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Role of Polycation Promoters in the Cobalt Phthalocyanine-Catalyzed Autoxidation of Thiols

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Introduction

When polymers are used as support for a catalyst, reaction rate, selectivity and even the reaction mechanism can be changed by polymeric effects.¹ The fact that polymers can be tailor-made, offers the opportunity to influence these effects due to specific macromolecular ligation. It appeared that several cationic polymers have large promoting effects on the cobalt(II) phthalocyaninetetra-sodiumsulfonate- ($\text{CoPc}(\text{NaSO}_3)_4$) (Fig. 1) catalyzed thiol autoxidation (Scheme 1). The best co-catalysts proved to be poly(quaternary ammonium)salts, the so-called ionenes (Fig. 2).² In the case of the addition of 2,4-ionene the highest rate enhancement is observed, i.e. by a factor of 40, as compared with the polymer-free system.³ Three polymer promoting effects are responsible for this rate increase. In this paper we will discuss their separate contributions to the overall activity. In order to elucidate which polymeric promoting effect has the largest contribution to this rate enhancement we will focus on substrate enrichment, which could perfectly be studied by using the water-soluble cobalt(II) phthalocyanineoctacarboxylic acid ($\text{CoPc}(\text{COOH})_8$). Also, in order to make separation of products and catalyst after the thiol oxidation possible, the catalytic system was immobilized on latices.

Experimental Part

The polymeric 2,4-ionenes were prepared according to the method developed by Rembaum et al.⁴ The monodisperse ionene oligomers were prepared according to earlier described procedures.⁵⁻⁷ $\text{CoPc}(\text{NaSO}_3)_4$ was kindly provided by dr. T.P.M. Beelen (Eindhoven University of Technology) and had been prepared according to a slight adaption of the original method described by Weber and Busch.^{8,9} $\text{CoPc}(\text{COOH})_8$ was kindly provided by prof. Shirai (Shinshu University, Ueda, Japan) and was synthesized according to a literature method.¹⁰ The catalytic thiol autoxidations were carried out batchwise as reported previously.¹¹

Results and Discussion

The effect of varying the 2,4-ionene/ $\text{CoPc}(\text{NaSO}_3)_4$ ratio, expressed as the N^+/Co ratio, on the mercaptoethanol oxidation rate is illustrated in Fig. 3. At low ionene concentrations low activities are observed due to the presence of the catalytically inactive dioxygen bridged μ -peroxo complex.¹² Further addition of polymer, the formation of the inactive μ -peroxo complex is strongly suppressed. Simultaneously, dimers of the $\text{CoPc}(\text{NaSO}_3)_4$ catalyst are formed, which are more active than the monomeric species.^{3,13} Furthermore,

the presence of the ionenes leads to substrate enrichment, i.e. higher local concentrations of the thiolate anions, the reactive species near the catalytic active sites in the polyelectrolyte domain. After an optimal N^+/Co ratio of 50 has been reached, further increase in the ionene concentration leads to a reduction in activity as a result of the decrease in the local thiolate anion concentration at the catalytically active sites.

It has been shown before that no μ -peroxo complexes are present at a N^+/Co ratio of 4 in the presence of polymeric 2,4-ionene.¹² The use of monodisperse oligomeric 2,4-ionenes showed that already small units of 2,4-ionene, with only two quaternary ammonium groups separated by four methylene groups, are capable of suppressing the formation of the μ -peroxo complexes and simultaneously inducing aggregation of the cobalt phthalocyanines.⁷ This was rather unexpected because this behaviour was thought to be characteristic of polymeric 2,4-ionene only. The chain length of the ionene appeared to have a minor effect on its excellent co-catalytic activity. The optimal polymer/catalyst ratio is dependent on the molecular weight of the ionene.⁷ The optimal N^+/Co ratio decreases with increasing chain length of 2,4-ionene and reaches a constant value of 50 for a 2,4-ionene with 8 N^+ .

Recently, we studied the spectroscopic and catalytic properties of mixtures of oppositely charged water-soluble cobalt phthalocyanines, which offered the possibility to elucidate the sole contribution of dimerization of the catalyst to the overall activity.¹³ A mixture of equimolar amounts of cobalt(II) phthalocyanine-tetra(trimethylammonium)iodide ($\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$) and $\text{CoPc}(\text{NaSO}_3)_4$ shows an increase in reaction rate for the 2-mercaptoethanol autoxidation as compared with an equal amount of one of the catalyst species separately. A mixture of $\text{CoPc}(\text{COOH})_8$ and $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4$ exhibits its maximum activity at a ratio of 1:2. The catalytic activities of these dimeric and trimeric catalyst complexes are the highest measured so far for any phthalocyanine-catalyzed mercaptoethanol oxidation in the absence of polycations. Upon addition of 2,4-ionene, to an equimolar dimeric $\text{CoPc}[\text{N}(\text{CH}_3)_3\text{I}]_4/\text{CoPc}(\text{NaSO}_3)_4$ complex lower reaction rates are obtained as those achieved for the conventional $\text{CoPc}(\text{NaSO}_3)_4/2,4$ -ionene system. Therefore, it can be concluded that the $\text{CoPc}(\text{NaSO}_3)_4$ -dimers, which are the most catalytically active species, most probably break up during the catalytic cycle.

The water-soluble $\text{CoPc}(\text{COOH})_8$ forms no aggregates or μ -peroxo complexes in the presence of 2,4-ionene under catalytic conditions. Hence this catalyst complex offers the possibility to study exclusively the effect of 2,4-ionene-induced substrate enrichment, i.e. higher local thiolate concentrations near the catalytic centre. Addition of 2,4-ionene to an aqueous $\text{CoPc}(\text{COOH})_8$ solution results in an enhancement by a factor of 2-3, which can entirely be ascribed to substrate enrichment. Applying the monodisperse ionene oligomers it appears that the optimal N^+/Co ratio as a function of the molecular weight of the ionene for the $\text{CoPc}(\text{COOH})_8/2,4$ -ionene system is similar to that of the $\text{CoPc}(\text{NaSO}_3)_4/2,4$ -ionene system. This leads to the conclusion that the optimal 2,4-ionene/ $\text{CoPc}(\text{NaSO}_3)_4$ ratio is predominantly determined by substrate enrichment.

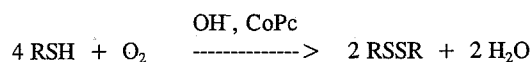
The excellent catalytic $\text{CoPc}(\text{NaSO}_3)_4/2,4$ -ionene combination for the autoxidation of thiols to disulfides does not allow continuous operation because of the homogeneity of the system. Therefore it is necessary to apply a support in order to immobilize the active system. The monodisperse amphiphilic polystyrene-ionene diblock

copolymers, which have been used before as co-catalysts in the hydrophobic thiol oxidation,^{5,6} appear to act as surfactant and are built in latex particles during the emulsion polymerization of styrene. The latices with ionene chains at the particle surface extending into the water phase, are stabilized electrostatically as well as sterically. After immobilization of the cobalt catalyst, high catalytic activities (500 mol O₂ / (mol Co · s)), fifteen times higher as compared with the polymr-free system, were achieved with relatively short ionene blocks with 7 quaternary ammonium groups at their particle surface. Despite relatively low surface charge densities, apparently enough ionene chains of sufficient length are present at the particle surface to stabilize the highly active CoPc(NaSO₃)₄ dimers and to achieve substrate enrichment.

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Scheme 1



where : RSH = thiol and CoPc = cobalt(II) phthalocyanine

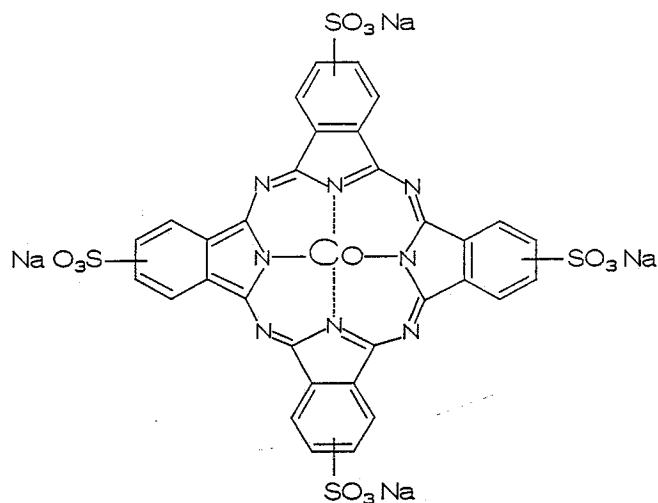


Figure 1 Structure of CoPc(NaSO₃)₄.

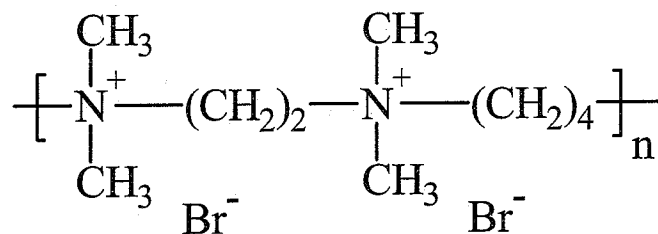


Figure 2 Structure of 2,4-ionene.

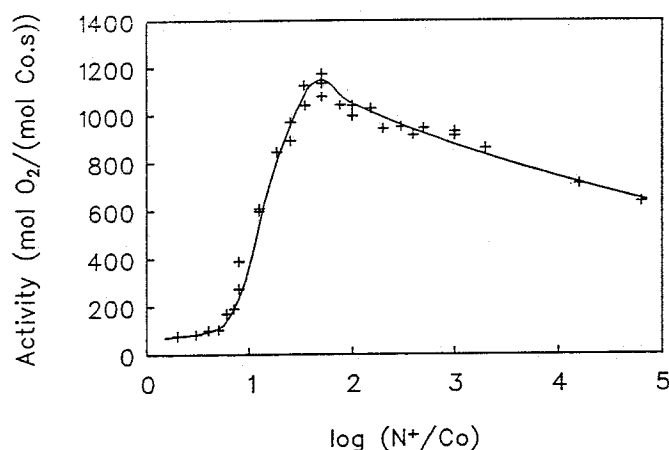


Figure 3 Effect of the 2,4-ionene concentration on the mercaptoethanol oxidation rate.
 [CoPc(NaSO₃)₄] = 2 · 10⁻⁷ mol · dm⁻³,
 pH = 9.0, [thiol] = 7.1 · 10⁻² mol · dm⁻³,
 M_n(2,4-ionene) = 6200 g · mol⁻¹.