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AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE TETRASODIUM SULFONATE ATTACHED TO POLY(VINYLAMINE). II. KINETIC MEASUREMENTS

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Summary

A kinetic study is presented of the autoxidation of 2-mercaptoethanol using cobalt(II) phthalocyanine tetrasodium sulfonate attached to poly(vinylamine) as a catalyst.

The main products appear to be 2,2'-dithiobis(ethanol) and hydrogen peroxide; the measured oxygen consumption was found to be in balance with the theoretical one, based on the exclusive formation of these compounds. The catalytic system exhibits a large activity and Michaelis-Menten kinetics are obeyed with respect to substrate concentration and oxygen pressure. The reaction rate was first order in polymeric catalyst.

Upon addition of salt a severe decrease in activity was observed. A comparison of the activation energies in the presence and absence of salt suggests that the local thiol anion concentration in the vicinity of the oxidation sites is lowered upon salt addition. Although an entropy change cannot be excluded, this may explain the fall in reactivity.

Addition of radical scavengers also led to a decrease in the reaction rate, indicating that radicals are reaction intermediates. Overall, the polymeric catalyst exhibits an enzyme-like behaviour and resembles the catalytic action of vitamin B₁₂ in the oxidation of thiols.

Introduction

During the past two decades much attention has been paid to the autoxidation of thiols using transition metal containing compounds as catalysts. Some of these investigations [1] originated from a wish to develop catalysts which could be used for the desulfurization of natural gas and oil. Other surveys [2, 3] dealt with the enzymatic conversion of thiols in order to clarify thiol metabolism in biological systems. It has been found that cobalt(II) phthalocyanine (CoPc) [4] in the presence of alkali is a very good catalyst for the conversion of thiols to disulfides, the alkali increasing the

Fig. 1. Structure of $\text{CoPc}(\text{NaSO}_3)_4$.

concentration of thiol anions which are the reactive species in the system. In many papers emphasis was laid on reaction kinetics and re-use of the catalysts. However large differences in kinetic behaviour were observed between homogeneous systems where CoPc derivatives in alkaline media were used as the catalyst [5, 6] and systems where CoPc was immobilized on porous solid supports [6, 7].

In our laboratory systems are being investigated where $\text{CoPc}(\text{NaSO}_3)_4$ (Fig. 1) is attached to basic polymers by complexation. In particular, the water-soluble poly(vinylamine) (PVAm) appears to be a very good promotor in the autoxidation of 2-mercaptoethanol (RSH) [8]. Thus, relative to the aqueous system $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$, the bifunctional polymeric system appears to be *ca.* 30 times more active. Our aim is to elucidate the contribution of the polymeric ligand to this increased catalytic action, and in order to achieve this systems with other basic polymers are being investigated.

We found earlier [9] that the coil conformation of the polymer prevents the formation of catalytically inactive dimeric oxo adducts of $\text{CoPc}(\text{NaSO}_3)_4$, and that the basic functionalities were an excellent substitute for the alkali commonly used in the homogeneous system with $\text{CoPc}(\text{NaSO}_3)_4$ [8]. Recently we have investigated the conformation of the polymeric catalyst during reaction and examined the influence of pH on the conformation of the polymeric catalyst and its reaction rate [10]. We now present a kinetic study of this polymeric system, the results being discussed in relation to data obtained from homogeneous and immobilized systems.

Experimental

Chemical reagents

PVAmHCl was purchased from Polysciences Inc. (Warrington U.S.A.; $\bar{M}_n(\text{PVAm}) = 5 \times 10^4 \text{ g mol}^{-1}$, from viscosity experiments in water containing 0.01 N NaOH and 0.1 M NaCl [11]). Aqueous solutions of PVAm were obtained by eluting a 3% solution of PVAmHCl through an Amberlite IRA-

401 anion exchange column. The equivalent amine concentration was determined by potentiometric titration with HCl solution (Merck, Titrisol ampoules) in 2 M NaCl (p.a.). CoPc(NaSO₃)₄ (kindly provided by Dr. T.P.M. Beelen) had been synthesised by a method analogous to that of Weber and Busch [12] as described by Zwart *et al.* [5]. 2-Mercaptoethanol was distilled before use and stored in the dark at 5 °C for periods not exceeding two weeks. The thiol content after storage was checked by iodometric titration [13] and was found 99% pure. Distilled water was used throughout.

Catalyst preparation

The catalyst was prepared by mixing aqueous solutions of PVAm and CoPc(NaSO₃)₄, resulting in a polymer-organometal complex. The solution of PVAm was initially added to the reaction vessel and the solution of CoPc(NaSO₃)₄ immediately afterwards. The mixture was degassed twice and saturated with oxygen over a period of 20 min while stirring vigorously.

Catalytic activity measurements

The reaction rate was determined by monitoring the oxygen consumption during the oxidation reaction.

Activity measurements were carried out at constant pressure in an all-glass double-walled thermostated Warburg apparatus, equipped with a powerful mechanical glass stirrer. Oxygen pressure was adjustable. A stirring speed of 2300 r.p.m. was maintained, although this was not critical since a somewhat higher or lower stirring speed did not affect the oxygen uptake. However at oxygen uptake rates exceeding 25 - 30 ml min⁻¹, for a reaction volume of 0.1 dm³ and oxygen pressure of 35 kPa, transport limitation problems occurred.

The Warburg apparatus was equipped with a pH electrode (Radiometer Copenhagen GK 2401 B), the pH being measured 15 s after addition of thiol. Calibrated buffer solutions were employed to check that this type of electrode was not harmed by the presence of thiol. Oxygen consumption rates were measured with a digital flowmeter (Inacom Veenendaal, The Netherlands).

The reaction was started by adding the substrate, 2-mercaptoethanol, to the reaction vessel by means of a syringe. Initial reaction rates were determined as the average consumption during the first minute.

Analysis of the H₂O₂ content

The hydrogen peroxide level in the reaction mixture was analysed by iodometric titration [14].

Results and discussion

Oxygen mass balance

Earlier studies of the autoxidation of thiols [5, 15] have investigated whether disulfide was formed exclusively as the reaction product; in other

words if the conversion obeyed eqn. (4) in Scheme 1. This reaction appears to be the principal one, but in some cases H_2O_2 could be also detected in the reaction mixture [3, 5]. Thus in the system $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ the existence of H_2O_2 at neutral pH was demonstrated spectrophotometrically [16].

Scheme 1. Overall reactions in the oxidation of 2-mercaptoethanol.

In order to check the oxygen mass balance for the $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ system, the total oxygen consumption for complete conversion, *i.e.* the integral of the oxygen uptake curve in Fig. 2, was measured and the peroxide content was determined iodometrically. From the weight of added substrate and from the remaining hydrogen peroxide content after oxygen consumption had stopped, *i.e.* after complete conversion of RSH, the corresponding moles of oxygen were calculated using eqns. (3) and (4) in succession (Scheme 1). The sum of these should be compared with the measured oxygen consumption, see Table 1. From a consideration of the stoichiometry of eqns. (3) and (4) in Scheme 1 and the results in Table 1 it appears that mainly RSSR, and to a lesser extent H_2O_2 , are formed during the catalytic oxidation of RSH, the hydrogen peroxide possibly as an intermediate product*.

It has been shown [16] that, in the absence of PVAm and at neutral pH, $\text{CoPc}(\text{NaSO}_3)_4$ decomposes rather slowly in the presence of H_2O_2 . As stated above, initial reaction rates have been obtained in this study from the oxygen consumption during the first minute of reaction on the basis that over such short periods of time no substantial decomposition of the catalyst will occur. However, the existence of an oxygen mass balance does not rule out the formation of very small amounts of sulfur-containing acids arising from the relatively high H_2O_2 levels during reaction. These acids were assumed to be responsible for catalyst deactivation during successive runs [16].

In some cases [5, 15] the presence of some RSH has been reported after oxygen consumption has stopped. However, in these studies, the detection of residual thiol (which has a strong smell even as extremely small traces) was not possible after cessation of the oxygen uptake. Furthermore,

*If reaction 2 occurs less frequently than reaction 1, some H_2O_2 will remain after the thiol is converted to RSSR. At this stage it is not possible to verify whether RSSR is formed exclusively through reactions 1 and 2 proceeding consecutively or via a mechanism involving several simultaneously occurring reactions.

Fig. 2. Oxygen uptake rate v' plotted against time. $c_{\text{CoPc}(\text{NaSO}_3)_4} = 1.92 \times 10^{-7} \text{ M}$; $c_{\text{—NH}_2} = 1.5 \times 10^{-3} \text{ N}$; [added thiol] = 18.5 mmol; reaction volume = 0.101 dm³; $T = 25.0 \pm 0.1^\circ \text{C}$; pH = 7.4; $P_{\text{O}_2} = 100 \text{ kPa}$.

TABLE 1

Oxygen mass balance in the oxidation of 2-mercaptoethanol

Amount of product (mmol) ^a	Amount of O ₂ consumed (mmol)	Mole fraction of O ₂ (%)
RSH converted (a) 18.558	O ₂ (RSSR) (a/4) 4.640	87.3 ± 1.8 ^b
H ₂ O ₂ remaining (b) 1.307	O ₂ (H ₂ O ₂) (b/2) 0.654	12.3 ± 0.6
	O ₂ (total calc.) 5.293	99.6 ± 1.8
	O ₂ (total meas.) 5.315	100.0

^aData after complete conversion of RSH.

^bAverage of four experiments; errors within 95% confidence limit.

because of the method of analysis employed for H₂O₂, any unconverted thiol would also react with iodine to yield RSSR, and thus not affect the calculated total oxygen consumption.

Effect of thiol concentration

The relationship between the reaction rate and the thiol concentration at a pH value of 7.2, a temperature of 25.0 °C and a Co/NH₂ mole ratio of 3.9×10^{-4} is shown in Fig. 3(a). At high concentrations a saturation effect is observed. Michaelis-Menten kinetics [17,18] (Scheme 2) appear to be obeyed, and the rate constants k_2 and K_m have been calculated from a Lineweaver-Burk plot, *i.e.* a double reciprocal plot of the initial reaction rate v against the initial substrate concentration [Fig. 3(b)].

From the intercept in Fig. 3(b) and the total catalyst concentration, the turn-over number of the enzyme-substrate complex, *i.e.* the catalytic con-

Fig. 3. (a) Reaction rate v plotted against the thiol concentration. $c_{\text{CoPo}(\text{NaSO}_3)_4} = 3.7 \times 10^{-7} \text{ M}$; $c_{\text{-NH}_2} = 0.95 \times 10^{-3} \text{ N}$; reaction volume = 0.105 dm^3 ; $T = 25.0 \pm 0.1^\circ \text{C}$; $\text{pH} = 7.2$; $P_{\text{O}_2} = 100 \text{ kPa}$. The reaction rate v is expressed in $\text{mol RSH dm}^{-3} \text{ s}^{-1}$, calculated on the basis of the stoichiometry of eqn. (4). (b) Lineweaver-Burk plot. Reaction conditions as given for Fig. 3(a).

stant, can be calculated from eqn. (7) of Scheme 2 and has the value $k_2 = 1.6 \times 10^3 \text{ s}^{-1}$. Similarly, from the slope in Fig. 3(b) and v_s it follows that $K_m = 0.07 \text{ mol dm}^{-3}$.

$$\frac{1}{v} = \frac{1}{v_s} + \frac{K_m}{v_s} \cdot \frac{1}{c_{\text{RSH}}} \quad (6)$$

$$v_s = k_2 \cdot E_0 \quad (7)$$

$$K_m = \frac{k_{-1} + k_2}{k_1} \quad (8)$$

$$K_s = \frac{k_1}{k_{-1}}$$

Scheme 2. Summary of Michaelis-Menten kinetics. In this scheme v_s is the maximum reaction rate at $c_{\text{RSH}} = \infty$; K_m is the Michaelis-Menten constant; K_s is the equilibrium constant for substrate binding; and E_0 is the concentration of added catalyst.

The occurrence of a saturation effect for the catalytic activity upon addition of excess substrate, which is common in enzymatic reactions, has also been observed in other systems involving polymeric catalysts [19], indicating that a complex is formed between the substrate and the catalyst before the actual reaction takes place.

The observed value of k_2 is remarkably high for a polymeric catalyst, while the value of K_m is in the usual range. Values of k_2 normally lie in the range $10^{-3} - 10^{-1} \text{ s}^{-1}$ and $K_m \approx 10^{-4} - 1 \text{ mol dm}^{-3}$ for polymeric catalysts obeying Michaelis-Menten kinetics [19 - 21]. The value of the turnover number for a polymeric catalyst observed in this work is of a magnitude which is only commonly encountered with enzymes.

Effect of ionic strength

Figure 4 illustrates the catalytic activity at a pH value of 7.2 and a temperature of 25.0°C as a function of the ionic strength μ (added NaCl). The addition of small amounts of salt leads to a severe reduction in the reaction rate. This behaviour may be explained by the considerable decrease in the concentration of the thiol anion (RS^-) adjacent to the polymer chain caused by repulsive forces between competitive anions (Cl^-) and shielding of the charge on the chain. Moreover, upon addition of salt the polymeric coils shrink considerably due to shielding of the chain charge, and this is reflected in a decreasing viscosity for solutions of the polymeric catalyst [22]. Hence, the occurrence of transport limitations of reactants, which would cause a lower (apparent) reaction rate, cannot be excluded. Similar electrostatic effects have been observed for other polymeric catalysts in aqueous solutions. Pecht *et al.* [23] have investigated the oxidation of ascorbate and other negatively charged ions with molecular oxygen in the presence of a copper(II)-poly(histidine) catalyst, the addition of salt again causing the reaction rate to diminish. Tsuchida *et al.* [24] have also reported that an increase of anion concentration caused by the addition of neutral salt led to a decrease of reaction rate in the electron transfer reactions of cobalt(III)-poly(4-vinylpyridine) complexes.

Fig. 4. Reaction rate as a function of the ionic strength (NaCl). pH = 7.2. Other reaction conditions as listed for Fig. 2.

Effect of temperature

In order to adduce further supporting evidence for the hypothesis that addition of salt lowers the local substrate concentration (RS^-), the temperature dependence of the reaction rate has been measured at $\mu = 0$ and $\mu = 0.1$ between 5 and 45 °C, at a fixed catalyst concentration and pH. Because the reaction rate largely depends upon the pH value of the system [10], this was controlled by addition of small amounts of HCl or NaOH to compensate for the thermal dissociation affects.

Plots of $\ln v$ against the reciprocal of the temperature are shown in Fig. 5, the overall activation energies being listed in Table 2. In the calculation of the activation energies, measurements above 40 °C were not taken into account since limitations of oxygen transport were observed at such temperatures. The difference in activation energy at $\mu = 0$ and $\mu = 0.1$ is small; however, the decrease in activity shown in Fig. 4 is quite large. For this reason the observed decrease in chemical reactivity must arise from a smaller activation entropy, smaller local reactant concentrations or both. At this stage of the investigation it is not yet possible to distinguish clearly between these effects since ionic strength and chain conformation may also affect the activation entropy. We have shown earlier [10] that at intermediate pH values no direct correlation exists between the conformation of the catalyst and reaction rate; however, this does not entirely exclude the

Fig. 5. A plot of $\ln v$ against the reciprocal of the temperature for different ionic strengths (NaCl). pH = 7.3 ± 0.1 ; other reaction conditions as listed for Fig. 2; ○: $\mu = 0$; ●: $\mu = 0.1$.

TABLE 2

Activation energies, E_a , at different ionic strengths

pH	μ (mol dm ⁻³)	E_a (kJ mol ⁻¹)
7.4	0	61 ± 7
7.2	0.1	49 ± 2

occurrence of a change in the conformational activation entropy. Hence, irrespective of the fact that the polymeric catalyst conformation is strongly influenced by salt addition, it is to be expected that a lower thiol concentration rather than a lower activation entropy will have the greater effect upon the reaction rate.

Effect of catalyst concentration

Important kinetic features have been obtained by investigating whether k_2 (eqn. (7), Scheme 2) and K_m (eqn. (8), Scheme 2) remain constant when the catalyst concentration is varied. Since variations in the Co/NH_2 ratio affect the reaction rate [9], this ratio was kept constant at 1.3×10^{-4} during the first set of experiments. Since polymer concentration varies, the pH value was controlled by the addition of small amounts of NaOH and was kept constant at 7.4. Lineweaver–Burk plots have been composed for several concentrations of the polymeric catalyst [Fig. 6(a)] and values of v_s , K_m and k_2 determined (see Table 3). The reaction rate at infinite substrate concentration, v_s , is plotted against catalyst concentration in Fig. 6(b). From the slope in Fig. 6(b) k_2 was derived: $k_2 = 2.8 \times 10^3 \text{ s}^{-1}$. The linear relationship found is in full accordance with eqn. (7) in Scheme 2. Also K_m does not change significantly within experimental error.

The higher value of k_2 at lower Co/NH_2 ratios ($k_2 = 1.6 \times 10^3$ and $2.8 \times 10^3 \text{ s}^{-1}$ at $\text{Co}/\text{NH}_2 = 3.9 \times 10^{-4}$ and 1.3×10^{-4} , respectively) may be ascribed to effects arising from different bulk pH values at the two ratios employed. Evidently, the calculated values of k_2 are apparent values, since the effective catalyst concentration diminishes at higher Co/NH_2 ratios. On this basis, an absolute value of k_2 should be obtained on extrapolation to $\text{Co}/\text{NH}_2 = 0$.

Fig. 6. (a) Lineweaver–Burk plots for several catalyst concentrations. $\text{Co}/\text{NH}_2 = 1.28 \times 10^{-4}$; pH = 7.4; reaction volume = 0.101 dm^3 ; $T = 25.0 \pm 0.1^\circ \text{C}$; $P_{\text{O}_2} = 100 \text{ kPa}$; $\circ$: $E_0 = 0.96 \times 10^{-7} \text{ M}$; $\bullet$: $E_0 = 1.92 \times 10^{-7} \text{ M}$; $\square$: $E_0 = 2.87 \times 10^{-7} \text{ M}$; $\blacksquare$: $E_0 = 3.83 \times 10^{-7} \text{ M}$. (b) Plot of the reaction rates at infinite substrate concentration against the catalyst concentration, E_0 , expressed as $\text{mol CoPc}(\text{NaSO}_3)_4 \text{ dm}^{-3}$. Reaction conditions as listed for Fig. 6(a). Experimental errors are within 95% confidence limits.

TABLE 3

Values of v_s , K_m and k_2 as a function of the catalyst concentration E_0

$10^7 E_0$ (mol dm ⁻³)	10^4Co/NH_2	$10^4 v_s$ (mol dm ⁻³ s ⁻¹)	K_m (mol dm ⁻³)	$10^{-3} k_2$ (s ⁻¹)
0.96	1.3	2.7 ± 0.5	0.11 ± 0.02	$2.8 \pm 0.6^{\text{a,c}}$
1.92	1.3	5.9 ± 0.8	0.11 ± 0.01	$3.1 \pm 0.4^{\text{a}}$
2.87	1.3	7.9 ± 0.9	0.09 ± 0.01	$2.8 \pm 0.3^{\text{a}}$
3.83	1.3	10.9 ± 1.9	0.08 ± 0.01	$2.9 \pm 0.5^{\text{a}}$
3.71	3.9	5.9 ± 0.9	0.07 ± 0.01	$1.6 \pm 0.3^{\text{b}}$

^aCalculated from the data in Fig. 6(a).^bCalculated from the data in Fig. 3(b).^cAll errors are within 95% confidence limits.

The value of K_m , however, is apparently not very sensitive to the Co/NH₂ ratio (see Table 3); obviously K_m is not dependent on the polymer concentration over the range studied.

Effect of oxygen pressure

The effect of oxygen pressure on reaction rate was investigated over the pressure range 10 - 100 kPa at fixed substrate concentration. The results are shown in Fig. 7(a). The occurrence of a saturation effect and the linear nature of the Lineweaver-Burk plot [Fig. 7(b)] indicate that Michaelis-Menten kinetics may apply to the rate dependence on oxygen pressure.

Special attention has been paid to the possibility of oxygen transport limitations to the reaction. A somewhat faster or slower stirring speed does not affect the oxygen uptake rate, even over the low pressure region, although the reaction rate was more dependent on oxygen pressure over this

Fig. 7. (a) A plot of the reaction rate against the oxygen pressure. Reaction conditions as listed for Fig. 2. (b) Lineweaver-Burk plot for results depicted in Fig. 7(a).

latter region [see Fig. 7(a)]. What is important, however, is that even at the low pressure of 24 kPa the reaction rate remained first order in the catalyst concentration, as found earlier at a pressure of 100 kPa. These observations exclude the possible occurrence of transport limitations on the passage of oxygen from the gas phase into the bulk solution.

Effect of the addition of p-benzoquinone

The addition of 13 mg of *p*-benzoquinone to the reaction vessel (containing 1.5 g of thiol) caused an 80% decrease in the rate of reaction. Although it is possible that *p*-benzoquinone may take a direct part in the oxidation of the thiol, it is more likely that radical intermediates are involved in the reaction process thus explaining why such a small quantity of free radical scavenger can have such a large effect on the reaction rate.

General discussion

The polymeric catalyst possesses many enzyme-like characteristics:

- (1) Michaelis–Menten kinetics with respect to RSH.
- (2) A dependence of the reaction rate on pH with a maximum rate at a pH value of 8–9 [10].
- (3) First order kinetics with respect to catalyst concentration.
- (4) A relatively high turnover number ($k_2 \approx 2-3 \times 10^3 \text{ s}^{-1}$).

The activation energy is similar to the values observed in the autoxidation of RSH by vitamin B₁₂, the latter system exhibiting the same kinetics as the present polymeric system [15].

The occurrence of a saturation effect in the relationship between the reaction rate and oxygen pressure in the present system indicates that, in contrast to the homogeneous system $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$, the amount of catalytically inactive binuclear oxo adducts of $\text{CoPc}(\text{NaSO}_3)_4$ is not increased by higher oxygen pressures. This confirms again that the $\text{CoPc}(\text{NaSO}_3)_4$ sites are effectively shielded from other oxidation sites on the polymer surface.

A comparison of the $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ system with the homogeneous $\text{CoPc}(\text{NaSO}_3)_4/\text{OH}^-$ system reveals that the kinetics of the two systems are entirely different. The latter system appeared to have a positive, nearly first order, dependence on RS^- [25], the reaction rate decreasing with increasing oxygen pressure [25] and increasing upon addition of comparable amounts of salt [26]. Furthermore, in the conventional system the reaction rate was relatively low and the binuclear oxo-adduct content high [9]. The existence of H_2O_2 was never established, probably because the high pH value caused a rapid conversion of the peroxide [16].

Immobilized conventional systems containing $\text{CoPc}(\text{NaSO}_3)_4$ behave differently from the polymeric catalysts reported here. For the former systems, the influence of RSH on the reaction rate varies from being almost linear for porous chloromethylated polystyrene, cross-linked with divinylbenzene [7], to the existence of saturation kinetics for cellulose anion-

exchange resins [6]. In all cases reported, the activity for these immobilized systems is much lower than that observed for the $\text{CoPc}(\text{NaSO}_3)_4/\text{PVAm}$ system.

Obviously, the freely accessible polymer conformation and the special polymeric features of PVAm, such as the basicity of the amine ligands and complexation properties towards $\text{CoPc}(\text{NaSO}_3)_4$, act together to provide a much more efficient catalytic system.

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