

Photooxidation of sulfide, thiol, phenols, and cyclopentadiene by artificial light and solar light irradiation

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ABSTRACT. The photooxidations of the toxic products sulfide, 2-mercaptoethanol and phenols under partial mineralisation in aqueous alkaline solution and the photooxidation of cyclopentadiene in ethanol in order to produce fine chemicals is described. Because the employed photosensitizers such as metal phthalocyanines, a tetraphenylporphyrine, rose bengal or methylene blue absorb in the visible region of light, an inexpensive slide projector was used under laboratory conditions.

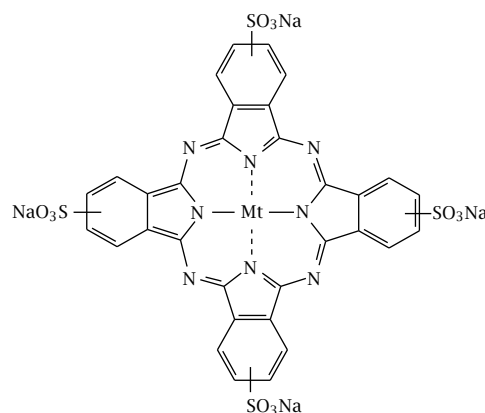
Experiments under solar radiation were carried out by concentrating the solar light with a reflective satellite bowl. The oxygen consumption over time is measured with a gas burette. The formation of singlet oxygen by energy transfer from the excited photosensitizer followed by oxidation of the substrates is responsible for the photoinduced oxidations. The applicability of the experimental conditions described here for other visible and solar light driven oxidation reactions is obvious.

1. INTRODUCTION

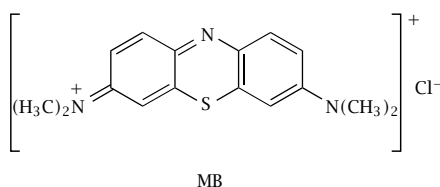
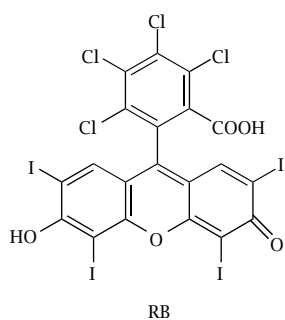
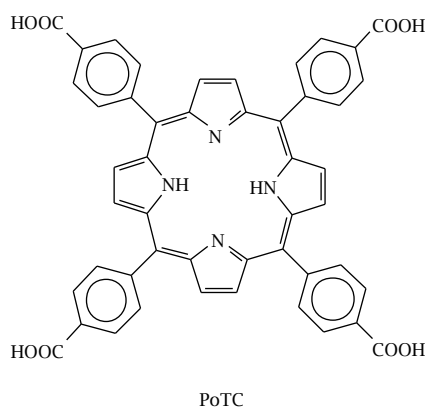
A well-known example for the cleaning of wastewater is the photocatalytic destruction of halogenated hydrocarbons and other hydrocarbons from water *via* exposure to solar radiation using TiO₂ as photoexcitable semiconductor [1-4]. But due to the band gap of the colorless TiO₂ (3.2 eV, \leq 387 nm), this process works in the UV region where only approximately 3% of solar radiation is effective. In order to overcome this disadvantage, photosensitizers absorbing in the visible region of light (\sim 49% solar radiation between $\lambda = 390$ -780 nm) must be used. Especially the photooxidation of organic and inorganic substrates by oxygen using visible light activation of photosensitizers is of increasing interest.

The synthesis of fine chemicals by solar radiation is one application. The photooxidation of α -terpine to (\pm)-ascaradiol in the presence of chlorophyll as photosensitizer has been described [5, 6]. Recently, the synthesis of 5-hydroxy-5H-furan-2-one from furfural and oxygen in the presence of methylene blue or rose bengal as photosensitizer in ethanol (SOLARIS reactor of the solar test center in Almeria, Spain) has been reported [7, 8]. Another example, now in the absence of oxygen, is the synthesis of pyridines from acetylenes and nitriles in the presence of a cobalt cyclopentadienyl complex in toluene (PROPHIS solar reactor of the DLR in Cologne, Germany) [9]. Finally, the photooxidation of cyclopentadiene with ¹O₂ *via* a [2+4]-cycloaddition to (Z)-4,5-epoxypent-2-enaldehyde has been described first in 1956 by G. O. Schenk [10]. The synthesis of this fine chemical as educt for further reactions [11, 12] by photosensitizers with high stability and activity is of increasing interest.

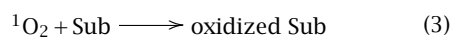
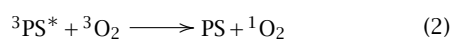
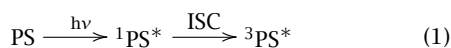
A second possible application is the cleaning of waste water. Employing water soluble photosensitizers, the photooxidation of sulfide [13], thiols [14], and phenols [15, 16] in water under visible light irradiation has been reported by us (other references cited in [13-15]). The advantage of these photoprocesses is the use of three for humankind "unexhaustible" resources: oxygen (from air), photons (visible light, solar radiation), water (as solvent). The only disadvantage is that the reactions are carried out in alkaline solutions. The following photosensitizers (PS) were employed: substituted phthalocyanines such as Al(III) and Zn(II) complexes of 2,9,16,23-tetrasulfophthalocyanine (AlPcTS, ZnPcTS), 5,10,15,20-tetrakis (4-carboxyphenyl) porphyrin (PoTC), rose bengal (RB), methylene blue (MB).



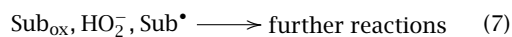
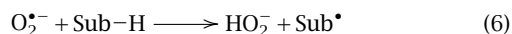
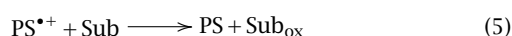
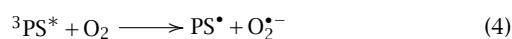
MtPcTS (Mt = Al[III], Zn[II], Co[III])



The photooxidation reactions include the following elementary step (equations (1), (2), and (3)). Excitation in the absorption region of the PS yields the excited singlet state ($^1PS^*$) and then by intersystem crossing (ISC) the excited triplet state ($^3PS^*$) [17-19]. Then the spin allowed triplet-singlet energy transfer from $^3PS^*$ to triplet oxygen (3O_2 , $^3\Sigma_g^-$) results in singlet oxygen (1O_2 , $^1\Delta_g$) followed by oxidation of the substrate (Sub) (so-called type II-reaction).



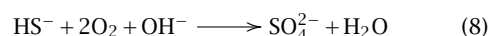
In addition to the singlet oxygen pathway, the formation of the superoxide anion radical ($O_2^{\bullet-}$) by photoinduced electron transfer cannot be ruled out as side reaction (equations (4), (5), (6), and (7); so-called type I-reaction) [17-19].



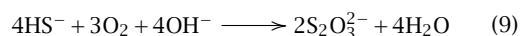
Sulfide and thiols can be oxidized in the dark in presence of a catalyst (*e.g.*, cobalt(II) phthalocyanine, CoPcTS) to yield thiosulfate [20], and disulfides [21], respectively (important processes in the petroleum industry for sweetening of gasoline fractions) (equations (9), (11)).

The more efficient photooxidations result in sulfate, sulfonic acids and—in the case of phenols—partially carbon dioxide [13-15], respectively (equations (8), (10), (12)).

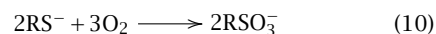
Photooxidation of sulfide:



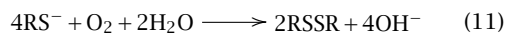
Catalytic oxidation of sulfide:



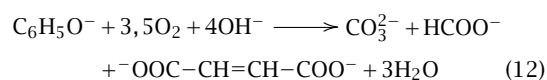
Photooxidation of 2-mercaptoethanol:



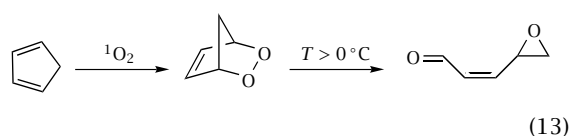
Catalytic oxidation of 2-mercaptoethanol:



Photooxidation of phenol:



The photooxidation of cyclopentadiene gives firstly an instable endoperoxyde as intermediate product. At higher temperatures the reaction ends in the formation of (Z)-4,5-epoxypent-2-enaldehyde (equation (13)).



This paper describes the photooxidation of sulfide, 2-mercaptoethanol (as example for thiols), phenols in aqueous alkaline solution and cyclopentadiene in ethanol. The O_2 consumption *versus* time is followed by a gas burette. For accurate measurements it is necessary that the reaction flask and the gas burette is thermostated. All employed photosensitizers are commercially available or can be synthesized according to the cited literature.

For the irradiation under laboratory conditions an expensive slide projector with a quartz-halogen lamp is used. Experiments under solar radiation are carried out by concentrating the solar light with an aluminium foil coated satellite bowl.

The experimental set-up allows to extend experiments to any photoreaction running in the visible region of light where gas consumption or evolution is measured.

2. MATERIALS AND METHODS

2.1. Chemicals

Photosensitizers. Aluminium(III)-hydroxy-2, 9, 16, 23-tetrasulfophthalocyaninetetrasodium salt, AlPcTS [14] (Porphyrin Products, P.O. Box 31, Logan, Utah 14321, USA), molecular weight 965 g mol^{-1} , UV/V is $\lambda = 343, 606, 674 \text{ nm}$ (in 0.1 mol l^{-1} CTAC at pH 13); zinc(II)-2,9,16,23-tetrasulfophthalocyaninetetrasodium salt, ZnPcTS [14] (Porphyrin Products), molecular weight 986 g mol^{-1} , UV/V is $\lambda = 341, 612, 680 \text{ nm}$ (in 0.1 mol l^{-1} CTAC at pH 13); 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin, PoTC [22, 23] (Porphyrin Products), molecular weight 791 g mol^{-1} , UV/V is $\lambda = 418, 516, 552, 588, 644 \text{ nm}$ (in 0.1 mol l^{-1} CTAC at pH 13); rose bengal disodium salt, RB (Alrich), molecular weight 1018 g mol^{-1} , UV/V is $\lambda = 326, 522, 561 \text{ nm}$ (in 0.1 mol l^{-1} CTAC at pH 13); methylene blue chloride, MB (Lancaster), molecular weight 320 g mol^{-1} , UV/V is $\lambda = 612 \text{ (sh)}, 661 \text{ nm}$ (in 0.1 mol l^{-1} SDS at pH 13).

Other chemicals. Detergents cetyltrimethylammonium chloride (CTAC, molecular weight 320 g mol^{-1}) and sodium dodecylsulfate (SDS, molecular weight 288 g mol^{-1}); borate (pH 9 and 10) and phosphate (pH 7) buffer solutions; substrates sodium sulfide nonahydrate, 2-mercaptoethanol, phenol, 2-chlorophenol (*p.a.*; employed as received), cyclopentadiene (distilled before use).

2.2. Equipment for photooxidation experiment. The apparatus consists of a two- or three-necked 100 ml reaction flask (containing a magnetic stirring bar), connected by a glass bridge to a 50 ml gas burette. All glass parts are double-walled to thermostate the temperature constant to 25°C . An equipment, available commercially, is the micro-hydrogenation apparatus Marhan (NORMAG, Postfach 1269, 65719 Hofheim, Germany). No additional filter to cut short and long wavelengths were used. Water is a good filter for IR light. The optical glass cut wavelength $< 300 \text{ nm}$. Therefore some UV light like in solar radiation is present.

For irradiation under *laboratory conditions* a 250 W slide projector with a quartz-halogen lamp was used. Quartz-halogen lamps emit photons between 300–2700 nm. In the visible region the light intensity is relatively continuous [24]. The light intensity was adjusted with a bolometer at $\sim 180 \text{ mW cm}^{-2}$ (distance lense of the slide projector to reaction flask between 5 and 10 cm).

For irradiation under *solar radiation* (for wavelength dependence of solar radiation see [7]) a parabolic reflector to concentrate the solar light was used. A simple plastic satellite receiver bowl (diameter 60 cm), which is available commercially, was carefully coated with a normal aluminium foil. The bowl was orientated to the sun and placed in such a distance from the reaction flask that the focus has a diameter of $\sim 10 \text{ cm}$. The solar light intensity of $\sim 55 \text{ mW cm}^{-2}$ was concentrated then to $\sim 1000 \text{ mW cm}^{-2}$ as determined with a bolometer.

2.3. Photooxidations

Photooxidation of sulfide and 2-mercaptoethanol. An aqueous solution of 50 ml containing the following compounds was employed: $5 \times 10^{-7} \text{ mol}$ photosensitizer (AlPcTS, ZnPcTS, PoTc, RB, or MB) for measurements at pH 13 0.24 g NaOH, at pH 10 and 9 25 ml borate buffer, at pH 7 25 ml phosphate buffer; for measurements in the presence of detergents 1.6 g ($5 \times 10^{-3} \text{ mol}$) CTAC or 1.44 g ($5 \times 10^{-3} \text{ mol}$) SDS to get solutions of 0.1 mol l^{-1} .

In all experiments the whole apparatus was thermostated at 25°C . After filling the reaction flask with 50 ml of the solution, the apparatus was flushed with pure oxygen for 10 min. Then $7 \times 10^{-4} \text{ mol Na}_2\text{S}$ (0.25 ml of a solution of 33.6 g (0.14 mol) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 50 ml water) or $50 \mu\text{l}$ ($7 \times 10^{-4} \text{ mol}$) 2-mercaptoethanol was added. The molar ratio substrate to PS amounts to 1400:1. The reaction flask was irradiated under intensive magnetic stirring up to 60 min, and the oxygen consumption over time was recorded.

Photooxidation of phenols. Only half amounts of PS and substrates were employed: $2.5 \times 10^{-7} \text{ mol}$ PS and $3.6 \times 10^{-4} \text{ mol}$ phenol or 2-chlorophenol in aqueous solution (0.25 ml of a solution of 6,74 g phenol or 9.1 g 2-chlorophenol (0.071 mol) in 50 ml ethanol). Again the molar ratio phenols to PS amounts to 1400:1.

Photooxidation of cyclopentadiene. The amount of PS was $1.25 \times 10^{-7} \text{ mol}$ dissolved in 50 ml ethanol. Cyclopentadiene was freshly distilled and then added to the 50 ml reaction solution in the amount of $1 \times 10^{-3} \text{ mol}$. The molar ratio cyclopentadiene to PS amounts to 8000:1.

3. RESULTS AND DISCUSSION

The results on the photooxidations are shown in Figures 1, 2, 3 and in Table 1 (for additional information see also [13–15]). The situation under the mentioned reaction conditions are as follows:

1. In the dark and in the absence of a catalyst or photocatalyst sulfide is slowly oxidized to thiosulfate [20], and 2-mercaptoethanol, phenols and cyclopentadiene are relatively stable.

2. In the dark and in the presence of a catalyst like CoPcTS catalytic oxidations of sulfide to thiosulfate [20], 2-mercaptoethanol to the disulfide [21] occur; phenol and cyclopentadiene are stable under these conditions (see equations (9), (11) and plots 1, 2 in Figure 1).

3. In the dark and in the presence of a photosensitizer the situation is comparable to the case (1) (see exemplarily plot 3 in Figure 1).

4. Under irradiation and now in the presence of a photosensitizer most efficient O_2 consumption is observed (see equations (8), (10), (12), (13), plot 4 in Figures 1, 2, 3, and Table 1).

5. The photooxidation of 2-chlorophenol is exemplarily included in Figure 2 and Table 1 also under conditions of solar radiation. Due to the higher light intensity of the concentrated solar light ($\sim 1000 \text{ mW cm}^{-2}$) compared to the slide projector ($\sim 180 \text{ mW cm}^{-2}$) the

photooxidations of phenols and cyclopentadiene under solar light are more rapid (Figures 2, and 3). 2-chloro-, 3-chloro- and 4-chlorophenol showed similar behaviour in photooxidation experiments [15].

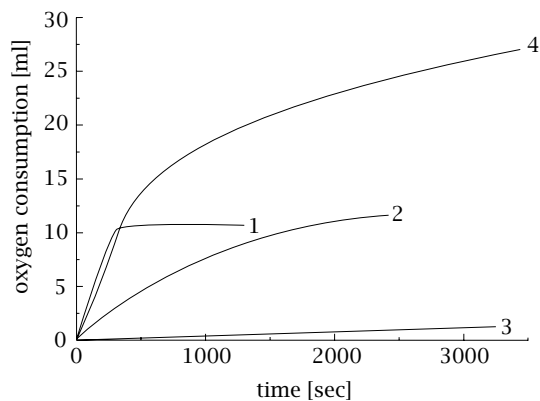


Figure 1. Catalytic and photocatalytic oxidation of 2-mercaptoethanol at pH 13. Plot 1: With 1.4 mmol thiol and 0.5 μmol CoPcTS (molar ratio: 2800) in the dark and under irradiation. Plot 2: Same like plot 1, only in the presence of 0.1 mol L⁻¹ CTAC. Plot 3: With 0.7 mmol thiol and 0.5 μmol ZnPcTS in the presence of detergent in the dark. Plot 4: Same like plot 3, only under irradiation with a slide projector.

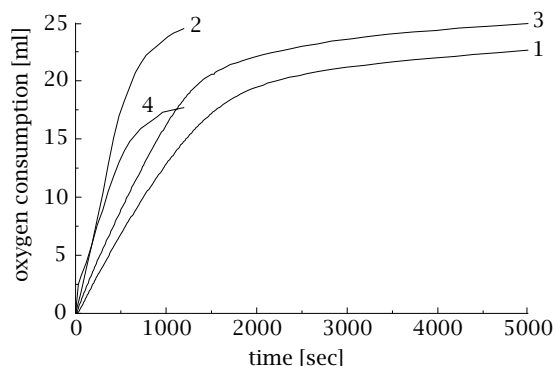


Figure 2. Photooxidation of 0.35 mmol 2-chlorophenol (i) Containing 0.25 μmol AlPcTS with irradiation by a slide projector (plot 1) or by solar radiation (plot 2). (ii) Containing 0.25 μmol ZnPcTS and 0.1 mol L⁻¹ CTAC with irradiation by a slide projector (plot 3) or by solar radiation (plot 4).

Depending on the reaction conditions, sulfide is photooxidized up to sulfate (observed and calculated molar-ratio consumed O₂ to employed sulfide ≤ 2 , equation (8)) [13]. In the case of the photooxidation of 2-mercaptoethanol, the isolated mixture consists of 80% 2-hydroxyethanesulfonic acid and 20% sulfate [14]. The oxygen consumed per mol employed thiol is ≤ 1.5 (equation (10)). For the photooxidation of phenol a molar ratio of consumed oxygen to employed phenol = $\sim 3.5\text{--}4$ was found (equation (12)) [15]. From Figures 1 and 2 it is seen that after a rapid initial phase of the photooxidation of 2-mercaptoethanol and phenol slow

subsequent steps are observed which may lead to further mineralization of the substrates. In the case of cyclopentadiene the oxygen consumption corresponds to a molar ratio of 1:1.

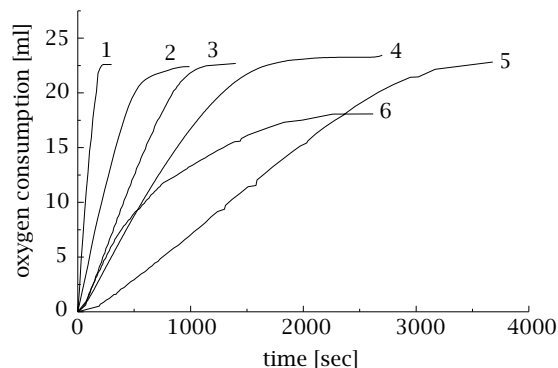


Figure 3. Photooxidation of 1 mmol cyclopentadiene in ethanol containing 0.125 μmol of different photosensitizers. (i) Slide projector: Plot 3: BR. Plot 4: ZnPcTS. Plot 5: PoTC. Plot 6: MB. (ii) Solar radiation: Plot 1: BR. Plot 2: AlPcTS.

Some additional results and comments are given:

- Photooxidation products of the employed substrates were—partly also quantitatively—determined from experiments carried out without detergent: sulfate from sulfide as BaSO₄ [13]; 2-hydroxyethanesulfonic acid and small amount of sulfate from 2-mercaptoethanol by IR spectroscopy and titration with Titriplex [14]; CO₂ and maleic/fumaric acid from phenol as BaCO₃ and by mass spectroscopy [15] and (Z)-4,5-epoxypent-2-enaldehyde from cyclopentadiene also by mass spectroscopy.

- For the photooxidations in aqueous solutions, the activities increase with higher pH value (see Table 1) which means that the anions S²⁻, RS⁻ and phenolate are more easily photooxidized than the protonated species. For phenol it was shown that the stabilities of the transition states of phenol or phenolate and singlet oxygen determine the rate of photooxidation [15].

- In some experiments detergents are added resulting in a strong increase of the activity for the photooxidations in aqueous solution. Without detergent the PSs are partly aggregating indicated by a shift of the λ_{max} absorption band. For a PS to be photoactive, it must exist as a monomer in solution because, in aggregates, dissipation of energy of the excited state occurs [13–15]. Detergents of opposite charge to the charge of the PSs are needed for monomerization (CTAC for ZnPcTS, PoTC, RB and SDS for MB). The tendency for aggregation of the employed PSs is in the order AlPcTS \ll PoTC \ll RB, MB < ZnPcTS. For photooxidation of cyclopentadiene no detergents were needed, because in ethanol the PS showed only very weak aggregation effects.

- During the photooxidation the PSs may also oxidatively decompose (see Table 1) [25, 26]. The degradation of the PSs was followed by measuring the UV/V is absorption intensity at the beginning and after

Table 1. Selected results on the photooxidation of sulfide, 2-mercaptoethanol, phenols and cyclopentadiene.

Photosensitizer (PS)	PH	Oxygen consumption in ml	Molar ratio consumed oxygen per substrate	Degradation of PS in %
1. Photooxidation of sulfide after 40 min irradiation slide projector				
AlPcTS ^a	13	25.4	1.5	3
AlPcTS ^b	13	34.4	2.0	22
AlPcTS ^a	9	>32.9	>1.9	87
ZnPcTS ^a	9	6.3	0.37	-
ZnPcTS ^b	9	33.2	>1.92	18
2. Photooxidation of 2-mercaptoethanol after 50 min irradiation slide projector				
AlPcTS ^a	13	21.5	0.96	-
AlPcTS ^b	13	32.0	1.43	3
ZnPcTS ^a	13	11.0	0.45	-
ZnPcTS ^b	13	27.0	1.2	50
3. Photooxidation of phenol after 1130 min irradiation slide projector				
AlPcTS ^a	13	32.4	3.7	0
AlPcTS ^b	13	34.6	3.9	21
ZnPcTS ^a	13	18.0	2.0	33
ZnPcTS ^b	13	33.6	3.8	97
ZnPcTS ^b	10	23.9	2.7	44
ZnPcTS ^b	7	6.4	0.7	65
POTC ^b	13	36.6	4.2	12
RB ^b	13	37.0	4.2	58
MB ^c	13	28.7	3.3	100
4. Photooxidation of 2-chlorophenol				
AlPcTS ^{a,d}	13	22.6	2.6	0
AlPcTS ^{a,e}	13	24.5	2.8	4
ZnPcTS ^{b,d}	13	24.9	2.8	71
ZnPcTS ^{b,e}	13	17.7	2.0	-
5. Photooxidation of cyclopentadiene				
AlPcTS ^{a,d}		23.1	0.94	15
ZnPcTS ^{a,d}		23.3	0.95	48
POTC ^{a,d}		22.9	0.94	-
RB ^{a,d}		22.7	0.93	39
MB ^{a,d}		18.1	0.74	100
AlPcTS ^{a,e}		22.4	0.92	14
RB ^{a,e}		22.6	0.92	60

^a Without detergent.

^b With CTAC.

^c With SDS.

^d After irradiation with slide projector.

^e After irradiation with solar radiation.

termination of the photooxidation. For a PS, high activity and good stability are fundamental prerequisites for a practical application. The tendency for the decomposition of the PSs are in most cases in the order AlPcTS < PoTC < ZnPcTS < RB < MB. AlPcTS exhibits the advantage of high activity, good stability and low aggregation

(use without detergent in aqueous solution).

• The activities of the PSs in the different photooxidations can be compared by calculation of the reaction rates (micromoles of consumed O₂ per minute) from the initial linear slope of the oxygen consumption over time [13–15]. Especially AlPcTS and rose bengal exhibit

good photosensitizing activities.

- It is important to show that the PSs are active at wavelengths of their absorptions in the visible region. Therefore, interference filters placed between the slide projector and the reaction flask were used to obtain so-called action spectra. The absorptions of the PSs correlate with their activities [13, 14].

- Further it is necessary to estimate the mechanisms of the photooxidation reactions. At the beginning of this article the singlet oxygen ($^1\text{O}_2$) and superoxide anion radical ($\text{O}_2^{\cdot-}$) pathways were pointed out (equations (2), (3), (4), (5), (6), and (7)). All employed PSs exhibit a high quantum yield of singlet oxygen formation: $\phi_{\Delta} = 0.2\text{--}0.7$ [26, 27]. The participation of singlet oxygen can be shown easily. Singlet oxygen has a longer lifetime in D_2O than in water. Therefore, the reaction rates and final oxygen consumptions are increased in D_2O (Figure 4). On the other side, the addition of sodium azide as physical quencher deactivates a fraction of $^1\text{O}_2$ and reduces the reaction rate and oxygen consumption (Figure 4) [13–15]. The additionally existing electron transfer pathway and, thus, the participation of superoxide anion radical in a side reaction was provided (i) by the formation of hydrogen peroxide (H_2O_2) and (ii) the reduction of methylviologen.

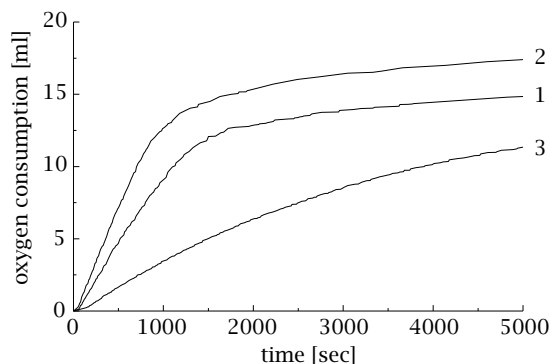
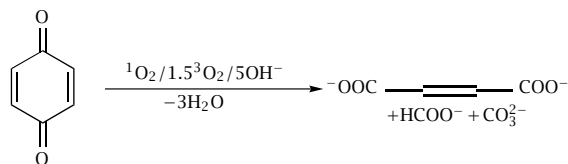
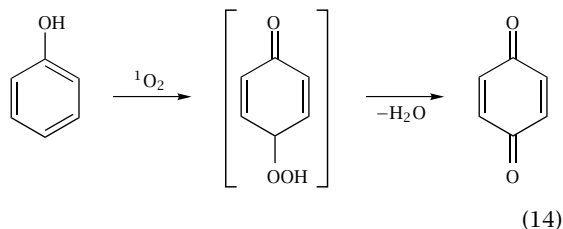


Figure 4. Photooxidation of 0.175 mol phenol in the presence of $0.125\ \mu\text{mol}$ AlPcTS in 25 ml aqueous solution at $\text{pH } 13$. Plot 1: In 25 ml H_2O without D_2O and NaN_3 . Plot 2: In 25 ml D_2O without NaN_3 . Plot 3: In 25 ml H_2O with 0.25 mmol NaN_3 without D_2O .

From detailed investigations of the mechanisms it came out that in the reaction sequences, *e.g.*, from sulfide to sulfate, thiol to disulfide and phenol to carbon dioxide and maleic/fumaric acid, several intermediates are involved [13–15]. Equations (14), (15) summarize some intermediates in the photooxidation of phenol using the singlet oxygen pathway.



4. CONCLUSION

The photooxidations of sulfide, 2-mercaptoethanol, phenols and cyclopentadiene demonstrate exemplarily that photoreactions (i) can easily be examined in the visible region of light and (ii) are applicable for waste water cleaning since, at least partial mineralisation can be obtained or can be used for the synthesis of fine chemicals. Especially AlPcTS combines good activity and stability, therefore it is more preferable than rose bengal and methylene blue. A simple satellite bowl allows to concentrate solar radiation and to carry out experiments under solar conditions after getting experiences using a slide projector under laboratory conditions. The use of thermostated reaction flask and gas burette allows to measure accurately the oxygen consumption. The applicability of the experimental conditions described here for other visible and solar light driven oxidation reactions is obvious. Presently, the immobilization of the most active photosensitizers at organic and inorganic macromolecules is under investigation. The photoactivities of these heterogenized PSs will be reported in a separate paper in near future.

ACKNOWLEDGEMENTS

The authors are grateful to the Government of Bremen for the financial support by the grants of the Material Science and Technology Research Cooperation, and the Energy Programme (No. 55-2/11).

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