

# The role of hydrogen peroxide during the autoxidation of thiols promoted by bifunctional polymer-bonded cobaltphthalocyanine catalysts

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## THE ROLE OF HYDROGEN PEROXIDE DURING THE AUTOXIDATION OF THIOLS PROMOTED BY BIFUNCTIONAL POLYMER-BONDED COBALTPHTHALOCYANINE CATALYSTS

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### Summary

Bifunctional catalysts composed of a polymeric base and a cobalt-phthalocyanine were applied to the oxidation of thiols (RSH) to disulphides (RSSR). During this reaction hydrogen peroxide ( $H_2O_2$ ) is produced and consumed simultaneously. A mechanistic interpretation of the production of  $H_2O_2$  is presented and it is furthermore demonstrated that the base catalyzed reaction of RSH with  $H_2O_2$  can account for the measured conversion of  $H_2O_2$ . The consumption of  $H_2O_2$  by the reaction of  $H_2O_2$  with the polymeric amine groups and the disproportionation of  $H_2O_2$  into  $O_2$  and  $H_2O$  (catalyzed by cobaltphthalocyanines) is found to be of minor importance in the investigated reaction system. The reaction of RSH with  $H_2O_2$  results mainly in the formation of RSSR, but it has been shown by IR measurements that also small amounts of sulphur-containing oxy-acids are formed. The observed deactivation of the bifunctional catalytic systems results from the poisoning of the essential basic sites of the catalysts by these sulphur-acids. Although some decomposition of the cobaltphthalocyanine by  $H_2O_2$  occurs, it is proved that this oxidative destruction is not the primary cause of the deactivation.

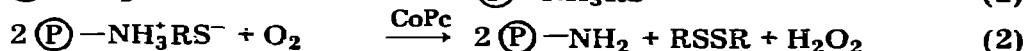
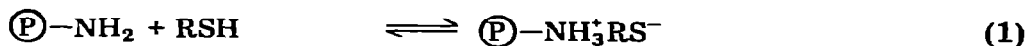
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### Introduction

The reaction of thiols with metal complexes has been known for over 50 years. Interest in the interaction of thiols with metals focusses on the biological importance of the sulphhydryl groups and the possible relationship of model systems to cytochrome P-450 [1, 2]. Furthermore, studies on the reaction of thiols with metals have also been performed with the aim of understanding the catalytic behaviour of metals in the oxidation of thiols. The knowledge concerning the catalytic oxidation of thiols is applied in industrial processes for the purification of oil products [3, 4]. In the petro-

leum industry the thiol contamination of hydrocarbons is a prevailing problem because thiols possess an obnoxious odour and corrosive properties.

It is now well established that thiols (RSH) can be readily oxidized to disulphides (RSSR) in basic media using metal ions [5, 6] or metal complexes [7, 8] as catalysts. Recently [9 - 11], we have shown that a particularly active catalytic system is obtained when using a polymeric base — instead of the commonly applied alkaline hydroxide — in combination with a cobalt-phthalocyanine (CoPc) as oxidation site. The reaction pathway for the oxidation of thiols in our system may be represented by a set of consecutive reactions (eqns. (1) - (3)).



While the activity of the bifunctional polymeric catalyst in aqueous media is appreciably higher than the activity of the traditional CoPc/NaOH system, a serious drawback limiting the practical applicability of the polymeric system is the loss of activity observed in successive runs [9, 10]. Rollmann [12] applied similar bifunctional catalysts composed of polymer-bonded porphyrins to the oxidation of thiols and noticed also a rather rapid ageing of his catalyst. He ascribed this deactivation to decomposition of the porphyrins by free radical processes.

We, however, have assumed [9, 10] that the deactivation of our polymeric catalytic system is caused by traces of sulphur-containing oxo-acids. A strong acid may occupy the basic groups of the polymer, thus hindering the thiolate groups from coordinating to the polymeric base (*i.e.* inhibition of reaction (1)). Presumably, these sulphur-containing oxo-acids ( $\text{RSO}_x\text{H}$ ) are formed in traces by the reaction of  $\text{H}_2\text{O}_2$  with RSH, while disulphide (RSSR) is the main product of this particular reaction (see eqn. (3a)).



$$(b \ll 1, x \leq 3)$$

This hypothesis is in agreement with literature data [13] revealing that in industrial processes for the removal of mercaptans problems might also occur (*i.e.* consumption of base and formation of coloured products), due to over-oxidation by  $\text{H}_2\text{O}_2$ .

It is the scope of the present article to describe the role of  $\text{H}_2\text{O}_2$  in the reaction system and to clarify the way of deactivation of the bifunctional catalysts. Obviously, a sound explanation of the behaviour of  $\text{H}_2\text{O}_2$  during the catalytic oxidation can only be obtained when taking into consideration all possible reactions of  $\text{H}_2\text{O}_2$ . Therefore, in this investigation we have studied not only the various reactions of  $\text{H}_2\text{O}_2$  with RSH, but also the reaction of  $\text{H}_2\text{O}_2$  with the amine groups of the polymeric carrier, the decomposition of CoPc by  $\text{H}_2\text{O}_2$  and the disproportionation of  $\text{H}_2\text{O}_2$  catalyzed by CoPc.

## Experimental

### *Reagents and methods*

The applied thiol, 2-mercaptoethanol (Merck), was distilled before use and carefully kept under nitrogen.  $H_2O_2$  (30%) was obtained from Brocacef B.V. and used as purchased. Distilled and deionized water was used throughout the experiments. The measurements on the activity of the catalysts for the oxidation of 2-mercaptoethanol were carried out as described in a previous article [10].

The concentrations of  $H_2O_2$  were determined spectrophotometrically using  $TiCl_3-H_2O_2$  as reagent [14]. In solutions containing thiol these latter measurements have to be carried out immediately after sampling. In this way a possible error due to the oxidation of RSH with  $Ti(III)-H_2O_2$  [1] can be avoided.

### *Preparation of the catalysts*

Details of the preparation of the tetrasodiumsalt of cobalt (II)-tetrasulphophthalocyanine ( $CoPc(SO_3Na)_4$ ), cobalt (II)-tetracarboxyphthalocyanine ( $CoPc(COOH)_4$ ), cobalt(II)-tetraaminophthalocyanine ( $CoPc(NH_2)_4$ ), poly(vinylamine) (PVAm) and of the coupling of cobaltphthalocyanines to PVAm have been described previously ([10, 15] and references therein).  $CoPc(NH_2)_4$  was coupled by means of 2, 4, 6-trichloro-s-triazine [16] to the amine groups of Enzacryl AA (*i.e.* a porous crosslinked poly(acrylamide) with aniline-substituted acrylamide groups supplied by Koch-Light Laboratories Ltd.).

$CoPc(NH_2)_4$  was also coupled (using the same method) to an Enzacryl AA sample which was modified by amine groups (*i.e.* with bis(3-amino-propyl)-amine) according to the method given by Inman and Dintzis [17]. The amine-modified Enzacryl AA sample contained  $2.1 \mu\text{mol}$  amine per mg (measured by titration with 0.1 N HCl).

### *Apparatus*

Optical spectra were recorded with a Unicam SP 800 spectrophotometer. IR spectra were measured on Hitachi EPI L and Grubb-Parsons IR spectrophotometers. The pH measurements were carried out using a Radiometer type TTT 1c apparatus.

## Results and discussion

### *(a) The concentration of $H_2O_2$ during the catalyzed oxidation of RSH*

In a previous article [11] we have shown that the activity of catalysts consisting of cobalt(II)-tetrasulphophthalocyanine ( $CoPc(SO_3Na)_4$ ) and poly(vinylamine) (PVAm) for the autoxidation of 2-mercaptoethanol (RSH) increases with increasing amine content at constant  $CoPc(SO_3Na)_4$  concentration. Our present measurements of the concentration of hydrogen per-

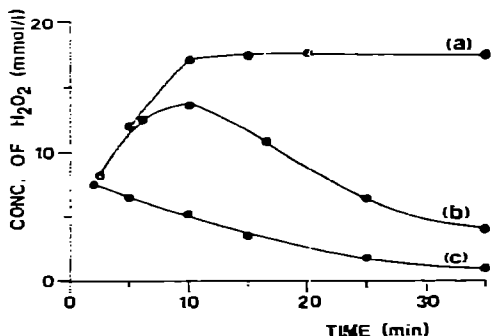


Fig. 1. The accumulation of  $\text{H}_2\text{O}_2$  as a function of the amount of poly(vinylamine) during the oxidation of 2-mercaptoethanol using  $10^{-8}$  mol  $\text{CoPc}(\text{SO}_3\text{Na})_4$  (conditions: 14.25 mmol thiol;  $T = 24^\circ\text{C}$ ;  $p(\text{O}_2) = 1$  atm; reaction volume, 75 ml). (a)  $10^{-5}$ , (b)  $10^{-4}$ , and (c)  $5 \times 10^{-4}$  mol amine.

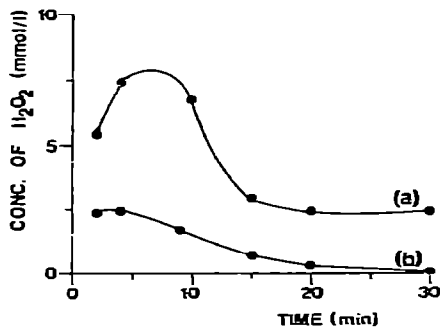


Fig. 2. The influence of the addition of NaOH on the concentration profile of  $\text{H}_2\text{O}_2$  during oxidation of 2-mercaptoethanol using PVAm with covalently attached  $\text{CoPc}(\text{COOH})_4$  ( $9 \times 10^{-5}$  mol amine/ $3 \times 10^{-8}$  mol Co) as catalyst (conditions, see Fig. 1). (a) no additional base, and (b) 0.1 mmol NaOH added.

oxide formed during reaction reveal that also the level of  $\text{H}_2\text{O}_2$  accumulation depends strongly on the content of polymeric amine in the reaction mixture. From the results presented in Fig. 1, it is obvious that the amount of  $\text{H}_2\text{O}_2$  present diminishes with increasing amine concentration. Evidently, the amount of polymeric base in the bifunctional catalyst is of considerable importance for both the catalytic activity and the level of  $\text{H}_2\text{O}_2$  accumulation. A relatively high excess of polymeric amine groups as compared to  $\text{CoPc}$  molecules favours the rate of oxygen uptake and diminishes the accumulation of  $\text{H}_2\text{O}_2$ .

The amount of  $\text{H}_2\text{O}_2$  in the reaction system decreases not only with increasing PVAm content (*cf.* Fig. 1), but decreases also substantially on addition of small amounts of NaOH. This is demonstrated by experiments performed with cobalt(II)-tetracarboxyphthalocyanine ( $\text{CoPc}(\text{COOH})_4$ ) covalently bonded to PVAm (see Fig. 2). Comparable results have also been obtained using  $\text{CoPc}(\text{SO}_3\text{Na})_4$ : the structural differences between  $\text{CoPc}(\text{COOH})_4$  and  $\text{CoPc}(\text{SO}_3\text{Na})_4$  are at least in this case of minor importance.

Obviously, the concentration–time dependence of  $\text{H}_2\text{O}_2$  (*cf.* Figs. 1 and 2) can only be explained when taking into consideration production as well as conversion of  $\text{H}_2\text{O}_2$ .

### (b) Production of $\text{H}_2\text{O}_2$

The overall stoichiometry of the oxidation of RSH by  $\text{O}_2$  in an alkaline solution with transition metal compounds as catalysts is represented by  $4\text{RSH} + \text{O}_2 \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O}$ . In such conventional systems no  $\text{H}_2\text{O}_2$  was detected [10] and so a direct four-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$  by means of the catalysts could not be excluded.

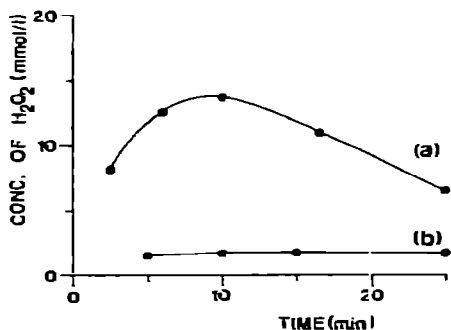


Fig. 3. The accumulation of  $\text{H}_2\text{O}_2$  as a function of the amount of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  during the oxidation of 2-mercaptoethanol using  $10^{-4}$  mol amine (as PVAm; conditions, see Fig. 1). (a)  $10^{-8}$ , and (b)  $10^{-9}$  mol.  $\text{CoPc}(\text{SO}_3\text{Na})_4$ .

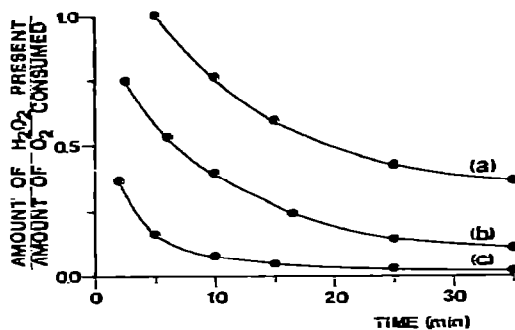
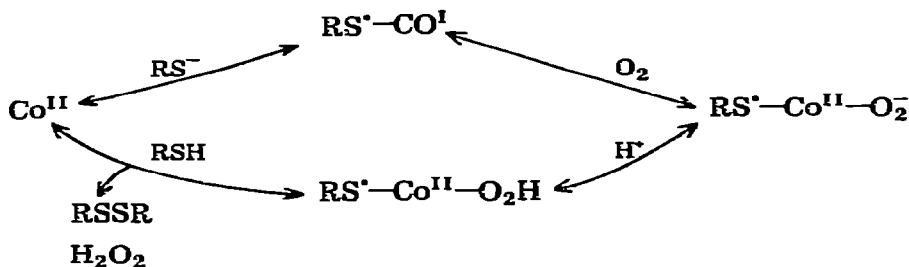


Fig. 4. The influence of the amount of amine on the ratio of the amount of  $\text{H}_2\text{O}_2$  and the amount of consumed  $\text{O}_2$  during the oxidation of 2-mercaptoethanol catalyzed by  $\text{CoPc}(\text{SO}_3\text{Na})_4(10^{-8}$  mol)/PVAm complexes (conditions, see Fig. 1). (a)  $10^{-5}$ , (b)  $10^{-4}$ , and (c)  $5 \times 10^{-4}$  mol amine.

On the other hand, we have found that with CoPc bonded on polymers with amine groups,  $\text{H}_2\text{O}_2$  was present as an intermediate and the amount of  $\text{H}_2\text{O}_2$  depended strongly on the amount of CoPc in the reaction mixture (see Fig. 3). From measurements at low  $[\text{amine}]/[\text{CoPc}]$  ratios (Fig. 4), it can even be concluded that all  $\text{O}_2$  consumed by the thiol oxidation is converted to  $\text{H}_2\text{O}_2$  before it is reduced to  $\text{H}_2\text{O}$ . Our results strongly indicate that the production of  $\text{H}_2\text{O}_2$  is catalyzed by CoPc and in analogy with a mechanism suggested previously [9], we present in scheme I a mechanistic interpretation of the production of  $\text{H}_2\text{O}_2$  during thiol oxidation with cobaltphthalocyanines.



Scheme I.

### (c) Conversion of $\text{H}_2\text{O}_2$

In order to establish the precise role of  $\text{H}_2\text{O}_2$  during the catalytic oxidation of thiols, the various possibilities for the conversion of  $\text{H}_2\text{O}_2$  have been investigated separately.

We have found that the uncatalyzed decomposition of  $\text{H}_2\text{O}_2$  according to eqn. (4) does not contribute considerably to the conversion of produced

$\text{H}_2\text{O}_2$ : the rate of reaction (4) is some orders of magnitude lower than the rate of  $\text{H}_2\text{O}_2$  conversion during thiol oxidation with bifunctional catalysts. Our results are in agreement with literature data [18] demonstrating that the decomposition of  $\text{H}_2\text{O}_2$  is a very slow reaction in the absence of transition metal ions.



The decomposition of  $\text{H}_2\text{O}_2$  according to eqn. (4) is catalyzed by various metal ions and metal ion complexes [19, 20]. In biological systems, peroxide decomposition is carried out by the enzyme catalase, which is a heme iron protein containing four heme groups per molecule, each heme moiety consisting of high-spin iron (III) in a protoporphyrin IX ring [20]. The catalase-like activity of various metallophthalocyanines has been investigated in recent years because of the structural similarity of phthalocyanines with the naturally occurring porphyrins. Also,  $\text{CoPc}(\text{SO}_3\text{Na})_4$  has shown catalytic activity for the  $\text{H}_2\text{O}_2$  disproportionation reaction, although it has been proved by several authors [21, 22] that Fe-phthalocyanines are considerably more active catalysts. However, the available turnover numbers for the decomposition of  $\text{H}_2\text{O}_2$  catalyzed by  $\text{CoPc}(\text{SO}_3\text{Na})_4$  are much lower than the turnover numbers usually encountered in the production of  $\text{H}_2\text{O}_2$  during RSH oxidation with polymer-bonded phthalocyanines. A typical value for the turnover number of the decomposition of  $\text{H}_2\text{O}_2$  in a polymer-free  $\text{CoPc}(\text{SO}_3\text{Na})_4$  solution (at pH = 8 and  $T = 25^\circ\text{C}$ ) is  $1 \text{ min}^{-1}$  [23], whereas with our bifunctional system the turnover number for the production of  $\text{H}_2\text{O}_2$  is of the order of  $10^4 \text{ min}^{-1}$ . Evidently, it is very unlikely that the  $\text{CoPc}$  is able to provide a significant contribution to the conversion of  $\text{H}_2\text{O}_2$  during the thiol oxidation experiments.

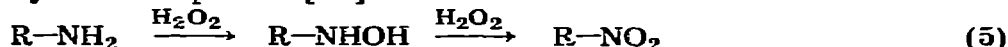
Moreover, in the presence of an excess of poly(vinylamine) (*i.e.*  $[\text{amine}]/[\text{CoPc}] > 200$  as is usual in catalytic experiments)  $\text{CoPc}(\text{SO}_3\text{Na})_4$  has virtually lost its catalytic activity for decomposition of  $\text{H}_2\text{O}_2$ . This is confirmed by visible light spectroscopy on solutions containing for example  $10^{-3} \text{ mol/l H}_2\text{O}_2$ ,  $10^{-3} \text{ mol/l amine}$  and  $2 \times 10^{-6} \text{ mol/l CoPc}(\text{SO}_3\text{Na})_4$  (see also ref. 11); even after 2 h no perceptible change occurred in the spectra. Nevertheless, bubbling of oxygen through these solutions immediately caused the formation of binuclear cobalt dioxygen adducts (see ref. 11), while in a polymer-free solution both the addition of  $\text{H}_2\text{O}_2$  as well as the bubbling through of oxygen immediately produced these binuclear dioxygen adducts.

Evidently, the presence of PVAm inhibits the interaction of  $\text{H}_2\text{O}_2$  with  $\text{CoPc}(\text{SO}_3\text{Na})_4$ . The above observations strongly suggest that amine groups of the polymeric base compete with  $\text{H}_2\text{O}_2$  for the 'free' coordination positions at the cobalt nucleus. Waldmeier *et al.* [23] have reported a fall in the catalase-like activity of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  on addition of imidazole. They explained this phenomenon by taking into account an obstruction of the two 'free' ligand positions at the catalyst by imidazole. Unfortunately, their explanation is not directly applicable to our system, because ESR-measure-

ments have shown that the formation of complexes of PVAm and a CoPc includes the coordinative interaction of amine groups of the polymer with only one apical site of the cobalt complex [10]. In such a case still one apical site of the cobalt complex is left available for an entering peroxide molecule.

However, Sigel *et al.* [24] and Barteri *et al.* [25] have shown recently a drastic loss of catalase-like activity of trans-Co and -Fe complexes when only one of the two available coordination positions is blocked by a ligand not displaceable by  $H_2O_2$  molecules. Our present experiments reveal that the addition of PVAm to  $CoPc(SO_3Na)_4$  results in a dramatic fall in catalase-like activity, and confirm the idea [24, 25] that an intramolecular dual-site mechanism for the catalytic  $H_2O_2$  decomposition is far more efficient than a single-site mechanism.

A third possibility for the conversion of  $H_2O_2$  is formed by its reaction with the primary amine groups of the carrier resulting in the formation of hydroxylamines, which in turn are susceptible to further oxidation into primary nitro compounds [26].



Experimental work has not given any indication that reaction (5) occurs with poly(vinylamine) under our catalytic conditions: IR measurements have demonstrated that PVAm is not affected in aqueous solutions containing peroxide in a concentration comparable with that usually encountered during oxidation experiments with bifunctional catalysts. Furthermore, we found that pretreatment of a bifunctional PVAm/ $CoPc(SO_3Na)_4$  catalyst with  $H_2O_2$  for 1 h before the start of a catalytic run results in the same high reaction rate as in the case that the catalyst is treated with  $H_2O_2$  immediately before the start of the RSH oxidation reaction.

Finally, the reaction of  $H_2O_2$  with RSH has been investigated. This reaction has already been proposed by us as being the main reason for the consumption of  $H_2O_2$  during thiol oxidation [10]. The results of the reaction of RSH with  $H_2O_2$  in the presence of NaOH and PVAm with exclusion of  $O_2$  and CoPc are presented in Fig. 5. It appears that the reaction rate strongly depends on the amount of added base. Comparison of the measurements performed with equivalent amounts of NaOH and amine groups (see Fig. 5) reveals that the reaction rate is higher when using NaOH. Comparing both types of base one has to realize that use of polymeric base has advantages as well as disadvantages: in the catalytic conversion of RSH the high local concentration of both  $RS^-$  and  $CoPc(SO_3Na)_4$  at the polymer gives the polymeric system a strong advantage compared with the system using NaOH. On the other hand, in case of reaction of RSH with  $H_2O_2$ , the  $H_2O_2$  will not become attached to the polymer and then the inhomogeneous distribution of basic sites in the solution is a disadvantage causing diffusional limitations. Addition of  $CoPc(SO_3Na)_4$  ( $10^{-7}$  mol) or bubbling of oxygen through the solutions had no noticeable influence on the observed rates of reaction of  $H_2O_2$  with 2-mercaptoethanol.



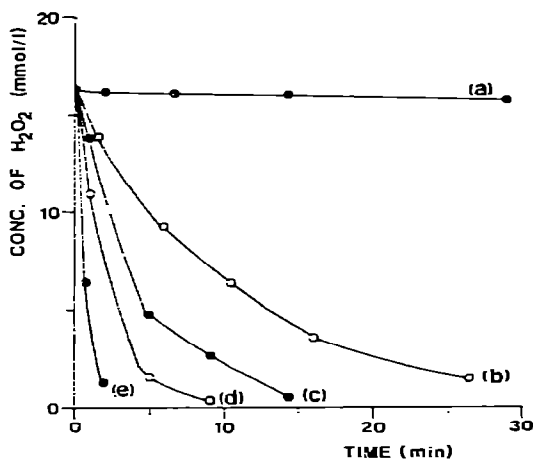


Fig. 5. The conversion of  $\text{H}_2\text{O}_2$  as a consequence of its reaction with 2-mercaptoethanol as a function of the added base (conditions:  $T = 23^\circ\text{C}$ ;  $p(\text{O}_2) = 1 \text{ atm}$ ; reaction volume, 75ml; 14.25 mmol thiol;  $[\text{H}_2\text{O}_2] = 1.6 \times 10^{-2} \text{ mol/l}$ ). (a) no base, (b)  $10^{-4} \text{ mol}$  amine (as PVAm), (c)  $10^{-4} \text{ mol}$  NaOH, (d)  $5 \times 10^{-4} \text{ mol}$  amine (as PVAm), and (e)  $5 \times 10^{-4} \text{ mol}$  NaOH.

Our results are in agreement with the literature data concerning the reaction of  $\text{H}_2\text{O}_2$  with other thiols [27, 28]. Barton *et al.* [27] have investigated the reaction of  $\text{H}_2\text{O}_2$  with cysteine and cysteamine in the pH range 6 - 11. These authors have demonstrated that their kinetic results can be explained by a mechanism in which the rate-limiting step consists of a nucleophilic attack of the thiolate anion on an oxygen atom of  $\text{H}_2\text{O}_2$ . Most probable the reaction of the nucleophilic  $\text{RS}^-$  species with  $\text{H}_2\text{O}_2$  occurs via simple  $\text{S}_\text{N}2$  substitution reactions, as shown in eqns. (6) and (7).

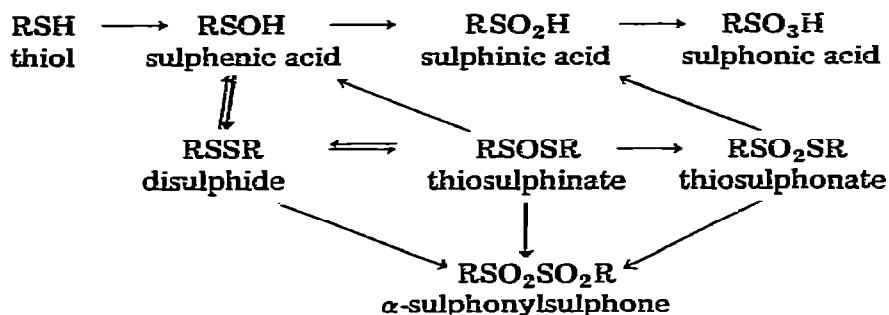


The rate of reaction of  $\text{H}_2\text{O}_2$  with RSH that is derived from Fig. 5 agrees with the rate of the consumption of  $\text{H}_2\text{O}_2$  during oxidation of RSH with the bifunctional catalysts. This demonstrates that this reaction is the main way for conversion of the  $\text{H}_2\text{O}_2$  formed.

#### (d) Deactivation of the catalysts

Although the reaction between RSH and  $\text{H}_2\text{O}_2$  results in a highly selective formation of disulphides, literature data [28] show that small amounts of higher oxidation products may be formed. Scheme II displays some interconversions which are possible between the sulphur functional groups starting from thiols [1]. Some of the steps shown in this scheme may be bypassed

and alternative hydrolytic products may be possible. The main end product to be expected is sulphonic acid due to the instability of most of the other oxidation products [26]



Scheme II.

In order to check the formation of sulphur-acids in our catalytic system we have carried out the following set of experiments. Firstly, an oxidation experiment has been performed with cobalt(II)-tetraaminophthalocyanine ( $\text{CoPc}(\text{NH}_2)_4$ ) coupled with the aid of 2,4,6-trichloro-s-triazine to Enzacryl AA (20 mg of this heterogeneous catalyst containing 0.25 wt.% of Co was applied) as a catalyst using 6 mmol of NaOH and 1 ml (14.25 mmol) 2-mercaptoethanol (RSH). As expected, during this experiment no  $\text{H}_2\text{O}_2$  accumulation could be detected and we assume the disulphide (RSSR) is produced with high selectivity. Having completed the conversion of RSH, the catalyst was separated and the reaction mixture neutralized with 0.1 N HCl. A small part of this solution was poured into a beaker and carefully concentrated by flushing with oxygen-free nitrogen. Application of this concentration method during one night resulted in a highly viscous product. The IR spectrum of one drop of this material between CsI discs is given in Fig. 6(a).

When 25 ml of an aqueous 0.1 M  $\text{H}_2\text{O}_2$  solution is added to 25 ml of the neutralized solution (containing 1.4 mmol RSSR) and the resulting mixture is concentrated at ambient temperature as just described, the material obtained shows an IR spectrum as depicted in Fig. 6(b). In the latter spectrum absorption peaks show up that are absent in Fig. 6(a) and which can be assigned to sulphur-containing oxo-compounds (see for instance ref. 29), *i.e.* 1312 ( $\text{O}=\text{S}=\text{O}$ , asymm.), 1118 ( $\text{O}=\text{S}=\text{O}$ , symm), 612 ( $\text{S}-\text{O}_2$ ), 560 and  $525\text{ cm}^{-1}$  ( $\text{S}-\text{O}_3$ ).

Subsequently, we have performed an RSH oxidation experiment using a bifunctional catalyst in the absence of additional alkaline base (*i.e.* Enzacryl AA modified by amine groups and  $\text{CoPc}(\text{NH}_2)_4$  coupled to this carrier using 2,4,6-trichloro-s-triazine as coupling agent, see experimental). Using 10.7 mg of this heterogeneous catalyst (containing 0.66 wt.% of Co) for the conversion of 1 ml (14.25 mmol) RSH under standard conditions we observe — as expected — the accumulation of  $\text{H}_2\text{O}_2$  in the reaction mixture.

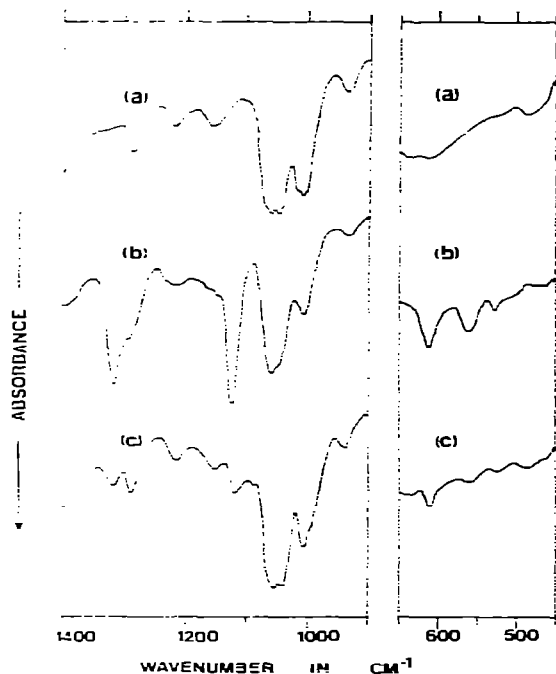


Fig. 6. IR analysis of the reaction products after oxidation of 2-mercaptoethanol under various conditions: (a) in the presence of catalyst and NaOH, (b) the product of (a) after additional treatment with  $\text{H}_2\text{O}_2$ , and (c) in the presence of bifunctional catalyst without additional NaOH.

When after complete conversion of the thiol the reaction mixture is subjected to the same concentration procedure as described above, we obtain a product which gives the IR spectrum shown in Fig. 6(c). Comparison of the latter spectrum with Fig. 6(a) and 6(b) reveals that the characteristic peaks of sulphur-containing oxo-acids are also present in spectrum 6(c). In conclusion, we have shown the possibility that small amounts of sulphur acids may be produced during the autoxidation of thiols with bifunctional catalysts.

In a previous article [9] we have demonstrated the essential role of the basic groups in our bifunctional catalysts. It was found that addition of a stoichiometric amount of HCl was sufficient for a dramatic decrease of the catalytic activity. Poisoning of the basic sites of the polymeric catalysts will also occur when strong sulphur-containing oxo-acids are formed during the catalytic oxidation of thiols. Due to the excess of RSH in relation to the amount of catalyst in our oxidation experiments, stoichiometric amounts of basic groups and strong sulphur acids are already obtained when a low percentage (<1%) of the amount of RSH is converted to sulphur acids.

The known sensitivity of metallophthalocyanines towards oxidative destruction prompted us to consider also deactivation of our bifunctional catalyst by means of decomposition of CoPc by  $\text{H}_2\text{O}_2$ . The instability of

metallophthalocyanines and related chelates is thought to be caused by direct demetallation and by hydroxylation of the mesoposition followed by ring cleavage and demetallation [30, 31].

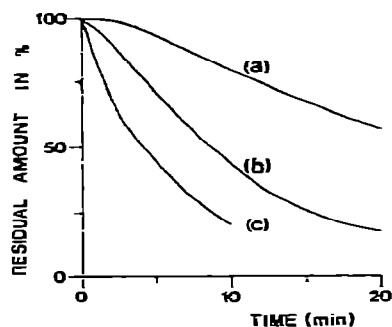


Fig. 7. The destruction of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  ( $2.5 \times 10^{-6}$  mol/l) by  $\text{H}_2\text{O}_2$  ( $1.3 \times 10^{-2}$  mol/l) according to visible light spectral measurements at  $15\,000\text{ cm}^{-1}$  determined as a function of pH (at ambient temperature). (a) pH 10.2, (b) pH 9.1, and (c) pH 5.8.

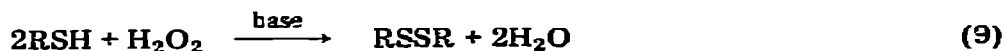
We have investigated the decomposition of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  as a function of the pH. It appears that in polymer-free solutions the stability of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  is increased at higher pH-values (see Fig. 7). However, in the presence of excess PVAm, as usual in our catalytic experiments, the degradation of the phthalocyanine did not show up. This shows once again that the presence of PVAm inhibits the interaction of  $\text{H}_2\text{O}_2$  with  $\text{CoPc}(\text{SO}_3\text{Na})_4$ . When the bonding interaction between the amine groups of PVAm and the CoPc is hindered, for instance by addition of acid, the interaction of  $\text{H}_2\text{O}_2$  with CoPc is not prohibited anymore. In the latter case decomposition of CoPc does occur. Such a situation may arise when during RSH oxidation with the bifunctional catalyst, a low pH ( $\text{pH} < 6$ ) is generated as a consequence of the formation of strong sulphur-containing oxo-acids.

An oxidation experiment with  $\text{CoPc}(\text{SO}_3\text{Na})_4$  ( $10^{-7}$  mol)/PVAm ( $10^{-4}$  mol amine) as catalyst has revealed that after five runs (each run carried out with 14.25 mmol 2-mercaptoethanol as substrate) 30% of the original amount of  $\text{CoPc}(\text{SO}_3\text{Na})_4$  is decomposed, according to visible light spectral measurements at  $15\,000\text{ cm}^{-1}$ . However, the catalytic activity in the fifth run is only  $\pm 2\%$  of the original activity, so it may be concluded that deactivation of the catalyst is not primarily caused by decomposition of  $\text{CoPc}(\text{SO}_3\text{Na})_4$ .

## Conclusions

During the catalytic oxidation of thiol (RSH) to disulphide (RSSR) the presence of  $\text{H}_2\text{O}_2$  can be accounted for by the reactions (8) and (9)





The relative rates of these reactions determine the amount of accumulated  $\text{H}_2\text{O}_2$  in the reaction system and these rates can be varied with respect to each other as is proven by the results given in Figs. 1 - 3. A crucial aspect of this coupled oxidation system is that only the production of  $\text{H}_2\text{O}_2$  (eqn. (8)) is catalyzed by CoPc, whereas the influence of CoPc on the conversion of  $\text{H}_2\text{O}_2$  is of negligible importance.

On the other hand, the role of base in the catalytic oxidation of thiols is a more complicated one. In addition to the conversion of RSH into reactive  $\text{RS}^-$  species, which is necessary for reaction (8) as well as for reaction (9), the base also takes care of the neutralization of the small quantities of sulphur acids formed according to scheme II.

The deactivation of the bifunctional catalysts in the absence of additional alkaline base is mainly the result of the poisoning of the basic sites by these sulphur acids. Although decomposition of the CoPc in the bifunctional catalysts has been observed, this is not the primary cause of the deactivation. Furthermore, the contribution of the conversion of the amine groups by  $\text{H}_2\text{O}_2$  to the poisoning can be neglected.

In reaction systems containing a surplus of NaOH a fair stability of the catalytic activity was observed under our conditions and in such systems also no perceptible  $\text{H}_2\text{O}_2$  accumulation occurred (see also ref. 10). However, the absence of a detectable amount of  $\text{H}_2\text{O}_2$  does not preclude its intermediate production, since our present measurements have demonstrated that the base catalyzed reaction of  $\text{H}_2\text{O}_2$  with RSH (eqn. (9)) can account for a rapid conversion of  $\text{H}_2\text{O}_2$ .

Since the deactivation of the bifunctional catalysts is apparently connected with the accumulation of  $\text{H}_2\text{O}_2$  our forthcoming research will be concerned with the *in situ* decomposition of the produced  $\text{H}_2\text{O}_2$  by means of compounds with a high catalase-like activity.

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