

# Oxidation and photooxidation of sulfur-containing compounds in the presence of water soluble phthalocyanine complexes

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Received 4 January 1995; accepted 6 June 1995

## Abstract

Water soluble cobalt(II) 2,9,16,23-tetrasulfophthalocyanine, zinc(II) 2,9,16,23-tetrasulfophthalocyanine, zinc(II) tetracarboxyphthalocyanine, and non-metallic sulfophthalocyanine complexes were studied as catalysts and photocatalysts for oxidation of sulfide, sulfite and thiosulfate ions by dioxygen. The cobalt phthalocyanine complexes exhibit high catalytic activity only in the oxidation of compounds containing sulfur in low oxidation state (sulfides). Oxidation is not complete and the activity of these complexes is not enhanced upon irradiation with visible light. Zinc and non-metallic phthalocyanine complexes demonstrate high catalytic activity only on irradiation with visible light. During interaction between dioxygen and the long-living triplet state of these complexes a chemically more reactive singlet dioxygen is formed which further interacts with compounds containing sulfur of various oxidation state. Upon photooxidation catalyzed by zinc or non-metallic phthalocyanine complexes the alkali sulfides, sulfites and thiosulfates are completely oxidized to sulfates. Aggregation of charged phthalocyanine complexes in aqueous medium decreases their effectiveness as photocatalysts because of lowering of the quantum yield of singlet dioxygen. In the presence of quaternary ammonium salts the equilibrium monomer–dimer is shifted to the monomeric form of the complexes, the photocatalytic activity being enhanced in this case. The mechanism of photocatalytic oxidation of sulfur-containing compounds and the catalyst destruction are briefly discussed.

*Keywords:* Photocatalysis; Oxidation; Phthalocyanine complexes; Sulphides; Sulphites; Thiosulphates

## 1. Introduction

Cobalt phthalocyanine complexes (CoPc) are effective catalysts for oxidation of thiols and hydrosulfides by dioxygen [1–7]. They have found wide application in the catalytic oxidation of mercaptans in oil fractions [4]. The redox process is catalyzed by the ground electronic state of the CoPc complexes and is the result of electron transfer from the sulfur-containing compound to dioxygen coordinated to the central Co(II) metal

atom [5–7]. The oxidation of thiols or alkali sulfides catalyzed by CoPc complexes is not complete, the end products being disulfides, sulfur and thiosulfates, respectively [4,5,8]. Of substantial importance, however, is the complete catalytic oxidation on removing alkali sulfides, sulfites and thiosulfates from industrial waste water [9] because effluent acidities can be properly controlled.

This work deals with the possibility for oxidation of alkali sulfides, sulfites and thiosulfates photocatalyzed by water soluble phthalocyanine complexes. The photocatalytic oxidation by sun-

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light is attractive especially on removing sulfur-containing pollutants from waste water. It is known [10–12] that upon irradiation with visible light the non-metallic phthalocyanine complexes and those containing metal ions with filled electron shells or d orbitals like Zn, Mg and Al manifest long lifetimes of the excited triplet state. They are sensitizers in electron or energy transfer reactions [10–13]. The dioxygen,  $^3\text{O}_2$  ( $^3\Sigma_g^-$ ), interacts with the excited triplet electronic state of the complexes and as a result of energy transfer is converted to singlet dioxygen,  $^1\text{O}_2$  ( $^1\Delta_g$ ) [12,13]. The formation of energetically rich singlet dioxygen is a prerequisite for complete oxidation of compounds containing sulfur of various oxidation states, such as mercaptans, hydrosulfides, sulfoxides, sulfites, and thiosulfates.

It has been shown [14] that the initial rates of oxidation of compounds containing sulfur in low oxidation state (thiols) do not differ significantly during catalysis by CoPc or photocatalysis by ZnPc complexes. Upon photocatalysis the redox process proceeds to a higher extent thus forming products of deep oxidation [14].

The catalytic and photocatalytic oxidation of sulfide, sulfite and thiosulfate ions was studied in homogeneous phase in the presence of sodium salts of the following complexes: cobalt(II) 2,9,16,23-tetrasulfophthalocyanine [ $\text{CoPc}(\text{SO}_3\text{Na})_4$ ], zinc(II) 2,9,16,23-tetrasulfophthalocyanine [ $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ], zinc(II) 2,9,16,23-tetracarboxyphthalocyanine [ $\text{ZnPc}(\text{COONa})_4$ ], and metal-free sulfophthalocyanine [ $\text{Pc}(\text{SO}_3\text{Na})_n$ ].

## 2. Experimental

$\text{CoPc}(\text{SO}_3\text{Na})_4$ ,  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  complexes were prepared from 4-sulfophthalic acid or trimellitic anhydride and purified according to methods described in the literature [15,16]. Non-metallic sulfonated phthalocyanine, containing 3 or 4 sulfo groups ( $n=3,4$ ), was prepared through sulfonation by oleum [17]. The concentrations of  $\text{K}_2\text{SO}_3$

(Fluka) and  $\text{Na}_2\text{S}_2\text{O}_3$  (Fluka) solutions were determined by iodometric titration.  $\text{Na}_2\text{S}$  content was determined by using copper perchlorate [18]. Dioxygen consumption was measured by means of a gas burette. The oxidation runs were carried out in aqueous medium at 293 K,  $\text{pH}=9.24$  and atmospheric pressure of dioxygen. An all-glass static reactor equipped with electromagnetic stirrer was used for the experiments. The photocatalytic oxidation was performed by exposure to a halogen lamp (12 V, 50 W), the illumination being  $38 \text{ mW/cm}^2$ .

Visible spectra of the phthalocyanine complexes in solution were recorded on a Hewlett Packard 89500 UV/VIS spectrophotometer. The sulfate ions formed upon complete photocatalytic oxidation of  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  were determined gravimetrically by precipitation with  $\text{BaCl}_2$ . The accuracy of the analysis was  $\pm 5 \text{ wt}\%$ .

## 3. Results

Charged phthalocyanine complexes form molecular associates as dimers and oligomers even in diluted solutions [12,19,20]. In photon-induced processes the self-association of the complexes is accompanied by quenching of the excited triplet state [10–12]. This has a substantial influence on the effectiveness of the phthalocyanine complexes as photocatalysts for redox processes taking place in the presence of dioxygen. It is well known that in solution the monomer–dimer equilibrium can be evaluated through the electron transitions in the Q band ( $\lambda=600\text{--}800 \text{ nm}$ ) that correspond to these two entities [12,20,21]. Under conditions of photooxidation the acquired visible spectra of aqueous solutions of  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  of equal concentration show that the monomerization of these complexes is different (Fig. 1). The monomer–dimer equilibrium is more strongly shifted to the monomeric form of  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  ( $\lambda=665 \text{ nm}$ ) in comparison with  $\text{ZnPc}(\text{COONa})_4$  ( $\lambda=675 \text{ nm}$ ). The  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  monomers

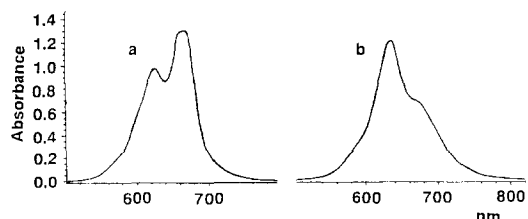


Fig. 1. Visible absorption spectra of equimolar aqueous solution (40  $\mu\text{mol/l}$ ). (a)  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ; (b)  $\text{ZnPc}(\text{COONa})_4$ .

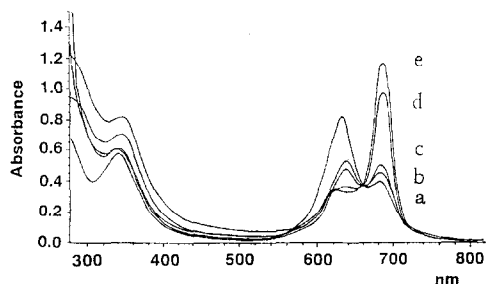
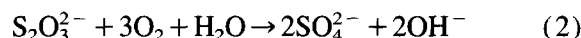
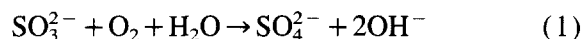


Fig. 2. Visible absorption spectra of  $\text{ZnPc}(\text{COONa})_4$  in aqueous solution in the presence of tetrabutylammonium chloride (mmol): (a) 0; (b) 0.3; (c) 0.6; (d) 1.2; (e) 1.8.

exhibit close values of the molar extinction coefficients, being  $\epsilon=48000$  [13] and  $\epsilon=60000$  [22], respectively. Thus, the results deduced from Fig. 1 allow us to interpret qualitatively the different activities of the two complexes in the photooxidation in aqueous solution (Table 1). The degree of association with  $\text{ZnPc}(\text{COONa})_4$  is controlled by adding bulky cations like tetrabutylammonium chloride (TBAC). The increase in intensity of the Q transition, specific of the mon-

omer Pc complex, with the increase in TBAC concentration is shown in Fig. 2.

The catalytic and photocatalytic activity of the  $\text{CoPc}(\text{SO}_3\text{Na})_4$ ,  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ,  $\text{ZnPc}(\text{COONa})_4$ , and  $\text{Pc}(\text{SO}_3\text{Na})_n$  complexes in the oxidation of  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (Table 1) is expressed by  $r$  ( $\text{mol O}_2 \text{ min}^{-1}/\text{mol Pc}$ ) or TOF ( $\text{mol oxidized substrate min}^{-1}/\text{mol Pc}$ ). The initial rates of catalytic and photocatalytic oxidation of the sulfur-containing compounds were determined from the linear part of the curve of dioxygen consumption with time (Fig. 3). The rate of photocatalytic oxidation of the sulfite or thiosulfate ion can be determined from the dioxygen consumption according to the stoichiometry of the following equations:



The kinetics of catalytic [23] or photocatalytic oxidation of  $\text{Na}_2\text{S}$  is somewhat more complex because the process is accomplished by series of parallel reactions. In this case the oxidation rate is evaluated by the dioxygen consumption irrespective of the total redox process. After stopping the consumption of dioxygen, it was found by means of iodometric titration or precipitation with  $\text{BaCl}_2$  that 92–97% of the amount of  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  was oxidized to sulfates. Therefore, upon photocatalytic oxidation  $\text{Na}_2\text{S}$  is also completely

Table 1

Catalytic and photocatalytic oxidation of alkali thiosulfates, sulfites and sulfides in aqueous medium at  $\text{pH}=9.24$

Complex 4 $\mu\text{mol}$	Condition	$\text{Na}_2\text{S}_2\text{O}_3^a$		$\text{K}_2\text{SO}_3^b$		$\text{Na}_2\text{S}^a$
		$r$ ( $\text{min}^{-1}$ )	TOF ( $\text{min}^{-1}$ )	$r$ ( $\text{min}^{-1}$ )	TOF ( $\text{min}^{-1}$ )	$r$ ( $\text{min}^{-1}$ )
–	dark	0	0	8.6	8.6	0.7
–	irradiation	0	0	23.4	23.4	1.3
$\text{CoPc}(\text{SO}_3\text{Na})_4$	dark	0	0	14.5	14.5	70.0
$\text{ZnPc}(\text{SO}_3\text{Na})_4$	dark	0	0	9.7	9.7	0.8
$\text{CoPc}(\text{SO}_3\text{Na})_4$	irradiation	0	0	11.2	11.2	66.0
$\text{ZnPc}(\text{SO}_3\text{Na})_4$	irradiation	8.4	2.8	111.6	111.6	31.3
$\text{ZnPc}(\text{COONa})_4$	irradiation	1.5	0.5	34.6	34.6	12.3
$\text{Pc}(\text{SO}_3\text{Na})_4$	irradiation	2.3	0.77	46.9	46.9	16.7

<sup>a</sup> 30 mmol.

<sup>b</sup> 3 mmol.

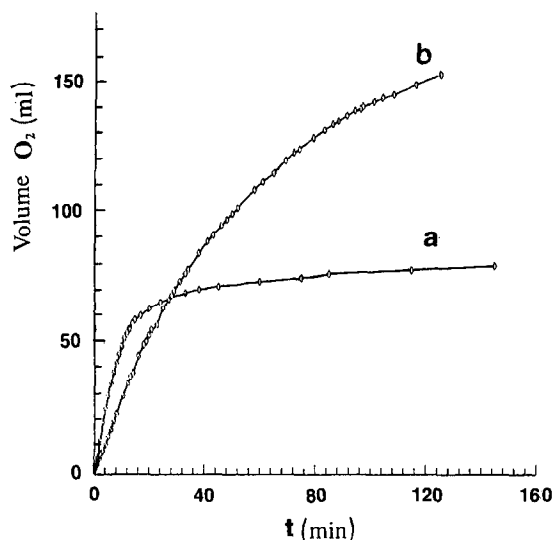


Fig. 3. Dioxygen consumption in the oxidation of  $\text{Na}_2\text{S}$ . (a) Catalyzed by  $\text{CoPc}(\text{SO}_3\text{Na})_4$ ; (b) photocatalyzed by  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ .

Table 2

Influence of  $\text{ZnPc}(\text{COONa})_4$  monomerization on its photocatalytic activity in  $\text{Na}_2\text{S}_2\text{O}_3$  oxidation<sup>a</sup>

$A_{\text{rel}}$	$\text{C}_{16}\text{H}_{36}\text{NCl}$ mmol	$r$ ( $\text{min}^{-1}$ )	TOF ( $\text{min}^{-1}$ )
0.24	0	1.5	0.5
0.39	0.3	3.9	1.3
0.43	0.6	5.0	1.7
0.81	1.2	6.7	2.2
1.00	1.8	13.4	4.5

<sup>a</sup> Reaction conditions:  $4 \mu\text{mol}$   $\text{ZnPc}(\text{COONa})_4$ ;  $30 \text{ mmol}$   $\text{Na}_2\text{S}_2\text{O}_3$ .

oxidized. In alkali aqueous solution  $\text{Na}_2\text{S}$  dissociates to hydrosulfide and sulfide ions which are oxidized according to the following general equations:

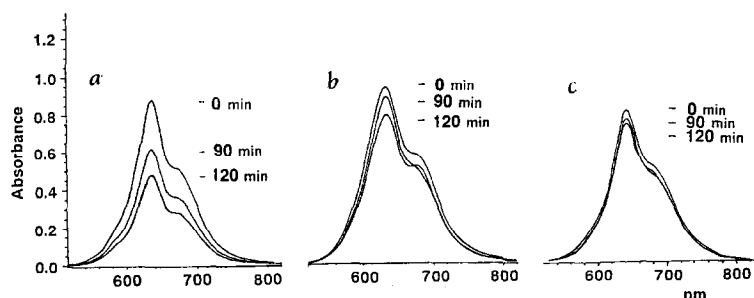
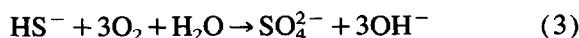


Fig. 4.  $\text{ZnPc}(\text{COONa})_4$  photodestruction (a) in the presence of dioxygen; (b) upon photocatalytic oxidation of  $\text{Na}_2\text{S}_2\text{O}_3$ ; (c) during photocatalytic oxidation of  $\text{Na}_2\text{S}$ .

The effect of  $\text{ZnPc}(\text{COONa})_4$  monomerization on its photocatalytic activity in  $\text{Na}_2\text{S}_2\text{O}_3$  oxidation is presented in Table 2. The variation of the concentration of the monomeric complex at different  $\text{H}_2\text{O}:\text{TBAC}$  ratios is expressed as a relative quantity  $[C]_{\text{rel}} = [C]_n / [C]_{\text{max}} = A_n / A_{\text{max}} = A_{\text{rel}}$ .  $[C]_n$  and  $[C]_{\text{max}}$  are the concentrations of the monomeric complex for absorptions  $A_n$  (curves a–e) and  $A_{\text{max}}$  (curve e), respectively, at  $\lambda = 675 \text{ nm}$  (Fig. 2). The relative variation of the  $\text{ZnPc}(\text{COONa})_4$  monomer concentration was evaluated on the assumption that the molar extinction coefficient of the complex at  $\lambda = 675 \text{ nm}$  was constant.

The photocatalytic oxidation of  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  was accompanied by decomposition of the complexes with time (Fig. 4). Data on  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  photodestruction in relation to the amount of monomeric complex and the presence of oxidizable substrate are shown in Table 3.

#### 4. Discussion

The oxidation and photooxidation of sulfur-containing compounds of different oxidation state, catalyzed by phthalocyanine complexes, proceeds with the participation of dioxygen. The activation of the dioxygen and the possibility of its participation in a catalytic or photocatalytic process is dependent upon the electronic structure of the phthalocyanine complexes and the central metal atom. Complexes containing cobalt or vanadyl ions can reversibly coordinate dioxygen in

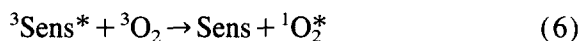
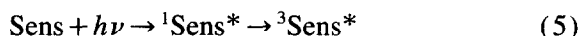
Table 3  
Chemical stability on photocatalytic oxidation of zinc phthalocyanine complexes

Complex 4 $\mu\text{mol}$	Compound 30 mmol	$\text{C}_{16}\text{H}_{39}\text{NCl}$ mmol	Decomposition (%) after		
			40 min	90 min	120 min
$\text{ZnPc}(\text{COONa})_4$	–	–	7.5	21.2	34.6
	$\text{Na}_2\text{S}_2\text{O}_3$	0	2.5	5.5	15.1
	$\text{Na}_2\text{S}_2\text{O}_3$	0.3	8.0	20.0	37.0
	$\text{Na}_2\text{S}_2\text{O}_3$	0.9	15.0	38.0	50.0
	$\text{Na}_2\text{S}_2\text{O}_3$	1.2	23.0	52.0	70.0
	$\text{Na}_2\text{S}$	1.8	0	3.6	6.4
$\text{ZnPc}(\text{SO}_3\text{Na})_4$	–	–	8.5	28.6	54.3
	$\text{Na}_2\text{S}_2\text{O}_3$	–	7.0	27.0	51.3

the dark which is the basis of the redox mechanism of catalytic oxidation of sulfur-containing compounds [5–7]. However, complete oxidation of mercaptans and hydrosulfides does not occur upon catalysis by cobalt phthalocyanine complexes [1–5,14]. This is reasonable bearing in mind the redox potentials of the catalyst and reagents [1]. The amounts of dioxygen consumed (Fig. 3) indicate that the oxidation of  $\text{Na}_2\text{S}$  catalyzed by  $\text{CoPc}(\text{SO}_3\text{Na})_4$  does not proceed completely to sulfates according to Eqs. 3 and 4. The lack of catalytic activity of  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  in the dark (Table 1) is due to the fact that these complexes do not coordinate and activate dioxygen [25,26].

Like thiols [14], the oxidation of  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$  catalyzed by  $\text{CoPc}$  complexes is not enhanced upon irradiation with visible light (Table 1). During photooxidation the catalytic activity is dependent on the lifetime of the excited triplet state and the possibility of formation of  $^1\text{O}_2$  ( $^1\Delta_g$ ). Complexes like  $\text{CoPc}(\text{SO}_3\text{Na})_4$  containing a central metal ion with unfilled d orbitals exhibit a very short lifetime of the excited triplet state ( $^1\sigma_{\text{Co}} \approx 0.065 \mu\text{s}$ ) [10] and because of this are not able to interact with  $^3\text{O}_2$  ( $^3\Sigma_g$ ). By contrast, those containing a metal ion with filled electron shells or d orbitals and non-metallic phthalocyanine complexes manifest long lifetimes of the excited triplet state,  $^1\sigma$  being 170 and 245  $\mu\text{s}$  for  $\text{Pc}(\text{SO}_3\text{Na})_n$  and  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ , respectively [10]. By means of energy transfer, these complexes are able to convert triplet dioxygen,  $^3\text{O}_2$

( $^3\Sigma_g$ ), into singlet dioxygen,  $^1\text{O}_2$  ( $^1\Delta_g$ ), according to the following scheme:



The energetically rich  $^1\text{O}_2^*$  molecule exhibits higher reactivity than triplet dioxygen ( $^3\text{O}_2$ ). The photocatalytic activity of  $\text{Pc}(\text{SO}_3\text{Na})_n$ ,  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  is associated with formation of  $^1\text{O}_2^*$  and its interaction with  $\text{Na}_2\text{S}$ ,  $\text{K}_2\text{SO}_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ :



The photocatalytic activity of the  $\text{Pc}(\text{SO}_3\text{Na})_n$ ,  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  complexes in aqueous medium is different (Table 1). This is due mainly to differences in the lifetimes and quantum yields of the excited triplet state of the complexes:  $^1\sigma = 170 \mu\text{s}$ ,  $\phi_{\text{T}} = 0.14$  and  $^1\sigma = 245 \mu\text{s}$ ,  $\phi_{\text{T}} = 0.56$  for  $\text{Pc}(\text{SO}_3\text{Na})_n$  and  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ , respectively [10]. Self-association of the  $\text{ZnPc}(\text{SO}_3\text{Na})_4$ ,  $\text{ZnPc}(\text{COONa})_4$  and  $\text{Pc}(\text{SO}_3\text{Na})_n$  complexes in aqueous solution has also substantial influence on the photocatalytic activity. Upon formation of dimers as a result of bimolecular triplet annihilation, the excited triplet state of the species is quenched and the quantum yield is decreased. The different aggregation degree of  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  and  $\text{ZnPc}(\text{COONa})_4$  in aqueous solution (Fig. 1) is the principal factor which affects the photocatalytic activity of both complexes (Table 1). The quantum yield of

$^1\text{O}_2^*$ , formed from the monomer  $\text{ZnPc}(\text{COONa})_4$  species, is 0.7 whereas that of the dimer is 0.1 [12]. On photooxidation of  $\text{Na}_2\text{S}_2\text{O}_3$  the enhancement of catalytic activity of  $\text{ZnPc}(\text{COONa})_4$  in the presence of TBAC (Table 2) is due to the increase in the amount of the monomer complex (Fig. 2) and the photogeneration of singlet dioxygen with higher concentration.

Upon irradiation with visible light in the presence of dioxygen the phthalocyanine complexes decompose with time. The photodestruction proceeds faster with complexes having a central metal ion with filled d orbitals or electron shells and is due to interaction with  $^1\text{O}_2$  ( $^1\Delta_g$ ) [13]. A photodecomposition of phthalocyanine complexes is also observed during catalytic photooxidation of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  by  $\text{ZnPc}(\text{SO}_3\text{Na})_4$  or  $\text{ZnPc}(\text{COONa})_4$  (Fig. 4). The rate of photodestruction of  $\text{ZnPc}(\text{COONa})_4$  is enhanced by increasing the amount of monomer species and is due to photogeneration of higher concentrations of  $^1\text{O}_2^*$  (Table 3). The photodecomposition of  $\text{ZnPc}(\text{COONa})_4$  in the presence of  $\text{Na}_2\text{S}_2\text{O}_3$  or  $\text{Na}_2\text{S}$  showed 2–7 times lower values (Table 3).

The mechanism of zinc porphyrins and zinc phthalocyanines oxidation by  $^1\text{O}_2^*$  has been studied in detail [13,24]. Singlet dioxygen interacts predominantly with unsaturated carbon–nitrogen double bonds of the peripheral ligand. In the presence of quenchers the reaction of photodestruction can proceed parallel to the reaction of substrate oxidation (Eq. 7) The lower photodestruction degree of the  $\text{Zn}(\text{II})$ –phthalocyanine complexes on photocatalytic oxidation of  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  (Table 3) is due to consumption of photogenerated  $^1\text{O}_2^*$  from these parallel interactions.

## 5. Conclusions

Phthalocyanine complexes with long lifetime of the excited triplet state exhibit high activity as photocatalysts for oxidation of sulfide, sulfite and thiosulfate ions in alkali solution. By contrast with cobalt phthalocyanine complexes, the photooxidation catalyzed by zinc or non-metallic com-

plexes proceeds completely to sulfates regardless of the sulfur oxidation state. The activity of the photocatalysts is dependent upon the lifetime of their excited triplet states and the related photogeneration of singlet dioxygen. Upon self-association in solution the photocatalytic activity of the phthalocyanine complexes is lowered because of decrease in the quantum yield of singlet dioxygen. As a result of singlet dioxygen consumption during oxidation of alkali sulfides, sulfites and thiosulfates the photodestruction of phthalocyanine complexes is decreased by 2–7 times.

## Acknowledgements

The authors are grateful to the Bulgarian National Scientific Research Foundation for financial support.

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