

## Effects of ionenes on catalytic activity and structure of cobalt phthalocyanine. Part 2. Kinetics as a function of thiol and oxygen concentrations

**Citation for published version (APA):**

Herk, van, A. M., Tullemans, A. H. J., Welzen, van, J., & German, A. L. (1988). Effects of ionenes on catalytic activity and structure of cobalt phthalocyanine. Part 2. Kinetics as a function of thiol and oxygen concentrations. *Journal of Molecular Catalysis*, 44(2), 269-277. [https://doi.org/10.1016/0304-5102\(88\)80037-3](https://doi.org/10.1016/0304-5102(88)80037-3)

**DOI:**

[10.1016/0304-5102\(88\)80037-3](https://doi.org/10.1016/0304-5102(88)80037-3)

**Document status and date:**

Published: 01/01/1988

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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**EFFECTS OF IONENES ON CATALYTIC ACTIVITY AND  
STRUCTURE OF COBALT PHTHALOCYANINE  
PART 2. KINETICS AS A FUNCTION OF THIOL AND OXYGEN  
CONCENTRATIONS**

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(Received May 18, 1987; accepted September 10, 1987)

**Summary**

The catalytic oxidation of 2-mercaptoethanol was investigated kinetically for the system cobalt(II) phthalocyanine-tetra(sodium sulfonate) in the presence of poly(quaternary ammonium salts). The kinetics follow the two-substrate Michaelis-Menten rate law, in which 2-mercaptoethanol is one substrate and oxygen the other. At low thiol concentrations, the decrease in the rate of oxygen consumption during a catalytic reaction can be described by an exponential decay curve. At higher thiol concentrations, the complete two-substrate Michaelis-Menten rate law must be used. A very high turnover number of  $4300 \pm 400 \text{ s}^{-1}$  was found. Furthermore, the equilibrium constant for the addition of thiol was found to be  $46 \pm 10 \text{ M}^{-1}$ .

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**Introduction**

In polymeric catalysis, the effects polymers exert on catalytic reactions are the subject of many investigations [1]. In our laboratory the catalytic oxidation of thiols has been a successful probe to study such polymeric effects [2]. As a catalyst for this process, porphyrins and phthalocyanines in particular appeared to be very active. The relation of this process to naturally-occurring reactions is obvious. Vitamin B<sub>12</sub> also catalyses the oxidation of thiols.

In our laboratory we used mainly cobalt(II) phthalocyanine-tetra(sodium sulfonate) [CoPc(NaSO<sub>3</sub>)<sub>4</sub>] in combination with a wide variety of water-soluble polymers and immobilized polymers [2]. Poly(vinylamine), for example, showed large rate-enhancing effects. The rate of conversion of 2-mercaptoethanol to the corresponding disulfide appeared to be governed by three important parameters: basicity of the polymer, polymer charge density and ionic strength [2]. Basic groups are needed to dissociate the

weakly acidic thiol, thus supplying thiol anions, which are generally considered as the reactive species. A high charge density on the cationic polymer causes an increase in the local concentration of both thiolate anions and the negatively charged catalyst, and thus enhances the reaction rate. Low ionic strength results in a high reaction rate, since then only little competition between  $RS^-$  and other anions is possible.

In the case of poly(vinylamine), both protonated and unprotonated amine groups are present under reaction conditions. Therefore, the ratio of basicity and charge density will vary strongly with changes in, for example, pH, ionic strength, temperature or chain length of the polymer. In our previous studies we made no effort to maintain constant ionic strength and pH, because no complete mechanistic study was pursued. In the present investigations, however, ionic strength and pH are kept constant. As a model system we are currently investigating  $CoPc(NaSO_3)_4$  in the presence of ionenes. This type of polymer is preferred over poly(vinylamine) because its cationic charge is independent of pH. As a consequence, the catalytic activity is less influenced by pH than in the case of poly(vinylamine) [3]. Furthermore, the maximum activity is even higher for ionenes, and their catalytic activity decreases less in successive thiol oxidation runs [3]. Since ionenes do not contain basic groups and still show high catalytic activities, the high charge density on the polymer seems to be one of the most important factors in the rate-enhancing effects of these polymers.

In order to obtain mechanistic information on this interesting catalytic process, all parameters studied must be varied independently. In particular, ionic strength and pH must be controlled under all conditions. In the mechanistic interpretation of the kinetic data, the structure of the catalyst  $CoPc(NaSO_3)_4$  must also be taken into account. Our first study [4] on this subject revealed that the catalyst is mainly present as a dimeric species in the presence of 2,4-ionene. Furthermore,  $\mu$ -peroxo-bridged dimers were shown to be absent in the presence of oxygen in this system. Therefore, the structure of the polymeric catalyst in the absence of thiol is clearly established. Whether the structure of the catalyst changes under influence of the substrate is not yet known and is currently under investigation in our laboratory. The elucidation of a reaction mechanism should be a combination of kinetic investigations and structural information.

Insight into the reaction mechanism and the structure of the catalyst can lead to tailoring of new polymers with higher activities in combination with catalysts and specific substrates. We now present a kinetic study of this polymeric system, focussed on two-substrate kinetics.

## Experimental

2,4-Ionene was synthesized according to Rembaum [5] in equivolume mixtures of dimethylformamide and methanol, containing stoichiometric amounts of *N,N,N',N'*-tetramethylethanediamine (TMEDA, Merck, pure) and 1,4-dibromobutane (Fluka, pure) (1.5 M). The solution was kept at

room temperature for two weeks without stirring. The polymer was precipitated in acetone, filtered and purified by washing with acetone. The product was dried under vacuum at 50 °C for ~12 h. To determine molecular mass, 2,4-ionene was terminated by adding 0.25 g TMEDA to 1 g product and 1 ml water. The *N*-terminated ionene was washed with acetone and dried at 50 °C under vacuum. 1 M HCl was added to a solution of the terminated ionene until pH was below 3, and titration with 0.01 M NaOH was carried out [6].

CoPc(NaSO<sub>3</sub>)<sub>4</sub>, kindly provided by Dr. T. P. M. Beelen, was synthesized according to an adaptation by Zwart *et al.* [7] of the method by Weber and Busch [8].

The polymer catalyst was prepared by mixing 10 ml of  $1 \times 10^{-2}$  M 2,4-ionene (concentration expressed as the amount of ammonium groups) and variable amounts of CoPc(NaSO<sub>3</sub>)<sub>4</sub> (varied between  $1.6 \times 10^{-7}$  and  $1.4 \times 10^{-6}$  M) to keep the oxygen consumption rate within measurable range. To maintain a pH of  $8.30 \pm 0.05$  and a constant ionic strength of 0.1 M, TRIS buffer was used, containing 0.214 M tris(hydroxymethyl)aminomethane (Janssen Chimica) and 0.1 M HCl (Merck). Ionic strength was considered to be 0.1 M, equal to the Cl<sup>-</sup> concentration. This solution was added to the catalyst until a total volume of 100 ml was obtained.

The reaction vessel was an all glass double-walled thermostatted apparatus ( $25.0 \pm 0.5$  °C), equipped with a powerful mechanical glass stirrer. The stirring speed was 2500 rpm, at which no diffusion limitation occurs for our catalytic system [3]. The mixture was degassed twice, and the vessel was filled with nitrogen gas between evacuations. When the desired oxygen partial pressure was lower than 1 atm, an oxygen-nitrogen gas mixture was supplied to a total pressure of 0.1 MPa. The solution was saturated with the gas mixture for 5 min under vigorous stirring. Concentrations of dissolved oxygen were calculated from the partial pressure of oxygen in combination with the solubility of oxygen in 0.125 M NaCl (0.0011 M at 1 atm O<sub>2</sub>) [9].

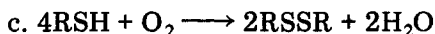
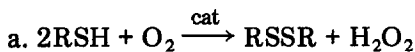
The reaction was started by adding 2-mercaptoethanol (purchased by Fluka) to the reaction vessel by means of a syringe. Mercaptoethanol was distilled prior to use and kept under nitrogen in a sealed ampoule. Distilled water was used throughout the whole experiment. The reaction rate was determined by monitoring oxygen consumption rate during the oxidation reaction. The oxygen consumption was measured with a digital flow meter (Inacom, Veenendaal). During reaction, pH was measured with a pHM 62 pH meter equipped with a GK 2401 B pH-electrode (Radiometer Copenhagen).

Prior to each reaction, the reactor was washed with water containing a soap solution (Hellma, Baden) while stirring for 5 - 10 min.

## Results and discussion

### *Initial rate as a function of substrate concentrations*

The reaction of thiols with oxygen generally proceeds according to the following stoichiometry:



In general, reaction 1b is considered as a fast consecutive reaction [10]. The initial rate is calculated as the amount of thiol converted per mole of catalyst, taking into account the stoichiometry of Scheme 1. First-order kinetics in  $\text{CoPc}(\text{NaSO}_3)_4$  were found.

At a pH of 8.30, the initial oxidation rate was measured at several partial oxygen pressures and thiolate anion concentrations. We used thiolate anion concentrations instead of thiol concentrations because we consider the thiolate anion as the reactive species. Thiolate concentrations at an ionic strength of 0.1 M were calculated from a  $\text{pK}_a$  value of 9.6 [11] at zero ionic strength and the Debye-Hückel equation [12]. The dependence of the reaction rate on both thiolate anion and oxygen concentrations showed Michaelis-Menten type curves, Figs. 1 and 2.

These results suggest two-substrate Michaelis-Menten kinetics [13], according to Scheme 2:

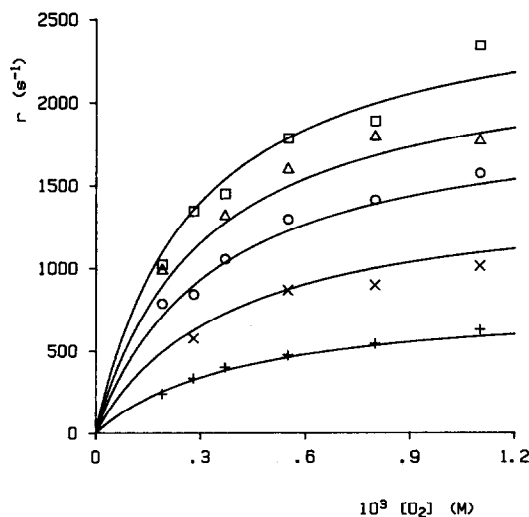


Fig. 1. Initial reaction rate as a function of oxygen concentration at thiolate anion concentrations of 0.00143 M (+), 0.00314 M (x), 0.0051 M (o), 0.0071 M ( $\Delta$ ) and 0.010 M ( $\square$ ). Curves calculated according to eqn. (4).  $T = 25.0 \pm 0.5$  °C,  $I = 0.1$  M,  $\text{pH} = 8.30 \pm 0.05$ .

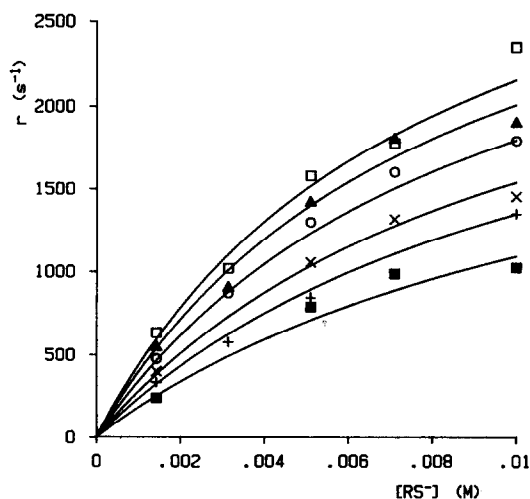
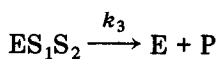
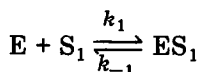


Fig. 2. Initial reaction rate as a function of thiolate anion concentration at oxygen concentrations of  $1.9 \times 10^{-4}$  M (■),  $2.8 \times 10^{-4}$  M (+),  $3.7 \times 10^{-4}$  M (x),  $5.5 \times 10^{-4}$  M (○),  $8.0 \times 10^{-4}$  M (▲) and  $1.1 \times 10^{-3}$  M (□). Curves calculated according to eqn. (4). Conditions as in Fig. 1.



where  $E = \text{CoPc}(\text{NaSO}_3)_4$ ,  $S_1$  and  $S_2$  are the two substrates, and  $P$  is the product.

If the reaction rate is given by:

$$V = \frac{dP}{dt} = k_3[ES_1S_2] \quad (3)$$

and steady state kinetics are assumed in both  $ES_1$  and  $ES_1S_2$ , it can be derived that [13]

$$-r = \frac{V}{[E]_{\text{tot}}} = \frac{c_1}{1 + \frac{c_3}{[S_1]} + \frac{c_2}{[S_2]} + \frac{c_2c_4}{[S_1][S_2]}} \quad (4)$$

with  $c_1 = 4k_3$ ,  $c_2 = (k_{-2} + k_3)/k_2$ ,  $c_3 = k_3/k_1$  and  $c_4 = k_{-1}/k_1$ .

It is customary to express the specific rate ( $r$ ) as the consumption of thiol per mol catalyst per second [2] (instead of mol product per mol

catalyst per second). Therefore,  $c_1$  is not equal to  $k_3$ , but, taking into account the stoichiometry of Scheme 1 and the fact that  $k_3$  refers only to the reaction step involving  $\text{CoPc}(\text{NaSO}_3)_4$  (Scheme 1, 1a),  $c_1 = 4k_3$ .

On the basis of formula 4, we cannot determine which substrate reacts first with the catalyst (Scheme 2). However, in our system no oxygen adducts can be detected in the absence of thiols [4]. Therefore we assume that prior to oxygen coordination a thiol must coordinate. Following the above-mentioned considerations, we assign  $S_1$  to the thiolate anion and  $S_2$  to oxygen.

Of course, Scheme 2 is an oversimplification of any correct reaction mechanism, because the valency of the cobalt in the catalyst changes during the reaction and radicals occur as intermediates [14]. Nevertheless, it is interesting to see if the reaction kinetics at different oxygen and thiol concentrations are in agreement with two-substrate Michaelis-Menten kinetics.

The lines drawn in Figs. 1 and 2 are calculated with constants obtained from a non-linear least squares calculation. The constants found were:  $c_1 = 4300 \pm 400 \text{ s}^{-1}$ ,  $c_2 = 1.4 \times 10^{-4} \pm 0.3 \times 10^{-4} \text{ M}$ ,  $c_3 = 6 \times 10^{-3} \pm 0.16 \times 10^{-3} \text{ M}$  and  $c_4 = 2.15 \times 10^{-2} \pm 0.5 \times 10^{-2} \text{ M}$ . In Table 1 the measured and calculated activities are shown. The average difference between measured and calculated activities is 5%.

From these data it can be concluded that the kinetics of the thiol oxidation, catalyzed by  $\text{CoPc}(\text{NaSO}_3)_4$  in the presence of 2,4-ionene, follow the two-substrate Michaelis-Menten kinetics. If indeed the first step in the reaction is the addition of the thiol, then  $c_4$  is equal to  $k_{-1}/k_1$ . The equilibrium constant is then equal to  $46 \text{ M}^{-1}$ . The turnover number ( $c_1$ ) is equal to  $4300 \text{ s}^{-1}$ , which is a very high number for this kind of reaction.

### *Oxygen consumption rate curves*

Because during the whole conversion the pH is maintained constant and the catalyst is not broken down during the reaction [3], the rate of oxygen consumption over the whole conversion contains kinetic information related to eqn. 4. If we assume that the concentration of thiol is low, then the rate of oxygen consumption varies linearly with the thiol concentration:

$$-r = k[\text{RSH}] = k \exp(-kt)[\text{RSH}]_0 \quad (5)$$

with  $k = c_1/(c_3 + c_2c_4/[\text{O}_2])$

Therefore the oxygen consumption should decrease according to an exponential decay curve. For comparison, the oxygen uptake rate curves for unbuffered and buffered systems are shown in Figs 3a and 3b respectively. Figure 3b also presents the exponential curve, which is fitted through the last part of the curve. From this fit, a value for  $k$  of  $4.1 \times 10^{-2} \text{ s}^{-1}$  is found, which, at a thiol concentration of 0.014 M (initial thiol concentration), gives an oxygen consumption rate of  $19 \text{ ml O}_2 \text{ min}^{-1}$ , a value which relates well to the oxygen consumption rate at the maximum of the curve ( $15 \text{ ml O}_2 \text{ min}^{-1}$ ).

TABLE 1

Measured and calculated activities at 25 °C;  $I = 0.1$  M,  $\text{pH} = 8.3$ ,  $1 \times 10^{-3}$  M 2,4-ionene

$10^3 [\text{RS}^-]$ (M)	$10^3 [\text{O}_2]$ (M)	$r_{\text{obs}}^a$	$r_{\text{calc}}^a$	Difference (%)
1.43	1.1	634	593	6.3
1.43	0.8	545	538	1.2
1.43	0.55	475	463	2.5
1.43	0.37	400	380	5.1
1.43	0.28	333	322	3.4
1.43	0.19	238	250	-5.2
3.14	1.1	1018	1101	-8.1
3.14	0.8	901	1008	-11.9
3.14	0.55	871	878	-0.7
3.14	0.28	577	624	-8.1
5.10	1.1	1578	1515	4.0
5.10	0.8	1414	1397	1.2
5.10	0.55	1296	1229	5.2
5.10	0.37	1054	1034	1.9
5.10	0.28	844	892	-5.6
5.10	0.19	788	709	10.0
7.10	1.1	1775	1825	-2.8
7.10	0.8	1797	1692	5.8
7.10	0.55	1598	1500	6.1
7.10	0.37	1314	1273	3.1
7.10	0.19	985	887	9.9
10.0	1.1	2347	2151	8.3
10.0	0.8	1893	2005	-5.9
10.0	0.55	1788	1793	-0.3
10.0	0.37	1450	1537	-6.0
10.0	0.28	1345	1345	0.0
10.0	0.19	1021	1089	-6.7

<sup>a</sup> $r$  expressed in units of mol thiol per mol catalyst per second;  $r_{\text{obs}}$ : observed initial rate,  $r_{\text{calc}}$ : initial rate calculated according to eqn. (4).

At higher thiol concentrations, the oxygen consumption rate curve can no longer be described in this way. There, the saturation kinetics in thiol must be taken into account (Fig. 4). In this case, eqn. 4 can be used to predict the oxygen consumption rate curve by numerically calculating the thiol concentrations in small time steps. In Fig. 4 a calculated curve is depicted which describes the experimental oxygen consumption rate curve rather well. At lower thiol concentrations differences occur between calculated and observed oxygen consumption rate curves. This indicates that the reaction stoichiometry of Scheme 1 is complicated, probably by hydrogen peroxide formation. Indeed,  $\text{H}_2\text{O}_2$  could be detected in the reaction mixtures. Therefore, we checked the oxygen mass balance for the  $\text{CoPc}(\text{NaSO}_3)_4/2,4\text{-ionene}$  system. The total oxygen consumption for complete conversion, *i.e.* the integral of the oxygen uptake curve, was



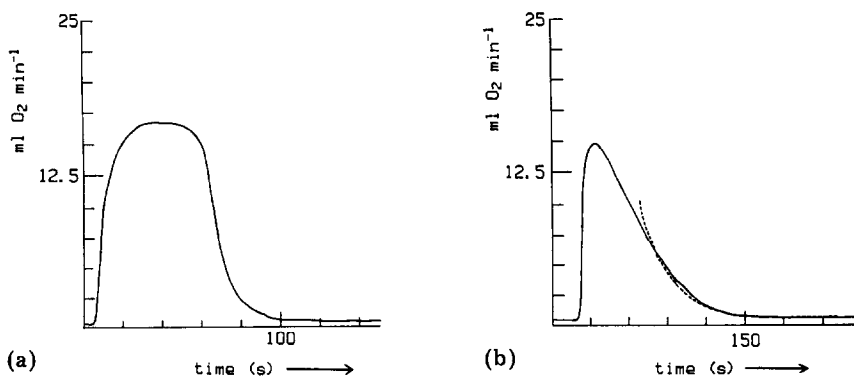


Fig. 3. Oxygen uptake rate *versus* time at low thiol concentration,  $T = 25^\circ\text{C}$ ,  $[\text{RSH}] = 0.014\text{ M}$ ; (a) Unbuffered system;  $I = 0\text{ M}$ , initial  $\text{pH} = 8.3$ ,  $[\text{CoPc}(\text{NaSO}_3)_4] = 2 \times 10^{-7}\text{ M}$ ,  $[\text{O}_2] = 0.0011\text{ M}$ ; (b) Buffered system;  $I = 0.1\text{ M}$ ,  $\text{pH} = 8.3$ ,  $[\text{CoPc}(\text{NaSO}_3)_4] = 1.1 \times 10^{-6}\text{ M}$ ,  $[\text{O}_2] = 3.7 \times 10^{-4}\text{ M}$ ; the dotted line represents the exponential fit according to eqn. (5).

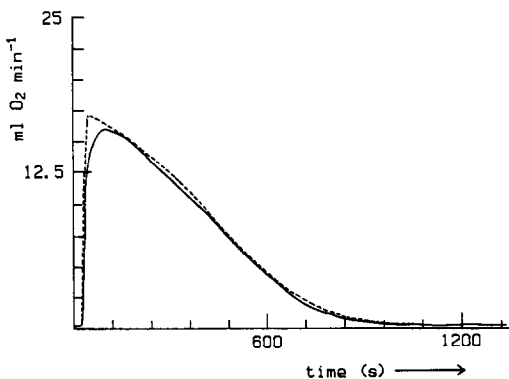


Fig. 4. Oxygen uptake rate *versus* time at high thiol concentration;  $[\text{RSH}] = 0.2\text{ M}$ ,  $[\text{O}_2] = 5.5 \times 10^{-4}\text{ M}$ ,  $[\text{CoPc}(\text{NaSO}_3)_4] = 2 \times 10^{-7}\text{ M}$ , other conditions as in Fig. 1. The dotted line represents the fit according to eqn. (4).

measured and the peroxide content was determined iodometrically. The number of moles of thiol together with the amount of hydrogen peroxide accumulated account for the total amount of oxygen consumed, within experimental error.

In general, only small amounts of peroxide could be detected. However, at low thiol concentrations the relative amount of hydrogen peroxide increased. This explains why at low thiol concentrations the exponential fit through the oxygen consumption rate curve gave a larger rate constant than expected from the initial rate.

## Conclusions

It can be concluded that the kinetics of the thiol oxidation follow the two-substrate Michaelis–Menten rate law, and that the initial rate and

oxygen consumption rate curve can be described by this rate law. The influence of pH on the rate constants and the interpretation of these rate constants in relation to the polymeric effects will be the subject of further investigations.

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