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POLYELECTROLYTE-PROMOTED CATALYTIC OXIDATION OF A HYDROPHOBIC THIOL

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Summary

The autoxidation of the hydrophobic 1-dodecanethiol was investigated using the hydrophilic $\text{CoPc}(\text{NaSO}_3)_4$ /ionene system in water as catalyst. It was found that reaction rate largely depends on the order of addition of reactants, stirring speed, pH, thiol concentration and ionene concentration. The observed dependencies indicate that the process proceeds via a phase-boundary mechanism.

Catalytic activity could be enhanced by coupling a hydrophobic group to the ionene chains, but not by introducing hydrophobic groups into the polymer backbone.

Stability of the catalyst system appeared to be poor, due to coprecipitation of the cobalt complex with the reaction product and, possibly, breakdown of the phthalocyanine by accumulated hydrogen peroxide.

Introduction

In our previous articles [1–5], an elaborate study was presented on the structural and kinetic aspects of the polyelectrolyte-promoted autoxidation of thiols using cobaltphthalocyanine–tetrasodiumsulfonate, $\text{CoPc}(\text{NaSO}_3)_4$ (1), as a catalyst. In order to obtain mechanistic information, a well-defined homogeneous system was investigated. Thus, 2-mercaptoethanol was chosen as a model substrate, since it is easily dissolved in the reaction medium (water), as is the corresponding disulfide.

However, it is also very interesting to study whether hydrophobic thiols can be oxidized using this type of catalyst system and, if possible, to determine how the mechanism of the process is affected by the thiol hydrophobicity.

Brouwer *et al.* [6] reported previously that the oxidation of 1-dodecanethiol is indeed enhanced by ionenes (polyquaternary ammonium salts, 2). Nevertheless, the efficiency of the process was found to be rather poor compared with that of 2-mercaptoethanol (the maximum observed rate

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1 cobaltphthalocyanine tetrasodiumsulfonate $\text{CoPc}(\text{NaSO}_3)_4$

2 ionenes

type	name	x	y	R
2a	2,4-ionene	2	4	CH_3
2b	2,10-ionene	2	10	CH_3
2c	3,3/ C_{12} -ionene	3	3	$\text{C}_{12}\text{H}_{25}$

was lower by a factor of ~ 10). Furthermore, the kinetic data were treated as for a homogeneous system, which may not be completely justified.

Therefore, this hydrophobic thiol oxidation has now been investigated in more detail and reaction conditions have been further optimized. In this report, the possibilities and limitations of ionenes in the catalytic conversion of dodecanethiol are discussed, as well as the mechanism of this process in comparison to its homogeneous counterpart.

Experimental

Ionene syntheses

2,4-Ionene (**2a**) and 2,10-ionene (**2b**) were prepared according to the method reported by Brouwer *et al.* [7]; 3,3/ C_{12} -ionene (**2c**) was synthesized according the method described in [8]. M_n -values were determined by titration with hydrochloric acid after terminating the products with amine groups by reaction with an excess of amine (0.25 g N,N,N',N' -tetramethylethylene diamine per gram of product) in water for 8 h [9]; the values obtained were 7300 for **2a**, 5600 for **2b** and 10^4 for **2c**.

Oleyl ionene (**3**) was synthesized as follows: 3.65 g dimethylaminopropyl-chloride (isolated from its hydrochloric salt, according to the method of Yen *et al.* [10]) and 0.69 g oleyl iodide (see below) were refluxed for 48 h in 5 ml water under nitrogen atmosphere. The iodide dissolved rapidly after the polymerization had started and a viscous reaction mixture resulted. After freeze-drying and washing the product with acetone, the chemical yield was found to be quantitative.

Synthesis of oleyl iodide

Oleyl iodide was prepared from oleyl alcohol via a two-step process. First, 5.0 g distilled oleyl alcohol $(\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-$

3 oleyl-ionene ($\text{X} = \text{Cl}^-$ or I^-)

CH₂OH) and 3.91 g *p*-toluenesulfonyl chloride were dissolved in 50 ml pyridine and stored overnight at 4 °C. A precipitate was formed during reaction. The reaction mixture was poured into ice and extracted several times with dichloromethane. The combined organic fractions were washed with a 5% HCl solution, followed by washing with water. After drying over MgSO₄, the solvent was removed under reduced pressure. The yield of oleyl *p*-toluene sulfonate (CH₃—(CH₂)₇—CH=CH—(CH₂)₇—CH₂OSO₂—C₆H₄—CH₃) was nearly quantitative. ¹H NMR showed the absence of the starting material oleyl alcohol.

5.5 g of the unpurified oleyl *p*-toluene sulfonate was dissolved in 75 ml acetone together with 2.1 g NaI and refluxed under nitrogen atmosphere for 3 h, during which a precipitate was formed. After filtration and evaporation of acetone a yellow oil remained (yield approx. 95%). ¹H NMR showed the absence of the *p*-toluenesulfonate group. The purity of the oleyl iodide (CH₃—(CH₂)₇—CH=CH—(CH₂)₇—CH₂I) was found to be better than 97% according to ¹H NMR, and thus satisfactory for synthesis of the oleyl ionene.

Other reagents

CoPc(NaSO₃)₄ (1), kindly provided by Dr. T. P. M. Beelen, was synthesized according to an adaptation by Zwart *et al.* [11] of the method described by Weber and Busch [12].

2-Mercaptoethanol and 1-dodecanethiol (Fluka) were (vacuum) distilled prior to use. All other reagents were of analytical purity and used without further purification.

Catalytic activity measurements

Thiol oxidations were carried out in an all-glass double-walled Warburg apparatus, equipped with a powerful mechanical glass stirrer and thermostatted at 25.0 ± 0.5 °C. The oxygen pressure was maintained at 100 kPa. The stirring speed was 2600 rpm unless stated otherwise. Reaction rate was measured by monitoring the oxygen uptake rate with a digital flow meter (Inacom, Veenendaal). During reaction, the pH was measured with a pHM 62 pH meter equipped with a GK 2401B pH-electrode (Radiometer, Copenhagen).

For 2-mercaptoethanol oxidations, reactions, were started by the addition of the thiol (by means of a syringe) to the oxygen-saturated catalyst mixture (containing ionene, cobalt complex and NaOH). For 1-dodecanethiol, it appeared to be more suitable to start reactions by injection of a concentrated CoPc(NaSO₃)₄ solution into the reactor containing an oxygen-saturated mixture of ionene, thiol and NaOH (see below). In all cases, the reaction volume was 0.1 dm³.

Determination of hydrogen peroxide concentration

After several oxidation experiments, the H₂O₂ content of the reaction mixture was determined spectrophotometrically using TiCl₃—H₂O₂ as reagent [13].

Results and discussion

Reaction procedure

When an oxidation experiment with 1-dodecanethiol is performed according to the method developed for mercaptoethanol (see Experimental), an oxygen uptake rate curve is obtained as depicted in Fig. 1a. It clearly demonstrates that, after the reaction has started, the reaction rate slowly increases, although the amount of thiol present is, of course, decreasing. Only when about 35% of the thiol is converted does the rate start to decrease again.

Apparently, optimum reaction conditions are reached after a relatively long period on a reaction time scale, most probably as a result of slow mixing of the thiol with the catalyst system, since the reaction is started by adding the thiol to the oxygen-saturated catalyst mixture. It can be expected that mixing of the hydrophobic substrate with the hydrophilic $\text{CoPc}(\text{NaSO}_3)_4/\text{ionene}$ system requires some time to reach equilibrium conditions.

In order to verify this assumption, the reaction procedure was somewhat adapted: first the ionene solution was mixed with the thiol and then the reaction was started by introducing the cobalt complex. The result of this procedure is illustrated in Fig. 1b. It is evident that the maximum reaction rate is now reached almost immediately after starting the reaction, confirming our hypothesis. Since the thiol concentration at this point is still high, the observed rate is also higher than was found for the conventional reaction procedure.

Fig. 1. Oxygen uptake rate curves for the catalytic oxidation of 1-dodecanethiol according to different reaction procedures (see text). Conditions: $\text{pH} = 13$, $[\text{RSH}]_0 = 0.021 \text{ mol dm}^{-3}$, $[\text{N}^+] = 10^{-3} \text{ mol dm}^{-3}$, $[\text{Co}] = 10^{-6} \text{ mol dm}^{-3}$, polymer promoter: 2,4-ionene ($M_n = 7400$). (a) Reaction started by thiol addition; (b) reaction started by $\text{CoPc}(\text{NaSO}_3)_4$ addition.

Because the method described above leads to less complicated kinetic behaviour, further experiments were performed according to this method.

Thiol dispersion in the reaction medium

On the basis of the very low solubility of dodecanethiol in aqueous media ($3 \times 10^{-5} \text{ mol dm}^{-3}$ at 50°C [14]), it was expected that a two-phase system would be formed upon mixing the thiol with the catalyst solution. Indeed, phase separation was observed without stirring, especially at low ionene concentrations. At high ionene concentrations an emulsion-like system was obtained, suggesting that the 2,4-ionene exhibits some surface-active characteristics.

Also at $\text{pH} = 13$ we observed a separate thiol phase, although in this case more thiol in the form of the thiolate anion may be present in the water phase.

In such a two-phase system, where the substrate exists mainly in one phase and the catalyst in the other, the reaction rate should depend largely on stirring speed, since this (at least partly) determines the contact surface between the two phases. However, reaction rate also depends on stirring speed because gas-phase oxygen must be sufficiently mixed with the reaction solution. To discriminate between these effects, the rate dependence on stirring speed was determined for both 2-mercaptoethanol and 1-dodecanethiol. The results are depicted in Fig. 2, which clearly shows that low stirring speeds lead to insufficient oxygen transport to the reaction solution, thus limiting reaction rate. At 1500 rpm this problem is overcome,

Fig. 2. Dependence of initial reaction rate, V_0 , on stirring speed in the 2,4-ionene-promoted oxidation of 2-mercaptoethanol (●) and 1-dodecanethiol (Δ). Conditions: (●) $\text{pH} = 8$, $[\text{RSH}]_0 = 0.19 \text{ mol dm}^{-3}$, $[\text{N}^+] = 10^{-3} \text{ mol dm}^{-3}$, $[\text{Co}] = 2 \times 10^{-7} \text{ mol dm}^{-3}$; (Δ): $\text{pH} = 13$, $[\text{RSH}]_0 = 0.013 \text{ mol dm}^{-3}$, $[\text{N}^+] = 5 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{Co}] = 2 \times 10^{-7} \text{ mol dm}^{-3}$ (reaction started by $\text{CoPc}(\text{NaSO}_3)_4$ addition).

as can be concluded from the constancy of reaction rate above this value for the mercaptoethanol system. On the other hand, dodecanethiol oxidation rate has not yet reached its maximum value, even at a stirring speed of 2000 rpm (where V_0 (initial oxidation rate) = $0.83 V_0^{\max}$), indicating that, indeed, the coexistence of two liquid phases enhances the rate dependence on stirring speed.

Obviously, it is necessary to apply high stirring speeds in the dodecanethiol system to avoid mass transfer problems during kinetic measurements. Therefore, all further experiments were carried out at a stirring speed of 2600 min^{-1} .

Concentration effects on kinetics

The reaction rate was studied as a function of substrate concentration and the concentrations of the catalyst components. The effect of varying pH was also investigated.

On lowering the pH starting from pH 13, it was found that the reaction rate decreased dramatically, reaching almost zero activity at $\text{pH} < 10$. This is in agreement with the fact that the thiolate anion is the reactive species, as was also established for mercaptoethanol [7]. Further experiments were therefore performed at pH 13.

Variation of the thiol concentration led to the behaviour depicted in Fig. 3. The kinetic order in thiol changed from 1 to 0 on increasing the amount of RSH, and thus it seems that the process can be described by a Michaelis-Menten model, analogous to the mercaptoethanol oxidation [2]. However, a Lineweaver-Burk plot of the obtained results (Fig. 3b) clearly demonstrates that the Michaelis-Menten rate law is not obeyed ($1/V_0$ versus $1/[\text{RSH}]$ should be linear). This is likely to be due to the non-linear relationship between the amount of thiol present in the reaction mixture and the thiolate anion concentration in the vicinity of the catalyst.

This local thiolate anion concentration appeared to be highly dependent on the ionene concentration, as becomes evident from Fig. 4. Effective conversion of dodecanethiol was observed to be possible over only a small range of ionene concentrations: $10^{-4} \text{ mol dm}^{-3} < [\text{N}^+] < 10^{-2} \text{ mol dm}^{-3}$, with a sharp optimum at $[\text{N}^+] \approx 10^{-3} \text{ mol dm}^{-3}$. For the oxidation of mercaptoethanol, the reported range was much larger and the optimum was less pronounced [9]. In our opinion, the results of Fig. 4 can be explained as follows:

The ionene interacts electrostatically with the thiolate anions that exist at the thiol-water interface. At low $[\text{N}^+]$, only a small part of the thiolate anions is in contact with the ionene that binds the cobalt catalyst complex, whereas the rest of the thiol remains separated in droplets from which only slow transport to the catalyst is possible. Therefore, the oxidation rate is rather low.

Upon increasing $[\text{N}^+]$, the contact surface between ionene and thiol (thiolate anion) is enhanced, resulting in increased activity. At $[\text{N}^+] \approx 10^{-3} \text{ mol dm}^{-3}$, an optimum contact surface appears to be reached; an

(a)

(b)

Fig. 3. (a) Initial dodecanethiol oxidation rate as a function of the amount of thiol per unit reaction volume; (b) Lineweaver-Burk plot of the results of (a). Polymer promoter: 2,4-ionene ($M_n = 7400$), pH = 13, $[N^+] = 5 \times 10^{-4}$ mol dm^{-3} , $[Co] = 8 \times 10^{-7}$ mol dm^{-3} , reaction started by $CoPc(NaSO_3)_4$ addition.

emulsion-like system is then obtained, in which the ionene apparently stabilizes small thiol droplets (stabilization was not sufficient to allow determination of particle size).

Further addition of ionene only leads to an increase in the ionene concentration in the aqueous phase (instead of in the phase-boundary layer).

Fig. 4. Effect of varying the 2,4-ionene concentration on the initial dodecanethiol oxidation rate. Conditions: pH = 13, $[RSH]_0 = 0.021 \text{ mol dm}^{-3}$, $[Co] = 8 \times 10^{-7} \text{ mol dm}^{-3}$ (reaction started by $CoPc(NaSO_3)_4$ addition).

Fig. 5. Schematic representation of the phase-boundary interaction of the catalyst system with the hydrophobic substrate.

Part of the cobalt complex will probably be bound to this aqueous ionene fraction and, thus, will not be susceptible to interaction with thiol. Therefore, the efficiency of the catalyst complex is lowered at high $[N^+]$ values. This explanation is in agreement with our observation that the rate optimum is shifted to lower $[N^+]$ upon decreasing the cobalt concentration. This also explains why the initial rate is not linear with $[Co]$, as was expected for a Michaelis–Menten type process.

Summarizing the observed concentration effects, it can be stated that the kinetics of the process under study are highly complicated due to the two-phase character of the reaction mixture. The mechanism of the reaction seems to be best characterized as a phase-boundary mechanism, as schematically given in Fig. 5.

Effect of varying the type of ionene

Since the contact surface between thiol and ionene appeared to be a very important factor determining the oxidation activity, attempts were made to improve this by building hydrophobic groups into the ionene, thus offering the possibility of hydrophobic interaction with the thiol. A more hydrophobic character of ionenes can be achieved by several methods: by introduction of longer alkyl segments into the polymer backbone, as in 2,10-ionene [5, 15] (**2b**) (1); by replacement of ammonium-ion attached methyl groups by longer side-groups, as in 3,3/ C_{12} -ionene [6, 16] (**2c**) (2); or

TABLE 1

Effect of varying the type of ionene on the initial rate of dodecanethiol oxidation^a

Ionene	Initial rate (mol O ₂ (mol Co) ⁻¹ s ⁻¹)
2,4-	250
2,10- ^b	17
3,3/C ₁₂ - ^c	50
oleyl ^c	410

^aConditions: pH 13, [RSH] = 0.021 mol dm⁻³, [Co] = 10⁻⁶ mol dm⁻³, [N⁺] = 5 × 10⁻⁴ mol dm⁻³.^b[N⁺] = 10⁻⁵ mol dm⁻³ (optimum).^c[Co] = 2 × 10⁻⁷ mol dm⁻³.

by coupling a hydrophobic moiety to one end of the ionene chains, as in oleyl ionene (3) (3).

The activities of these soap-like ionenes were measured and compared to that of 2,4-ionene (see Table 1). It was found that 2,10-ionene and 3,3/C₁₂-ionene exhibit rather low activities, whereas oleyl ionene was somewhat more active than 2,4-ionene.

The 2,10-ionene was expected to be relatively inactive since it stabilizes CoPc(NaSO₃)₄ in the catalytically not very active monomeric form [5]. For the same reason, the oxidation rate in the 3,3/C₁₂-ionene system was observed to be low, as it was established spectroscopically that this poly-soap also enhances monomerization of the catalyst complex.

On the other hand, oleyl ionene enhances aggregation of the phthalocyanine analogous to 2,4-ionene, in spite of its soap-like blocks. This can be

Fig. 6. Initial oxidation rate versus the oleyl ionene concentration. Conditions as in Fig. 4, except [Co] = 2 × 10⁻⁷ mol dm⁻³.

easily understood, since the oleyl segments that might lead to interaction with the lipophilic substrate particles are separated from the ionene blocks that electrostatically bind the cobalt complex. Thus, the oleyl ionene system is comparable to 2,4-ionene, as is also obvious from Fig. 6 in which the effect of varying $[N^+]$ is shown. The general features of this curve are the same as that of Fig. 4, but the optimum activity is higher and above the optimum the rate decrease is less drastic. Presumably, these differences are the results of a better interaction between the thiol and the catalyst system.

From Table 1 and Fig. 6 it is evident that dodecanethiol is oxidized most efficiently by a polymer containing a high charge density polyelectrolyte block (binding $\text{CoPc}(\text{NaSO}_3)_4$ in its active aggregated form and electrostatically interacting with RS^-) and a separate hydrophobic block (leading to hydrophobic interaction with the substrate).

Side reaction, deactivation of the catalyst

It has been reported previously [7] that mainly one side-reaction may occur in the polymer-promoted thiol oxidation, *viz.* the formation of hydrogen peroxide according to reaction (a) in Scheme 1.

Scheme 1.

The occurrence of this reaction in the present thiol oxidation system was investigated and, indeed, could be demonstrated. The amount of accumulated peroxide appeared to be higher than was found for mercaptoethanol under the same conditions. It was determined that for dodecanethiol the amount of accumulated H_2O_2 equals the amount of oxygen consumed during oxidation ($\text{H}_2\text{O}_2:\text{O}_2 = 1:1$). This implies that the thiol oxidation process completely follows reaction step 1a, and that step 1b does not occur, whereas in the mercaptoethanol oxidation step 1b is a fast consecutive reaction [2]. This difference is caused by the fact that hydrogen peroxide and thiol exist in two different phases in the dodecanethiol system. It appears that H_2O_2 is immediately transported to the bulk of the aqueous phase after it has been formed, so that no interaction with RSH is possible.

The accumulation of peroxide may be a serious problem in catalytic thiol conversion, since H_2O_2 may cause breakdown of the $\text{CoPc}(\text{NaSO}_3)_4$ complex [17].

Another way in which catalytic activity may be lost is by entrapment of the catalyst during the precipitation of the insoluble disulfide. The occurrence of this process could be easily seen from the blue color of the disulfide. It could not be established whether the ionene coprecipitates as well. Nevertheless, it is clear that the cobaltphthalocyanine/ionene system is not an ideal system for the oxidation of dodecanethiol, since inactivation occurs rapidly.

However, the study of this system in combination with dodecanethiol has revealed two phenomena that may be of general importance:

- hydrophilic polymers such as 2,4-ionene may efficiently interact with hydrophobic substrates on a purely electrostatic basis, leading to emulsion-like systems; thus, in this respect, polyelectrolytes, when combined with oppositely-charged substrate moieties, may gain surface-active properties.

- in order to improve such polymer-substrate interaction, preferably block-copolymers, consisting of a hydrophobic and a hydrophilic part, should be used, rather than random-type copolymers.

Conclusions

From the results presented above it can be concluded that the ionene-promoted oxidation of a hydrophobic thiol proceeds at the boundary of the thiol and aqueous phase. Therefore, the order of addition of reactants and the stirring speed highly affect reaction rate. The coexistence of two phases also leads to kinetics that deviate from the Michaelis–Menten model. Furthermore, reaction of thiol with the produced hydrogen peroxide (Scheme 1b) is prohibited.

The pH-dependence of the process revealed that thiolate anions are necessary for efficient oxidation. This explains why ionenes, in spite of their hydrophilicity, enhance reaction rate: they electrostatically interact with the thiolate anions, probably according to the schematic representation of Fig. 5, and also interact with the cobalt catalyst. If one of these interactions is not optimal, the reaction rate dramatically decreases and, therefore, only a very small ionene concentration range results in efficient thiol oxidation (Figs 4 and 6). Similar results were obtained by Hassanein and Ford [18] in their study of the autoxidation of 1-decanethiol with $\text{CoPc}(\text{NaSO}_3)_4$ in the presence of positively charged latex particles. Interaction of ionene with the thiolate anions can be improved by coupling hydrophobic blocks to the ionene chains.

Finally, it was established that the investigated catalyst system is not suitable for practical application, since deactivation of the catalyst occurs. A possible solution for this problem may be the use of other solvents, leading to a homogeneous reaction mixture.

The combination of the hydrophobic substrate and the hydrophilic catalyst appears to be an interesting system for the study of hydrophobic and electrostatic interactions in emulsion.

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