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Role of Polycation Promoters in the Cobalt(II) Phthalocyaninetetracarboxylic and -Octacarboxylic Acid-Catalyzed Autoxidation of Mercaptoethanol

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SYNOPSIS

The promoting effects of 2,4-ionene on the cobalt(II) phthalocyaninetetracarboxylic acid-[CoPc(COOH)$_4$] and cobalt(II) phthalocyanineoctacarboxylic acid-[CoPc(COOH)$_8$] catalyzed autoxidation of 2-mercaptoethanol were studied. Dimerization of the CoPc(COOH)$_4$ catalyst, combined with the disappearance of the catalytically inactive μ-peroxo complex and the appearance of substrate enrichment in the presence of 2,4-ionene, results in a 40-fold enhancement of the oxidation rate as compared with the polymer-free system. UV–VIS spectroscopy indicates that CoPc(COOH)$_8$ is incapable of forming μ-peroxo complexes or 2,4-ionene-induced dimeric catalyst species under normal reaction conditions. Thus, it was possible to study exclusively the ionene-induced effect of substrate enrichment. Addition of 2,4-ionene to an aqueous CoPc(COOH)$_8$ solution results in an activity enhancement by a factor of 2–3, which can be ascribed to substrate enrichment. Additionally, using monodisperse ionene oligomers showed a molecular weight dependence of 2,4-ionene on the catalytic activity of CoPc(COOH)$_8$, as was observed for the conventional 2,4-ionene/cobalt phthalocyaninetetrasodiumsulfonate system. The optimal polycation/catalyst ratios of both systems decrease with increasing chain length of 2,4-ionene, until a constant value is reached. This leads to the conclusion that the optimal polymer/catalyst ratios are predominantly determined by substrate enrichment. © 1995 John Wiley & Sons, Inc.

Keywords: 2,4-ionene • poly(quaternary ammonium)salt • cobalt(II) phthalocyaninetetracarboxylic acid • cobalt(II) phthalocyanineoctacarboxylic acid • mercaptoethanol • autoxidation • catalysis

INTRODUCTION

In catalytic reactions polymers can play different roles. Aside from acting as support for a catalyst, or functioning as catalysts themselves, polymers can exert different types of promoting effects on catalytic reactions.[1-5] One of the most important polymeric promoting effects on catalytic reactions is substrate enrichment caused by electrostatic or hydrophobic interactions, resulting in higher local substrate con-

centrations and therefore leading to higher reaction rates.[1,6,7] Substrate enrichment is also one of the three promoting effects polycations exhibit on the cobalt(II) phthalocyaninetetrasodiumsulfonate-[CoPc(NaSO$_3$)$_4$] (Fig. 1) catalyzed autoxidation of thiols to disulfides.[8-11] Since the thiolate anions and the catalyst are both negatively charged, the presence of polycations, especially ionenes (poly-(quaternary ammonium)salts)[8] (Fig. 2), results in higher local concentrations of the thiolate anions near the catalytically active sites in the polyelectrolyte domain. Besides, the formation of the catalytically inactive dioxygen bridged μ-peroxo complex is suppressed; simultaneously, aggregates of CoPc-(NaSO$_3$)$_4$ are formed due to the presence of ion-
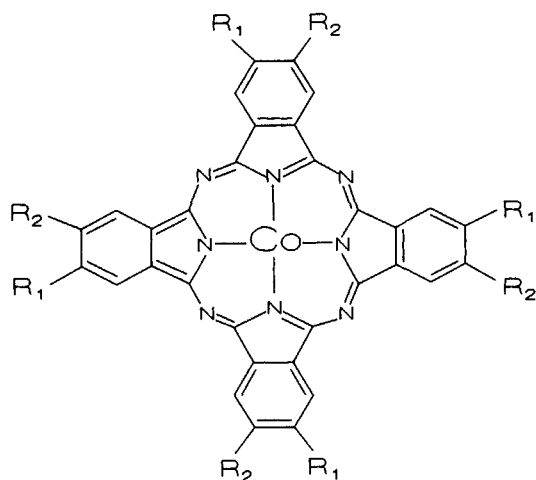
	R_1, R_2
CoPc(NaSO$_3$)$_4$	SO$_3$Na, H
CoPc(COOH)$_4$	COOH, H
CoPc(COOH)$_8$	COOH, COOH

Figure 1. Structures of CoPc(NaSO$_3$)$_4$, CoPc(COOH)$_4$, and CoPc(COOH)$_8$.

enes.[12] These three effects collectively contribute to an increase in the catalytic activity induced by polycations. In the case of the addition of 2,4-ionene, the highest rate enhancement is observed, i.e., by a factor of 40, compared with the polymer-free system.[9]

To elucidate which polycationic promoting effect has the largest contribution to this rate enhancement, we recently investigated the role of dimerization of the catalytic species by means of studying the spectroscopic and catalytic properties of mixtures of oppositely charged water-soluble cobalt(II) phthalocyanine complexes.[13] From these results it was concluded that the dimeric CoPc(NaSO$_3$)$_4$ species is the catalytically active species, which will probably break up after the first reaction step. The second effect, the suppression of inactive μ-peroxo complex formation in the presence of ionenes, appears to occur already at a low polymer/catalyst ratio.[12] In this article we are focused on the third ionene promoting effect, i.e., substrate enrichment.

It appears that cobalt(II) phthalocyanineoctacarboxylic acid [CoPc(COOH)$_8$] (Fig. 1), a catalyst which has been used before to study H$_2$O$_2$ decomposition,[14] the thiol oxidation[15] and after immobilization on cellulose fibers for the application of odor-removers,[16] provides valuable insight into this

ionene promoting effect. The spectroscopic properties of CoPc(COOH)$_8$ in the presence of ionene will be discussed here. In addition, the promoting effect of 2,4-ionene on the CoPc(COOH)$_8$-catalyzed mercaptoethanol oxidation will be studied. Moreover, we investigated the influence of the chain length of 2,4-ionene on the process of substrate enrichment, which was found to have a large influence on the conventional 2,4-ionene/CoPc(NaSO$_3$)$_4$ system.[17] Furthermore, the catalytic properties of CoPc(COOH)$_8$ were compared with those of cobalt(II) phthalocyaninetetracarboxylic acid (CoPc(COOH)$_4$) (Fig. 1), containing four negative charges.

EXPERIMENTAL

Materials

CoPc(NaSO$_3$)$_4$ was kindly provided by T.P.M. Beelen (Eindhoven University of Technology) and had been prepared according to the method described by Weber and Busch.[18,19] CoPc(COOH)$_8$ was kindly provided by H. Shirai (Shinshu University, Ueda, Japan) and was synthesized according to a literature method.[20]

The synthesis of cobalt phthalocyaninetetracarboxylic acid [CoPc(COOH)$_4$] was carried out with a few modifications according to the procedure described by Shirai et al.,[21] and by Wöhrle et al.[22] First, cobalt phthalocyaninetetracarboxamide [CoPc(CONH$_2$)$_4$] was prepared: trimellitic anhydride (1,2,4-benzenetricarboxylic anhydride) (10.0 g) (Janssen Chimica, 97%), urea (30.0 g) (Merck, p.a.), cobalt(II) chloride (3.9 g) (Janssen Chimica, 97%), and ammonium molybdate(VI)-tetrahydrate (1.3 g) (Janssen Chimica, p.a.) were thoroughly mixed with 50 mL of nitrobenzene, and this mixture was added to 100 mL of nitrobenzene in a round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser. The mixture was heated in an argon atmosphere for 3 h at 160°C. After filtration, the crude reaction product was washed with methanol, followed by extraction with methanol for 48 h in a soxhlet apparatus to remove the remaining nitrobenzene. Subsequently, most of the inorganic contaminants were removed by extraction with water
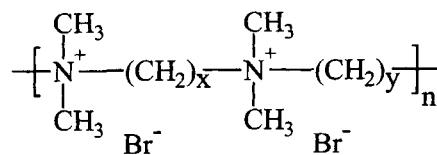

Figure 2. Structure of x,y-ionene.

for 4 days. This product was acidified with 600 mL of 6M HCl and stirred for 24 h, followed by filtration. Next, the product was extracted with an acetone/water mixture for 16 h. The blue-green solid obtained was dried at reduced pressure at 50–70°C for 5 days. Yield of CoPc(CONH$_2$)$_4$: 8.08 g (87%).

Subsequently, CoPc(CONH$_2$)$_4$ (2.0 g), KOH (50 g), and water (50 mL) were refluxed in a round-bottomed flask for 24 h. After this, the following purification procedure was carried out: first, the reaction mixture was acidified with 6M HCl to pH 2. Then, the blue precipitate was filtered off and washed with 0.1M HCl, acetone and ether. The obtained product was dissolved in 500 mL of water at pH 10. This solution was filtrated and the filtrate was again acidified. After repeating this procedure three times, the product was washed with water, ethanol, and ether, and dried at reduced pressure at 70°C for 24 h. Yield of CoPc(COOH)$_4$·4H$_2$O: 1.2 g (60%).

ANAL. Calcd for CoPc(COOH)$_4$·4H$_2$O: C, 52.76%; H, 2.95%; N, 13.68%. Found: C, 52.65%; H, 2.93%; N, 13.71%.

2,4-Ionene ($\bar{M}_n$ = 6200 g/mol) was synthesized according to the method described by Rembaum et al.[23] The preparation procedure for oligomeric ionenes has been described recently.[17,24,25]

Visible Light Absorption Spectroscopy

All VIS spectra were recorded on a Hewlett-Packard diode array 8451 A spectrophotometer at 25°C, using a 1 cm cell of quartz.

Catalytic Activity Measurements

The catalytic thiol autoxidations were carried out batchwise as reported previously,[26] in an all-glass double-walled Warburg apparatus (250 mL), equipped with a powerful mechanical glass stirrer (the stirring speed was 2600 rpm) and thermostated at 25.0 ± 0.1°C. The catalyst solution (consisting of the cobalt phthalocyanine complex, polymers, and doubly distilled water) was added to the reactor, followed by adjustment of the pH by the addition of a concentrated KOH (Merck, p.a.) solution (total reaction volume was always 0.10 dm^3). The reaction vessel was degassed, followed by saturation of the solution with oxygen. After repeating this procedure twice, the mixture was stirred vigorously for 5 min. The reaction was started by addition of 2-mercaptoethanol (ME) by a syringe into the reactor. Prior to use, ME (Janssen Chimica, 98%) was distilled in

an argon atmosphere, stored in the dark, and kept under argon in sealed flasks at 5°C.

Reaction rates were monitored by measuring the oxygen uptake with a digital mass flow controller (Inacom, Veenendaal), having a maximal capacity of 10 or 50 cm^3/min, at constant oxygen pressure at 100 ± 0.05 kPa. The pressure was kept constant with a Micro Switch 142PC01D pressure meter. The initial reaction rate, determined as the maximum in the oxygen flow, was measured immediately after ME was added. During the reaction, the pH was monitored by a GK 2401B pH electrode (Radiometer), connected to a pHM 62 pH meter.

RESULTS AND DISCUSSION

Effects of 2,4-Ionene on the Spectroscopic Behavior of CoPc(COOH)$_4$ and CoPc(COOH)$_8$

Because ionenes showed a large influence on the aggregation behavior of CoPc(NaSO$_3$)$_4$,[12,17] it is necessary to study the spectroscopic properties of CoPc(COOH)$_8$ in the presence of ionene before performing catalytic experiments. The visible light absorption spectrum of CoPc(COOH)$_8$ under neutral conditions [(pH 7, ionic strength (I) = 0.1M] is depicted in Figure 3. Two main absorption bands can be detected, i.e., at 618 and at 682 nm.[27] At pH 7.0 all carboxyl groups in the peripheral site of the phthalocyanine ring will be dissociated into carboxylates.[15] Varying the conditions (pH = 13, O$_2$ atmosphere) a spectrum was obtained comparable with the spectrum at pH 7. No formation of a dioxygen-bridged dimeric μ-peroxo complex was detected, which in the case of CoPc(NaSO$_3$)$_4$ normally appears
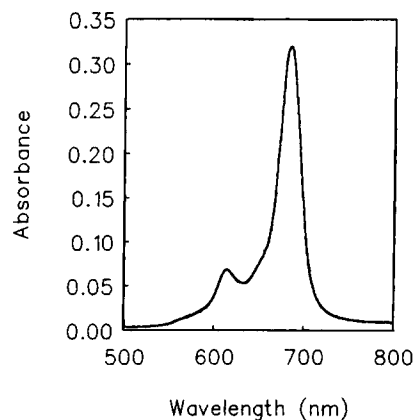

Figure 3. Absorption spectrum of an aqueous solution of CoPc(COOH)$_8$ at pH 7 (I = 0.1M). [CoPc(COOH)$_8$] = 5 × 10^{-6} mol dm^{-3}.

at high pH under aerobic conditions.[28] Presumably, it may be stated that $CoPc(COOH)_8$ is unable to form μ-peroxo complexes.

Additionally, dissolving $CoPc(COOH)_8$ in N,N-dimethylformamide under anaerobic conditions (argon atmosphere), a solvent in which phthalocyanine aggregates are known to dissociate into monomeric species upon addition,[29] did not lead to any shift in the VIS spectrum.

The question arises if the highly charged $CoPc(COO)_8^{8-}$ is capable of forming dimeric complexes. Aggregation of charged phthalocyanine complexes normally can be achieved in the presence of high electrolyte concentration[30-32] or induced by polyelectrolytes.[12] No dimerization of the catalyst was observed after addition of KCl or 2,4-ionene to an aqueous $CoPc(COOH)_8$ solution (pH > 7): the absorption spectrum was unaffected. Obviously, the neutralizing of the negative charges by cations or ionene proceeds inefficiently, so the repulsive forces between the two cobalt phthalocyanine anions remain too large to form a dimeric complex. Thus, it can be stated that in an alkaline solution no aggregation of $CoPc(COOH)_8$ can be attained upon addition of salts or polysalts. Thus, no aggregation of $CoPc(COOH)_8$ will occur during the catalytic experiments.

In addition, we studied the spectroscopic behavior of $CoPc(COOH)_4$ in the presence of 2,4-ionene. It should be expected that the spectral properties of $CoPc(COOH)_4$ in the presence of 2,4-ionene would not differ from those of $CoPc(NaSO_3)_4$, because only electrostatic interactions determine aggregation behavior. In Figure 4 the ratio of the absorbances at 620 nm (monomer) and 672 nm (dimer) of the $CoPc(COOH)_4$ is depicted, as a function of the 2,4-ionene/$CoPc(COOH)_4$ ratio, expressed as the $N^+/$Co ratio. As $N^+/$Co increases from 0 to 4, it appears that the A_{620}/A_{672} ratio, which is a measure of the relative amount of aggregated cobalt species,[12] increases. At $N^+/$Co = 4 [i.e., $\log(N^+/$Co$)$ = 0.6], where no μ-peroxo complexes could be detected, a discontinuity in the plot arises, suggesting the formation of an ionene/$CoPc(COOH)_4$ complex with fixed stoichiometry. Raising the amount of ionene does not influence the A_{620}/A_{672} ratio: the existing complex is not further affected. An analogous aggregation phenomenon has been observed for the conventional 2,4-ionene/$CoPc(NaSO_3)_4$ system.[12,17] Van Welzen et al. also showed that when NaBr is used instead of ionene, no formation of strongly interacting complexes occurred.[12]

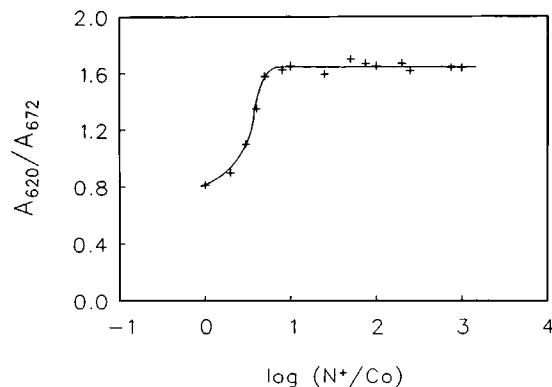These results clearly show that replacement of the peripheral sulfonate group by a carboxylic acid

Figure 4. Ratio of absorbances at 620 and 672 nm as a function of the $N^+/$Co ratio for a 2,4-ionene/$CoPc(COOH)_4$ system. [$CoPc(COOH)_4$] = 2 × 10^{-6} mol dm^{-3}, pH 9 (buffer, I = 0.1M), $\bar{M}_n$(2,4-ionene) = 6200 g mol^{-1}.

group has no influence on the aggregation behavior of the cobalt complex, because purely electrostatic shielding of charges is involved. In a similar way, it has been demonstrated that ionenes also strongly enhance the aggregation for other phthalocyanines, viz. iron(II), manganese and vanadyl phthalocyaninetetrasodium-sulfonates.[33]

Influence of 2,4-Ionene on the Catalytic Properties of $CoPc(COOH)_4$ and $CoPc(COOH)_8$

The incapability of $CoPc(COOH)_8$ to form ionene-induced aggregates under catalytic conditions gives us the opportunity to study solely the effect of substrate enrichment in the $CoPc(COOH)_8$-catalyzed thiol autoxidations. The effect of varying the N^+ concentrations on the 2,4-ionene promoted mercaptoethanol oxidation catalyzed by $CoPc(COOH)_8$ is depicted in Figure 5. At low ionene concentrations low oxidation rates are observed, similar to the activities obtained for a polymer-free system. At a $N^+/$Co ratio of 8, where an electrostatic neutral complex is formed, the oxidation rate increases. A further increase of the N^+ concentration leads to higher reaction rates until the highest catalytic activity is reached at an optimal $N^+/$Co ratio of 50, a value which has also been found for the 2,4-ionene/$CoPc(NaSO_3)_4$ system.[17]

Solely responsible for this rate increase is substrate enrichment, i.e., higher concentrations of the thiolate anions, near the active catalytic sites. Subsequently, a further increase of the polycation concentration leads to a small decrease in the catalytic activity. When large excesses of 2,4-ionene are used,
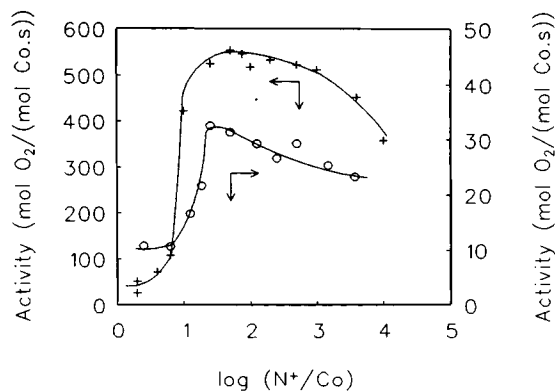
Figure 5. Effect of N^+/Co ratio on the mercaptoethanol oxidation rate: (+) $CoPc(COOH)_4$, $[CoPc(COOH)_4] = 2 \times 10^{-7}$ mol dm^{-3}; (O) $CoPc(COOH)_8$, $[CoPc(COOH)_8] = 2 \times 10^{-6}$ mol dm^{-3}. pH 9.0, [ME] $= 7.1 \times 10^{-2}$ mol dm^{-3}, $\bar{M}_n$(2,4-ionene) $= 6200$ g mol^{-1}.

many thiolate anion rich domains will not contain the catalyst and thus be less effective.

The rate enhancement after addition of 2,4-ionene to $CoPc(COOH)_8$, caused only by substrate enrichment is a factor of 2–3. Similar rate enhancements as compared with ionene-free systems have been observed in other phthalocyanine-containing systems. Addition of 2,4-ionene to a dimeric CoPc-$[N(CH_3)_3I]_4/CoPc(NaSO_3)_4$ complex also raised the reaction rate.[13] Despite a net zero charge of this complex, an acceleration factor of 2–3 was obtained, indicating that this dimeric complex is totally present in the polyelectrolyte domain, and addition of 2,4-ionene only results in substrate enrichment. Additionally, a similar rate increase by a factor of 2 was noticed for a dimeric $CoPc[N(CH_3)_3I]_4/CoPc(COOH)_8$ complex in the presence of 2,4-ionene.[13] An analogous acceleration factor for substrate enrichment, purely caused by electrostatic interactions, has been regarded earlier for the interionic reaction between phenolate and glyoxylic acid to α,4-dihydroxybenzene-acetic acid in the presence of 3,3-ionene.[6,7,34]

In comparison, the dependence of the catalytic activity of $CoPc(COOH)_4$ as a function of the 2,4-ionene concentration is also shown in Figure 5. This figure clearly shows that the influence of polycation addition on the catalytic activity of $CoPc(COOH)_4$ is a result of the three 2,4-ionene promoting effects.[9,17] At low ionene concentrations, the low catalytic activity is comparable with a polymer-free system. At a N^+/Co ratio of 4 higher reaction rates are achieved due to suppression of the catalytically inactive μ-peroxo complexes and simultaneously formation of $CoPc(COOH)_4$ dimers. Upon raising the co-catalyst amount the oxidation rate further
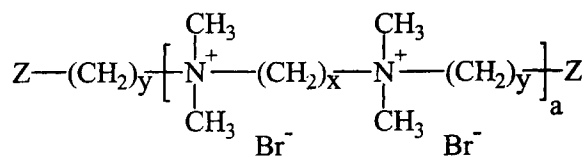
increases which was ascribed to substrate enrichment and mainly to enhanced aggregation of the catalyst, i.e., higher aggregates of dimeric CoPc-$(COOH)_4$ species.[9,12] The optimal catalytic conditions, where the highest reaction rates are observed, are reached at a N^+/Co ratio of 50. After an optimal N^+/Co has been realized, the decrease in activity is a result of a decrease in the local thiolate anion concentration at the catalytically active site.

Moreover, two other important aspects should be remarked. First, when comparing the catalytic properties of $CoPc(COOH)_4$ and $CoPc(COOH)_8$ both in the presence of 2,4-ionene, it can be observed that despite the expected higher activities for $CoPc(COOH)_4$ than for $CoPc(COOH)_8$, the shapes of both curves are quite similar and the maximal catalytic activities are reached at N^+/Co ratios of 50 (Fig. 5). Secondly, similar rate enhancements are observed upon addition of 2,4-ionene to CoPc-$(COOH)_4$ as well as to the conventional CoPc-$(NaSO_3)_4$ system.[9,17]

It was demonstrated before that the molecular weight of 2,4-ionene plays a major role in achieving the optimal N^+/Co ratio at the highest oxidation rate.[17] By using monodisperse oligomeric 2,4-ionenes it was found that the optimal N^+/Co ratio for a 2,4-ionene/$CoPc(NaSO_3)_4$ system decreases while the chain length of the ionene increases till a constant value of 50 is reached at eight N^+ per chain. From a mechanistic point of view these monodisperse ionene oligomers (Fig. 6) are excellent tools to provide insight into the molar mass dependence on the process of substrate enrichment in the case of the thiol oxidation catalyzed by $CoPc(COOH)_8$.

In Figure 7 the mercaptoethanol oxidation rates are presented as a function of the N^+/Co ratio for two monodisperse oligomers, containing two quaternary ammonium groups, i.e., the Br- and N-trimers (Fig. 6). A maximum in the catalytic activity at very high trimer concentrations can be noticed for the Br-trimer, indicating that substrate enrichment occurs only at these high oligomer concentrations. Compared with the polymer-free system addition of Br-trimer leads to a rate increase by a factor of 2. The very high optimal N^+/Co ratio, which is necessary to achieve effective substrate enrichment, is similar as revealed for the Br-trimer/CoPc-$(NaSO_3)_4$ combination.[17]

Surprisingly, no rate enhancement can be observed upon addition of N-trimer to an aqueous $CoPc(COOH)_8$ solution (Fig. 7). This implies that apparently the Br-trimer is capable of inducing substrate enrichment in contrast to the N-trimer, which probably can be ascribed to the difference in the

$$Z—(CH_2)_y\left[\begin{array}{c} CH_3 \\ | \\ N^+—(CH_2)_x—N^+—(CH_2)_y \\ | \\ CH_3 \quad Br^- \end{array} \begin{array}{c} CH_3 \\ | \\ \\ | \\ CH_3 \quad Br^- \end{array} \right]_a Z$$

(name)	a	x	y	Z
Br-trimer	1	2	4	Br
N-trimer	1	4	2	N-(CH₃)₂
Br-pentamer	2	2	4	Br
N-heptamer	3	4	2	N-(CH₃)₂
H-trimer-2C	1	2	4	H
H-trimer-3C	1	3	4	H
N-trimer-6C	1	6	2	N-(CH₃)₂

Figure 6. Structures of the different monodisperse ionene oligomers.

distance between the two quaternary ammonium groups in both trimers, i.e., approximately 4.1 and 6.1 Å for the Br- and N-trimers, respectively.

To elucidate the role of the distance between the two quaternary ammonium groups, we used other trimeric ionenes with three and six methylene groups between the two ionic sites (Fig. 6). The H-trimer-3C, where the distance between the charges is approximately 5.3 Å, is also unable to cause substrate enrichment: no raise in the activity can be observed while increasing the co-catalyst concentration (Fig. 7). Also for the N-trimer-6C, in which the positive charges are separated by six methylene groups an analogous behavior can be observed. The fact that the end group of a trimeric ionene plays no role was demonstrated by the H-trimer-2C, which achieved a similar rate increase as the Br-trimer. The addition of N,N,N',N'-tetramethylethylenediamine to the Br-trimer promoted thiol oxidation neither affected the rate acceleration.

Apparently, only trimeric ionene oligomers, where the distance between the two quaternary ammonium groups is less than about 5.3 Å, are capable of inducing substrate enrichment. Considering the distance between the two carboxylic end groups ($\sim$ 4.2 Å) attached to one phenyl ring, the reason of the incapability to induce substrate enrichment by tri-
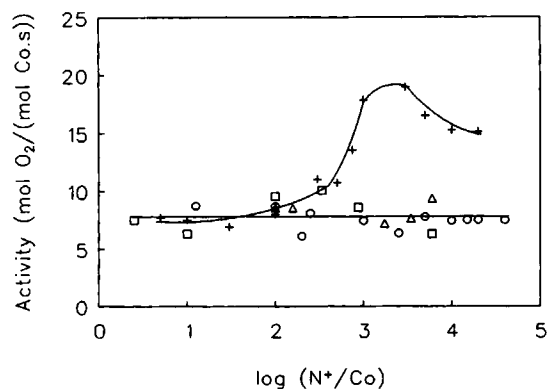

Figure 7. Effect of N^+/Co ratio on the mercaptoethanol oxidation rate: (+) Br-trimer, (○) N-trimer, (△) H-trimer-3C, (□) N-trimer-6C. [CoPc(COOH)$_8$] = 2 × 10^{-6} mol dm^{-3}, pH 9.0, [ME] = 7.1 × 10^{-2} mol dm^{-3}.

meric oligomers, where the ionic sites are separated by more than three methylene groups, lies in the fact that both quaternary ammonium groups are able to neutralize the two carboxylate groups attached to one phenyl ring. In such a case no extra N^+ is available for substrate enrichment. Obviously, the gap between the ionic sites in the Br-trimer ($\sim$ 4.1 Å) is too short to interact with both carboxylate groups, so one quaternary ammonium group is involved in binding the cobalt complex and the residual N^+ is available for substrate enrichment.

The influence of the N^+/Co ratio of two other oligomers, i.e., Br-pentamer and N-heptamer (Fig. 6), with four and six N^+, respectively, on the mercaptoethanol oxidation rate is shown in Figure 8. For both oligomers, rate increases by a factor of 2–3 are detectable upon addition of the ionene-oligomer. The optimal N^+/Co ratios for both Br-penta-
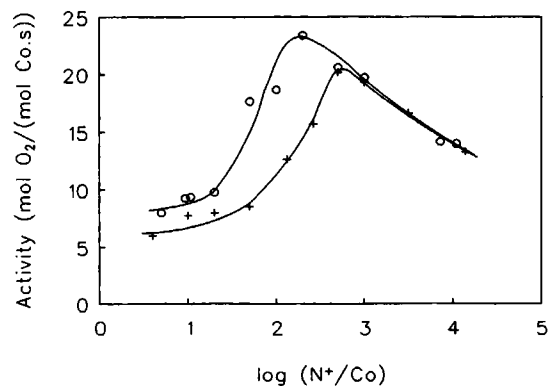

Figure 8. Effect of N^+/Co ratio on the mercaptoethanol oxidation rate: (+) Br-pentamer, (○) N-heptamer. [CoPc(COOH)$_8$] = 2 × 10^{-6} mol dm^{-3}, pH 9.0, [ME] = 7.1 × 10^{-2} mol dm^{-3}.

mer and N-heptamer are higher than those measured for high molecular weight 2,4-ionene and lower than determined for the Br-trimer. Furthermore, the optimal N^+/Co ratios and the shapes of both curves are identical to those obtained for the corresponding oligomer/CoPc(NaSO$_3$)$_4$ systems.[17]

Considering all results we have seen that the 2,4-ionene molecular weight dependence on the values of the N^+/Co optima for the CoPc(COOH)$_8$ is similar as for the CoPc(NaSO$_3$)$_4$ system. Despite lower catalytic activities, the shape of the curves are similar. Only the N-trimer deviates from this observation. Therefore, we may conclude that the values for the optimal N^+/Co ratio in a 2,4-ionene/CoPc(NaSO$_3$)$_4$ system,[17] where all three polycation promoting effects are involved, is exclusively determined by substrate enrichment and not by formation of higher aggregates of CoPc(NaSO$_3$)$_4$, which was thought before.[9]

Furthermore, we investigated the pH dependence of the thiol oxidation rate at the optimal N^+/Co ratio for both 2,4-ionene containing CoPc(COOH)$_4$ as well as CoPc(COOH)$_8$ systems (Fig. 9). With respect to CoPc(COOH)$_4$ a typical "bell-shaped" curve can be observed, similar to the curve for the 2,4-ionene/CoPc(NaSO$_3$)$_4$ system.[8] The pH optimum of CoPc(COOH)$_8$ is shifted to a somewhat larger value, probably due to the larger repulsion between the phthalocyanine and the thiolate anions. From this figure it becomes evident that the oxidation rate increases on raising the pH, because the reactive species is the thiolate anion and not 2-mercaptoethanol ($pK_a = 9.6$)[35] itself. However, after reaching an optimum the catalytic activity decreases: a simultaneous increase in ionic strength and hydroxide concentration leads to a competitive ion effect.

CONCLUSIONS

In the case of the 2,4-ionene/CoPc(COOH)$_4$ system the three polycation promoting effects result in a 40-fold rate enhancement as compared with the polymer-free system. UV-VIS spectroscopy experiments showed that CoPc(COOH)$_8$ was incapable of forming μ-peroxo complexes, or ionene-induced dimeric catalyst complexes. Thus, it was possible to study exclusively the ionene promoting effect substrate enrichment. The addition of 2,4-ionene to an aqueous CoPc(COOH)$_8$ solution therefore leads to a rate acceleration of a factor 2–3 ascribed completely to substrate enrichment, i.e., higher local concentrations of the thiolate anions.
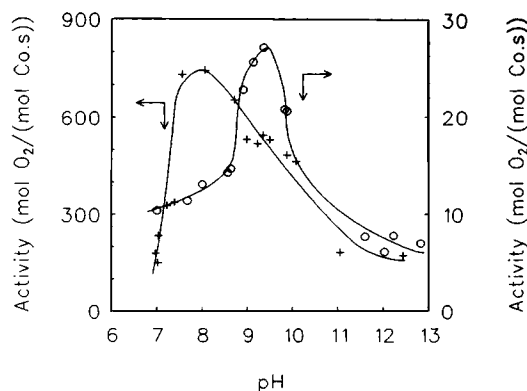

Figure 9. Catalytic activity as a function of pH: (+) CoPc(COOH)$_4$, [CoPc(COOH)$_4$] = 2 × 10^{-7} mol dm^{-3}, [N^+] = 1.5 × 10^{-5} mol dm^{-3}; (O) CoPc(COOH)$_8$, [CoPc(COOH)$_8$] = 2 × 10^{-6} mol dm^{-3}, [N^+] = 2.5 × 10^{-4} mol dm^{-3}. [ME] = 7.1 × 10^{-2} mol dm^{-3}.

Using monodisperse ionene oligomers a molecular weight dependence was found, resulting in a shift of the optimal N^+/Co ratios to lower values with increasing chain length of the ionene. The results showed that similar molar mass dependent optimal polymer/catalyst ratios were realized for both 2,4-ionene containing CoPc(COOH)$_8$ and CoPc(NaSO$_3$)$_4$ systems. Comparing both systems, we were able to conclude that substrate enrichment is the leading factor determining the optimal N^+/Co ratio.

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