1** at pH 9 (0.1 M CTAC).

was not much influenced by the latex sample (Fig. 6). The sensitizer was completely degraded during the photo-oxidation in the presence of any latex particles.

The dynamic light-scattering experiments in water revealed the latex solutions to consist of monodispersed particles [79]. In 0.2 M borate buffer, coagulation of the particles was observed for **11e** according to the polydispersity measurements. The same effect on addition of salt had already

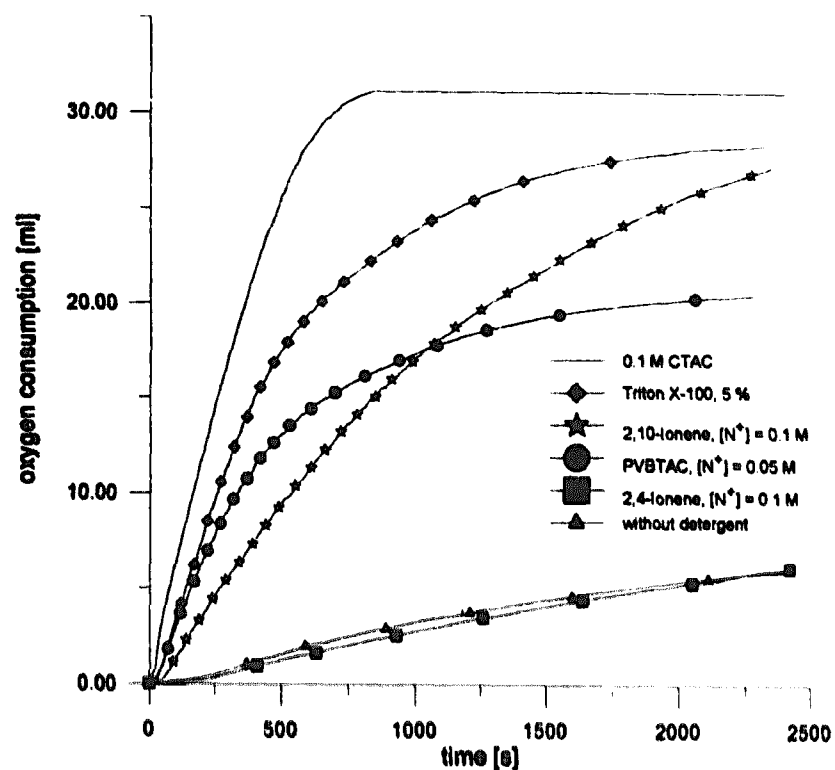


Fig. 5. Photo-oxidation of 0.71 mmol sodium sulfide using 0.5 μmol of **1** at pH 9 in the presence of different detergents or detergent substitutes.

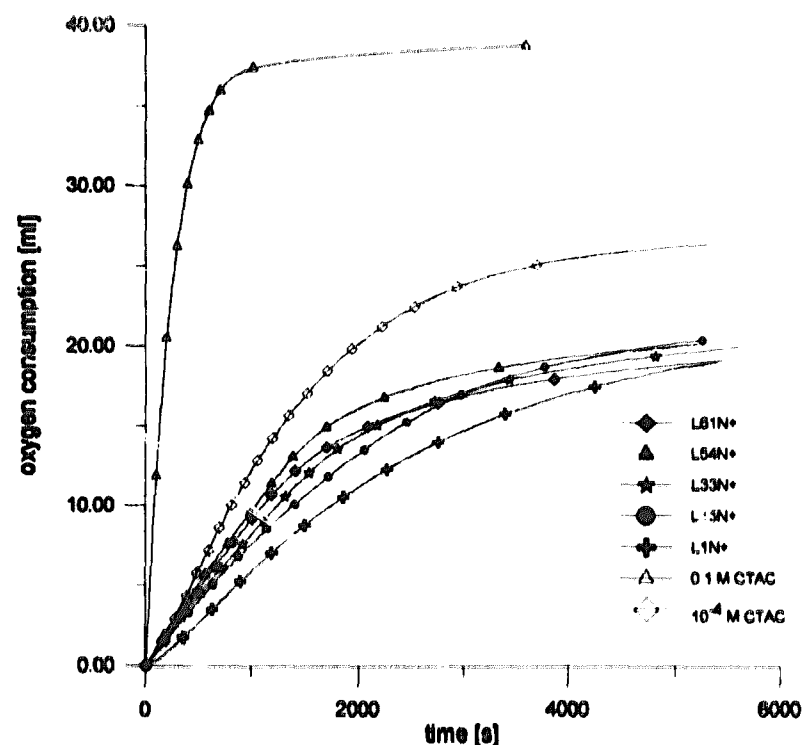


Fig. 6. Photo-oxidation of 0.71 mmol sodium sulfide using 0.5 μmol of **1** at pH 12 in the presence of different latexes ($[\text{N}^+] = 10^{-4} \text{ M}$, $\text{N}^+/\text{Zn} = 10$) in comparison to the photo-oxidation in the presence of 0.1 M CTAC ($\text{N}^+/\text{Zn} = 10^4$) and 10^{-4} M CTAC ($\text{N}^+/\text{Zn} = 10$), respectively.

been shown in previous experiments for L33N+ as well as for the more hydrophobic samples **11a** and **11b** [79]. In the case of **11d** and **11e**, the particles remained predominantly monodispersed in the buffer. Addition of **1** led to coagulation of the latexes L54N+ and L61N+ at a ratio of $\text{N}^+/\text{Zn} \geq 50$, indicated by the increased polydispersity.

The photo-oxidation rate was studied as a function of the N^+/Zn ratio with constant concentration of **1** (varying amount of latex) and with constant amount of latex (varying concentration of **1**) using **11d**. These reactions were carried out at pH 12 since the dark oxidation was strongly influenced by the amount of latex at pH 9. With constant amount of photocatalyst, the results indicated that the course of the

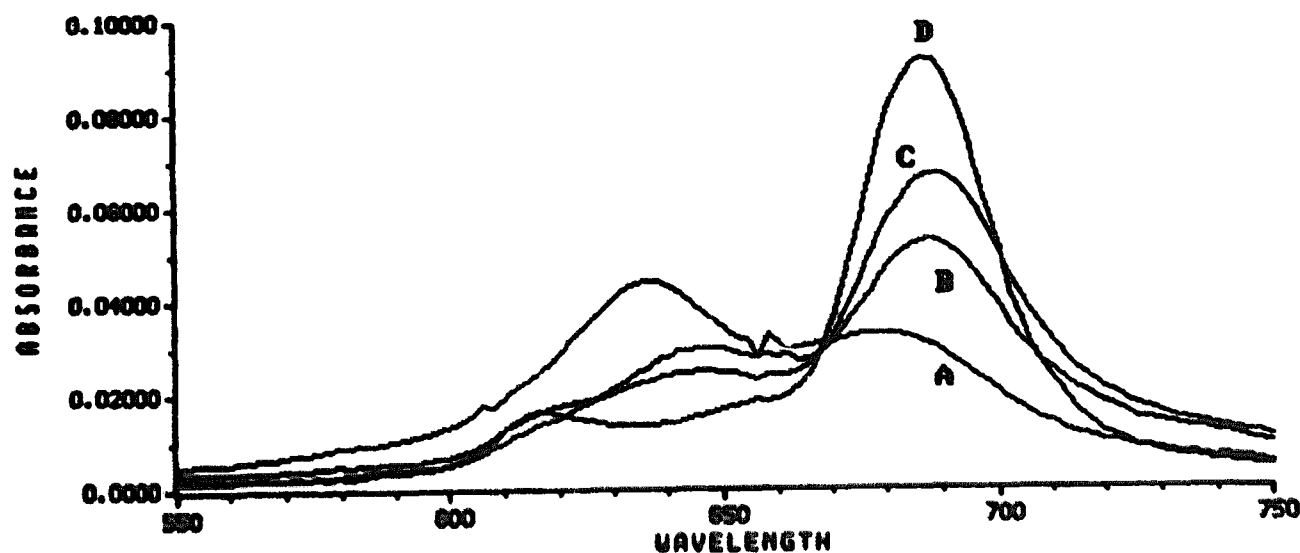


Fig. 7. Dependence of the UV-Vis spectrum of a 1 μ M aqueous solution of **1** on the latex used at $N^+/Zn = 10$: curve (A), latex LIN+; curve (B), latex L15N+; curve (C), latex L33N+; curve (D), latex 54N+.

photo-oxidation is largely independent of the N^+/Zn ratio at $N^+/Zn \geq 10$ (Fig. 8(a)). Below this value the reaction rate decreased, since the phthalocyanine became more and more aggregated. Using **1** at the same concentration without latex, some aggregated catalyst remained even after 90 min of irradiation in contrast to the experiments in the presence of **11d**. The initial reaction rate was slower than in the cases of $N^+/Zn \geq 10$. However, the oxygen consumption for long times without latex exceeded the oxygen consumption of each of the experiments with latex, owing to the lower degradation rate of **1** in the absence of latex.

Varying the catalyst concentration with a constant amount of latex, the results obtained are depicted in Fig. 8(b). At a higher concentration of **1**, higher conversion of sulfide was observed, according to the oxygen consumption measured. The initial reaction rate increased with the amount of sensitizer up to a concentration of 10^{-5} M ($N^+/Zn = 10$). At 2×10^{-5} M the photo-oxidation rate slightly decreased owing to a higher portion of aggregated phthalocyanine. This is confirmed by UV-Vis spectra of **1** as a function of the N^+/Zn ratio, which revealed an increasing aggregation tendency of the sensitizer with decreasing N^+/Zn ratio in solutions containing latex **11d**.

The addition of sodium chloride up to a concentration of 0.3 M did not affect much the course of the oxygen consumption, using **11d** at $N^+/Zn = 10$ and pH 12 (results not shown).

Hydrogen peroxide was found as by-product of the observed reaction for most of the photocatalysts studied. The course of development of detectable molecules H_2O_2 is depicted in Fig. 9 using **1** under standard conditions (pH 13 instead of pH 9). No hydrogen peroxide could be detected at the beginning of the photocatalytic process. As the oxygen consumption was almost terminated, more and more H_2O_2 was found. The detectable amount of peroxide did not significantly increase after completion of the oxidative process. The result leads to the conclusion that H_2O_2 reacts fast with sulfide or its first-formed oxidation products under these con-

ditions. In no experiment with latex particles could hydrogen peroxide be detected.

In order to get insight as to whether singlet oxygen is involved in the photooxidative process or not, different experiments were carried out. When D_2O instead of H_2O was used as solvent for the photo-oxidation of sulfide with **1** in the presence of 0.05 M CTAB **6**, the initial rate slightly increased. Adding sodium azide to the reaction solution under standard conditions decreased the photoactivity (Table 1). With 0.1 M NaN_3 , the activity was almost reduced to the activity in the dark. This phenomenon is not due to the increasing ionic strength, since $NaCl$ did not show the same effect (Table 3). When 0.01 M sodium azide was added, a reduced photo-oxidation rate was also found for **2** and **4** in the presence of detergent as well as for **1** in the presence of latex **11d**. **3**, which is not active as photocatalyst (see above) did not exhibit a significantly lower photoactivity in the presence of 0.01 M NaN_3 .

A photochemical system consisting of 2-mercaptoethanol as donor, zinc phthalocyanine as photocatalyst and methylviologen dication (MV^{2+}) as acceptor was developed as model system for photo-induced electron-transfer processes under oxygen-free conditions [2,18,21,82]. The redox potential of MV^{2+} $E^0(MV^{2+}/MV^{\cdot+}) = -0.45$ V(NHE) [83] is located near the reduction potential of dioxygen ($E^0(O_2/O_2^{\cdot-}) = -0.33$ V(NHE) [84,85]). Therefore the generation of $MV^{\cdot+}$ radicals which can be followed spectroscopically ($\lambda_{max} = 395$ nm, 605 nm) is a hint that electron transfer to oxygen is possible upon irradiation of the photocatalyst. In a system using sodium sulfide as donor and **1** as photocatalyst under standard conditions, a small quantity of $MV^{\cdot+}$ radicals with an initial rate $d[MV^{\cdot+}]/dt = 3 \times 10^{-7}$ M min^{-1} was determined. In contrast, the initial rate $-d[O_2]/dt$ is around $(1-2) \times 10^{-4}$ M min^{-1} (Table 1). In accordance with the above-mentioned results it can be concluded that energy transfer from the excited photosensitizer is the primary step of the process.

In Fig. 10 the photoaction spectrum of **1** in the presence of 0.1 M CTAC based on normalized initial reaction rates is

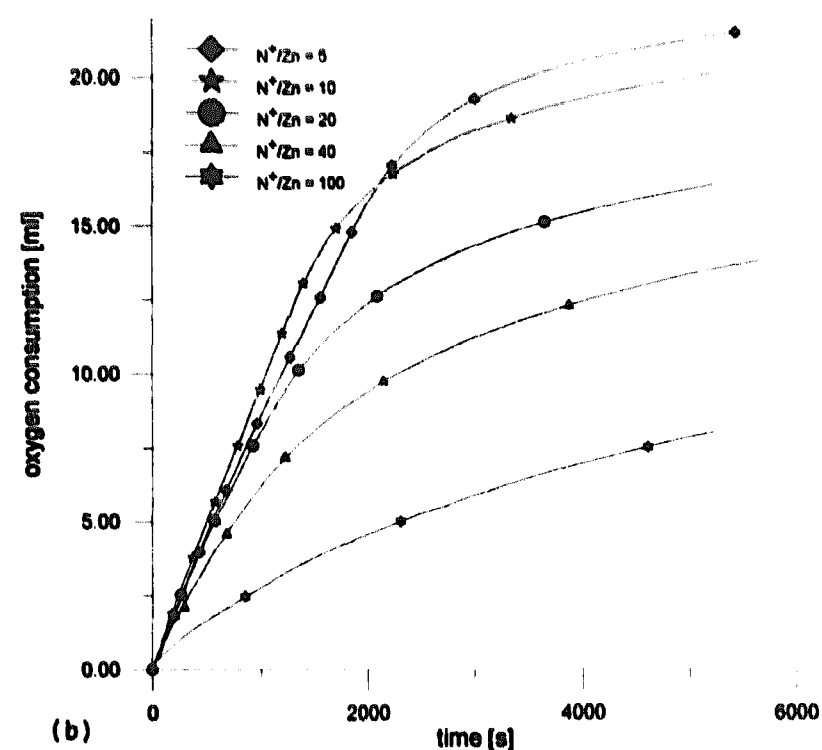
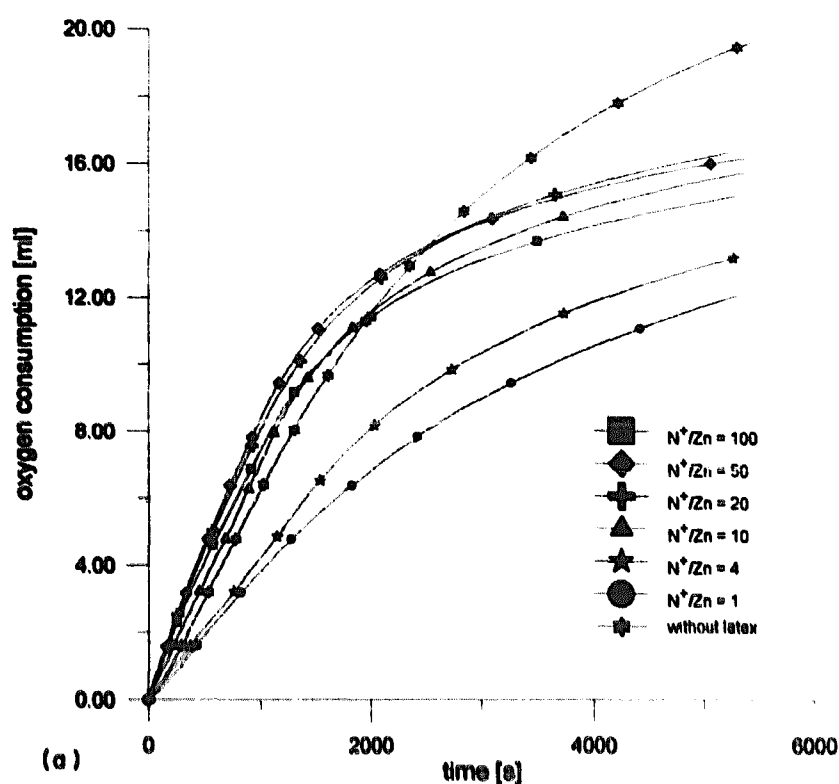


Fig. 8. (a) Photo-oxidation of 0.71 mmol sodium sulfide using latex 11d ($[N^+] = 10^{-4}$ M) with varying concentrations of 1 and pH 12. (b) Photo-oxidation of 0.71 mmol sodium sulfide using 0.25 μ mol of 1 with varying amounts of latex 11d and pH 12.

compared with the absorption spectrum. The highest activity was found in the Q-band transition. The quantum efficiency was calculated from the initial reaction rate of oxygen consumption over time vs. the absorbed photon flux at 680 nm. A high quantum yield of about 0.4 was found at pH 13 (otherwise standard conditions).

4. Discussion

In the system studied, the cationic micelles take over several functions. The negatively charged photocatalysts are monomerized and their precipitation in solutions of high ionic strength is avoided. Monomerization is a prerequisite for the

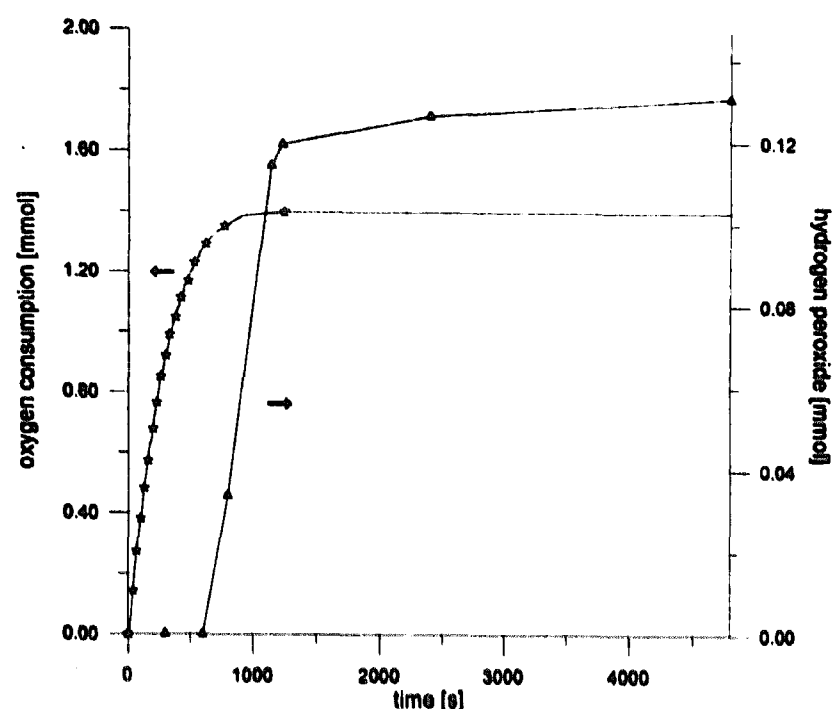


Fig. 9. Course of the development of detectable amounts of hydrogen peroxide (Δ) in comparison to the oxygen consumption over time ($*$) for the photo-oxidation of 0.71 mmol sodium sulfide using 1 under standard conditions (pH 13 instead of pH 9).

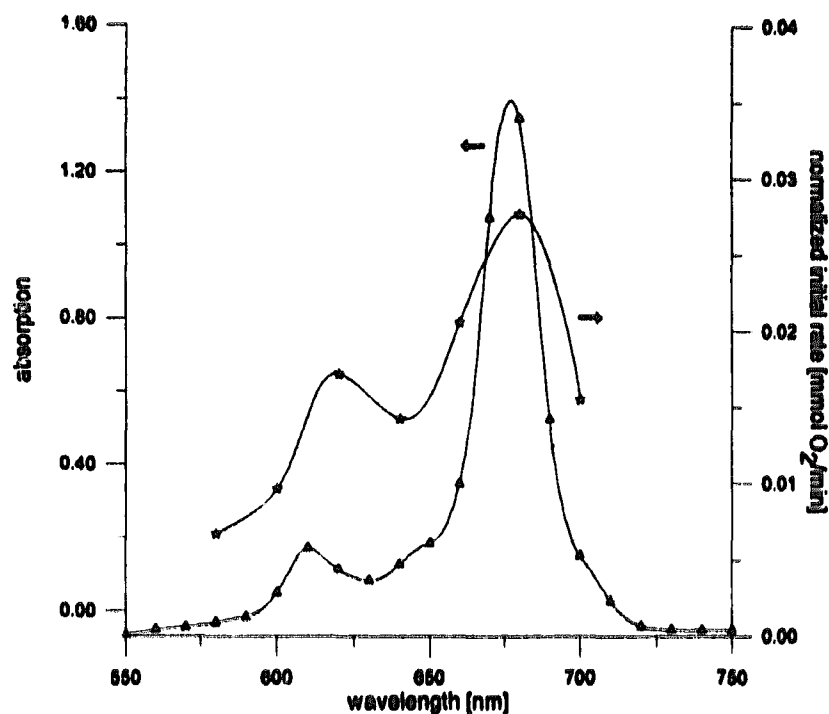


Fig. 10. Photoaction spectrum ($*$) for the photo-oxidation of 0.71 mmol sodium sulfide using 1 at pH 13 (otherwise standard conditions) in comparison to the absorption spectrum of 1 (Δ).

photoactivity of all sensitizers studied. Owing to attractive ionic interactions of the positively charged micellar surface with the anionic substrate, the local concentration of sulfide close to the sensitizer is increased, yielding higher reaction rates for the photo-oxidation. This phenomenon is revealed by the reduced photoactivity in the presence of high amounts of added sodium chloride (Table 3). The substrate and the chloride anion compete for binding sites at the micelle surface. Furthermore the solubility of oxygen is known to be enhanced in micelles supporting the photocatalytic process. For aqueous solutions of CTAB and SDS, an increase of the oxygen solubility by factors of 4 and 2.8, respectively, are reported in comparison to detergent-free solutions [86]. At a CTAC concentration of 0.1 M, about 2.4×10^{19} micelles

were present in 50 ml of reaction solution, taking a mean aggregation number of 124 [87] and neglecting effects of added electrolytes and bound photocatalyst. Provided that all sensitizer molecules were bound to micelles, every eightieth micelle contained one phthalocyanine molecule on average. Therefore the photocatalyst was highly distributed under standard conditions. Lowering the surfactant concentration led to an increase in the number of micelles containing more than one phthalocyanine, and to aggregation of phthalocyanines (Fig. 3). (The critical micelle concentration (CMC) for CTAC in water is $CMC_{CTAC} = 1.28 \times 10^{-3}$ M [88], but is known to be decreased by added electrolyte.) As a consequence, the photo-oxidation rate and the stability of the catalyst during the photocatalysis decreased (Table 2).

2 is predominantly monomeric even without CTAC. Therefore this catalyst can be used for photo-oxidation experiments in nonmicellar solutions. However, its photoactivity was lower in comparison to the measurement in the presence of surfactant, owing to the lack of substrate accumulation. The stability of **2** was drastically reduced if CTAC was present in the reaction solution. Even storing the solution in the dark, the catalyst underwent degradation (about 25% within 4 h and 30 min). This phenomenon has not been understood so far. The solutions of all the other photocatalysts studied were stable upon storing in the dark for several hours.

The photo-oxidation as well as the autoxidation in the dark were affected by the pH (Table 3). At the same ionic strength, the photo-oxidation rate increased with the pH. This indicates that the hydrogen sulfide ion (HS^- , $pK_a^1 = 7$ [62]) is less reactive than the sulfide ion (S^{2-} , $pK_a^2 = 13-14$ [62]) under the conditions applied. The presence of CTAC enhanced the autoxidative process owing to accumulation of the sulfide anions at the micelle/water interface and the increased oxygen solubility. Immediately after addition of the substrate, polysulfides ($\lambda_{max} = 290$ nm) occurred in the reaction solution under standard conditions, indicated by a color change. This phenomenon could not be observed at high pH and in the absence of surfactant. The reaction rate for the uncatalyzed oxidation was reduced.

The dependence of photoactivity of **1** on the sensitizer concentration was not linear (Fig. 4). Instead the slope of the graph decreased with increasing catalyst concentration. This phenomenon was not due to hindered mass transport of dioxygen or substrate, but due to the power of the light source. The penetration depth of the photons emitted with a wavelength around 680 nm was not sufficient. Because of the high absorption coefficient of the phthalocyanine, the photons were completely absorbed before passing through all of the reaction vessel at high concentrations of **1**. As a consequence, relatively lower reaction rates were observed with increasing concentrations of **1**, since an increasing number of the sensitizer molecules were not excited and could not contribute to the photooxidative process. For that reason the initial conversion ($mmol O_2 \text{ min}^{-1}$) and not the turnover frequency ($mol O_2 \text{ mol photocatalyst per minute}$) was used as measure for the photoactivity.

The destruction of **1** was 18% after 40 min of photooxidation in the presence of sulfide and 0.1 M CTAC (Fig. 2(a)). When the reaction solution was irradiated without substrate under otherwise identical conditions, only 12% were degraded. The sensitizer had been expected to be less stable under the conditions of the photo-oxidation without sulfide, since the fraction of the singlet oxygen which is quenched by the substrate cannot contribute to the decomposition of the photocatalyst. The result indicates that radical intermediates of the photooxidative process could be responsible for the destruction of **1** in addition to singlet oxygen [89].

The situation in latex is determined by the high local concentration of **1** within the particles and an assumed low binding of sulfide ions to the N^+ sites of the particles. The assumption is based on the fact that the photo-oxidation experiments were almost independent of the ionic strength (as determined with different concentrations of NaCl). The phthalocyanine molecules were completely bound to the latex particles at a ratio $N^+/Zn = 10$ except for sample **11a**. Only in this case was the UV-Vis absorption spectrum of a phthalocyanine observed in the ultrafiltrate (0.1 μm filter) after separation of the latex, whereas in all other cases the ultrafiltrate was colorless. This behavior is comprehensible, since most of the N^+ sites of **11a** must be at the surface to stabilize the charged colloidal particles. Therefore the sensitizer could be bound only to the surface but not to the core of the **11a** particles. Since the total area of the phthalocyanine molecules exceeded that of the $L1N^+$ particles by a factor of three, the photocatalyst could not be bound completely to latex **11a**. In contrast, the phthalocyanines bind completely to the other latexes, which have large fractions of internal as well as surface N^+ sites.

In comparison to the experiments with CTAC, the degradation of **1** was much faster in the presence of latex (Fig. 2(b)). This phenomenon is based on the fact that the local catalyst concentration is much higher in the latex particles than in the micelles. Under the experimental conditions, the total volume of **11d** in which all of the phthalocyanine was bound was estimated to be 4 μl in 50 ml of the reaction mixture. About 9×10^5 phthalocyanine molecules were present in each of the latex particles, and the local concentration of **1** within the polymer colloids was 0.125 M, in comparison to 10^{-5} M considering the whole reaction solution and to 0.19 mM in the micellar phase of 0.1 M CTAC (see above).

Once singlet oxygen was generated upon irradiation of the sensitizer, 1O_2 could readily react with a phthalocyanine in latex because of the short mean distance between the sensitizer molecules. As a consequence, the degradation rate was fast. The slower degradation with NaN_3 present also indicates that the decomposition reaction is due to singlet oxygen. When the photo-oxidation was carried out in a solution containing 10^{-4} M CTAC ($N^+/Zn = 10$, as in the case of the latex experiments), the activity was drastically reduced (Fig. 6, Table 2) and was comparable with that in latex solutions. However, the photo-oxidation rate in the presence of CTAC was still slightly higher than in case of the latex sample, and

degradation of **1** did not go to completion within 40 min. On the other hand, photo-oxidation reactions with latex under conditions comparable with the standard conditions of the CTAC experiments ($N^+/Zn = 10^4$) could not be carried out because too little light would penetrate into such a highly concentrated latex dispersion.

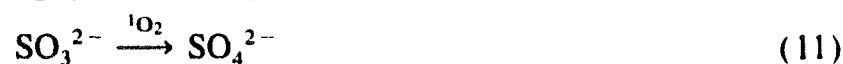
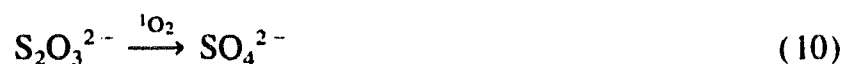
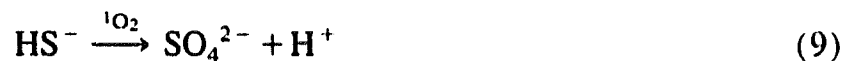
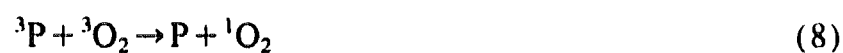
Although the exact mechanism of the sulfide photo-oxidation has not been elucidated so far, and the photophysical studies are still in progress, some important statements can be made. If thiosulfate or sulfite are intermediates of the process, these compounds are oxidized to sulfate (see Section 3). The phenomena observed in the presence of sodium azide and in D_2O instead of H_2O as solvent indicate that 1O_2 is involved in the photocatalytic process [86,90–93] except for **3**. This conclusion is supported by the facts that sodium azide is reported not to affect the triplet lifetime of **1** under nitrogen [31], that NaN_3 as well as oxygen did not change the fluorescence intensity of **1** under the experimental conditions, and that comparably reduced photoactivity was not observed in the presence of sodium chloride as in the presence of NaN_3 . In the case of **3**, which exhibits no photocatalytic effect, an electron-transfer mechanism takes place in which the $Co(II)$ is reduced to $Co(I)$ after coordination of the substrate, indicated by an additional absorption around 480 nm [67]. In contrast to the Co complex, no favorable coordination of the sulfide and change of the oxidation state of Zn and Al chelates is possible. Therefore these compounds are not active in the dark.

The kind of metal ion in the center of the phthalocyanine influences the photophysical properties of the compound. Closed-shell metallophthalocyanines exhibit long triplet lifetimes τ_T and high quantum yields of the triplet state Φ_T (e.g. **1** ($M = Zn^{2+}$), $\tau_T^{300K} = 245 \mu s$, $\Phi_T = 0.56$; **2** ($M = Al^{3+}$) $\tau_T^{300K} = 500 \mu s$ [16]). On the other hand, the triplet lifetimes of complexes with paramagnetic transition-metal ions are much shorter (e.g. **3** ($M = Cu^{2+}$ instead of Co^{2+}), $\tau_T^{300K} = 0.06 \mu s$, $\Phi_T = 0.92$ [16]). This behavior is also reflected by the singlet oxygen quantum yields ϕ_Δ . For $M = Zn^{2+}$ (**1**), Al^{3+} (**2**), $2H^+$ (**4**), Cu^{2+} and Co^{2+} (**3**) values of $\phi_\Delta = 0.45$, 0.34 , 0.14 , 0 and 0 , respectively, are reported [94]. Aggregated phthalocyanines exhibit much lower singlet oxygen quantum yields [23,30].

In comparison to the formation of singlet oxygen (energy transfer), the production of superoxide radical anions $O_2^{\bullet-}$ by electron transfer from the excited sulfophthalocyanine to oxygen is reported to be two orders of magnitude less [23,26]. This result is confirmed by the photochemical methylviologen test exhibiting only a slow rate for the formation of methylviologen cation radicals [18,21], even though the experiment has only a qualitative value since the interaction between the sensitizer accumulated at the positively charged CTAC micelle and MV^{2+} may be weak. The electron transfer to triplet oxygen is only possible from the excited singlet state [26]. Charge-recombination processes between $O_2^{\bullet-}$ and the positively charged phthalocyanine radical were suggested to take place readily [26].

It is well known that, in general, high oxygen concentrations favor the type-II photo-oxidation (energy transfer to triplet oxygen) and high substrate concentrations favor type-I reactions (electron transfer to the substrate). The experiments described in this paper were carried out in solutions saturated with oxygen. A solubility of oxygen in water $[O_2] = 1.28 \text{ mM}$ is reported (calculated from Ref. [95]). In surfactant solutions the oxygen solubility is increased. The total sulfide concentration in the reaction solution was 14 mM under standard conditions. However, its distribution is non-uniform owing to accumulation at the positively charged micelles. Therefore the local sulfide concentration at the micelle surface is much higher than the oxygen concentration. In this point of view the type-I photo-oxidation should be favored. However, experiments at pH 13 (otherwise standard conditions) revealed that triplet state **1** is very efficiently quenched by oxygen [18]. Under inert gas a triplet lifetime of $100 \mu s$ was determined, whereas in air the lifetime decreases to $3.4 \mu s$. On the other hand, the triplet lifetime of the sensitizer was not affected much when 14 mM 2-mercaptoethanol was present in the solution ($94 \mu s$). A similar result is expected for sulfide, and detailed photophysical investigations are now in progress.

The fundamental processes occurring in the photo-oxidation of sulfide, thiosulfate and sulfite are summarized in Eqs. (7)–(11) ($P = \text{phthalocyanine}$):



The course of the reaction between sulfide and singlet oxygen could not be elucidated within the framework of these investigations. Jensen [96] proposed that thiadioxirane or peroxy sulfoxide occur as intermediates, according to a theoretical study. The latter one might be slightly favored in solution. We suppose that the singlet oxygen generated upon irradiation of the sensitizer reacts with hydrosulfide ions to give sulfide radicals and superoxide (Eq. (12)). The oxidizing power of superoxide leads to the formation of peroxide (Eq. (13)). Sulfide radicals are oxidized in an unknown way via several intermediates (Eq. (14)). Electron-transfer processes upon irradiation contribute insignificantly to the reaction studied, according to the results of the photochemical methylviologen test. Among these photocatalytic processes, autoxidation by ground-state triplet oxygen and oxidation by hydrogen peroxide (Eqs. (3) and (4)) generated during the irradiation have to be considered. Therefore the mechanism is very complex, and the exact kinetics are very difficult to describe, especially in the presence of detergent where different local concentrations have to be taken into consideration.



5. Conclusions

The study reveals that a high photogenerated oxidation activity is not necessarily correlated to a high rate of photodegradation of the sensitizer, although both reactions are favored by singlet oxygen as intermediate reactant. The ratio of photoreactivity and photodegradation depends sensitively on the distribution of sensitizers, oxidants and substrates in the reaction space. This distribution is mediated by the detergent micelles or the latex dispersity, resulting in different accumulation ratios for the reactants and the sensitizer. The supramolecular chemistry, influencing this non-uniform distribution of the reaction partners in the reactor space, enables a control of optimum reaction conditions, e.g. maximum reactivity and minimum degradation.

Acknowledgements

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