

Effects of ionenes on structure and catalytic activity of cobalt phthalocyanine. Part 7. Dependence of reaction kinetics on pH, type of polymer and type of thiol

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EFFECTS OF IONENES ON STRUCTURE AND CATALYTIC ACTIVITY OF COBALT PHTHALOCYANINE PART 7. DEPENDENCE OF REACTION KINETICS ON pH, TYPE OF POLYMER AND TYPE OF THIOL

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Summary

The cobalt phthalocyanine (1)-catalyzed autoxidation of thiols in the presence of ionenes (2) was investigated kinetically, using the two-substrate Michaelis-Menten model. Effects of pH, type of ionene and type of thiol on the overall reaction rate were established, as well as their effects on the individual kinetic parameters.

Overall reaction rate appeared to be mainly determined by k_1 , the rate constant for complexation of the thiolate anion with the catalyst, and especially k_3 , the rate constant of the product formation step (see Scheme 1). Since k_1 is related to the local thiolate anion concentration, it could be increased by increasing the pH, the effective ionene charge density and the negative charge on the R-group of the thiol. Regarding k_3 , it was found that this rate constant decreases at $\text{pH} > 11$ or when negatively-charged thiols are used.

From the results obtained for different ionenes, it was concluded that the degree of phthalocyanine aggregation is an important factor, presumably affecting the ease of oxidation of the cobalt complex.

A detailed reaction mechanism, combining all observed dependencies is proposed and discussed.

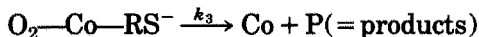
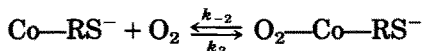
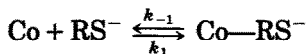
Introduction

Recently we have been studying the kinetics of the oxidation of thiols in the presence of cobalt phthalocyanine (1) and ionenes (2). It was established that the process can be described by the two-substrate Michaelis-Menten

*Part 6: see [1].

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model [2] according to Scheme 1, where Co represents $\text{CoPc}(\text{NaSO}_3)_4$:



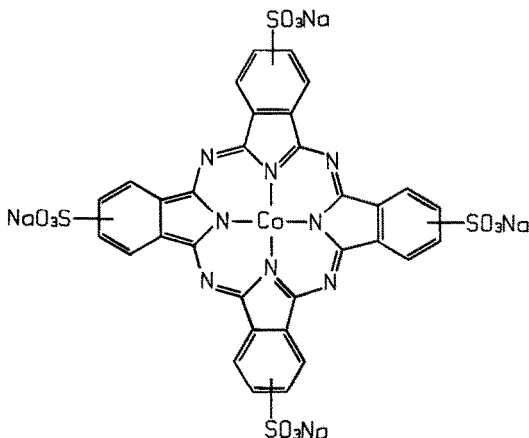
Scheme 1.

leading to the kinetic equation (1):

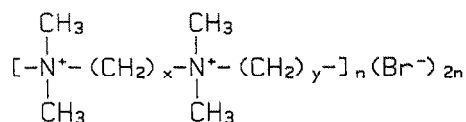
$$v = d[\text{P}]/dt = \frac{C_1[\text{Co}]}{1 + C_2/[\text{O}_2] + C_3/[\text{RS}^-] + C_2C_4/([\text{O}_2][\text{RS}^-])} \quad (1)$$

where $C_1 = k_3$, $C_2 = (k_{-2} + k_3)/k_2$, $C_3 = k_3/k_1$ and $C_4 = k_{-1}/k_1$.

It was found that only one side-reaction occurs, *viz.* the formation of hydrogen peroxide [1, 2]. In a previous article [1] a calculation model was presented to account for this peroxide accumulation.



1: cobalt phthalocyanine-tetrasodiumsulfonate, $\text{CoPc}(\text{NaSO}_3)_4$



2: ionenes

type	name	x	y
2a	2,4-ionene	2	4
2b	2,6-ionene	2	6
2c	6,4-ionene	6	4
2d	6,6-ionene	6	6
2e	2,xyl-ionene	2	$\text{CH}_2-\phi-\text{CH}_2$ (xylyl) instead of $(\text{CH}_2)_y$

Using the derived relationships, the effects of several reaction conditions on the kinetic parameters can now be investigated further, in order to obtain mechanistic information about the process. We discuss here the effects of varying the pH, the type of ionene and the type of thiol.

Experimental

Ionene syntheses

The ionenes **2a**, **b** and **d** were prepared as described previously [3]; 6,4-(**2c**) and 2,xyl-ionene (**2e**) were synthesized analogously, using the starting materials *N,N,N',N'*-tetramethyl-1,6-hexanediamine and 1,4-dibromobutane for **2c** and *N,N,N',N'*-tetramethylethanediamine and α,α' -dichloro-*p*-xylene for **2e**. M_n values were determined as published before [4] and were found to be: 8600 for **2a**, 7000 for **2b**, 6200 for **2c**, 13 000 for **2d** and 5300 for **2e**.

Ionene concentrations were always expressed as amounts of ammonium groups per unit volume ($[N^+]$ in mol dm⁻³).

Other materials

CoPc(NaSO₃)₄ (**1**), kindly provided by Dr. T. P. M. Beelen, was synthesized according to an adaptation by Zwart *et al.* [5] of the method described by Weber and Busch [6].

The thiols 2-mercaptoethanol (R⁰SH), mercaptoacetic acid (R⁻SH) and aminoethanethiol (R⁺SH) were distilled prior to use. All other reagents were of analytical grade and used without further purification.

Catalytic activity measurements

Catalytic measurements were performed according to the method described in [2]. The following buffer compounds were used: TRIS (tris(hydroxymethyl)aminomethane, pH 7.9–8.85), sodium tetraborate (pH 9.5), sodium carbonate (pH 10.5), sodium phosphate (pH 11.5 and 12.3) and sodium hydroxide (pH 13). The ionic strength of all buffers was 0.1 mol dm⁻³, achieved by dissolving the appropriate amounts of buffer compounds. No other salts were added, in order to obtain maximum buffer capacities. For the buffers of pH 10.5 and 11.5, buffer capacities were still found to be insufficient. Therefore, the results presented for these pH values are somewhat less reliable.

Calculation procedures

The degrees of thiol dissociation were calculated from the applied pH and the pK_a values at 0.1 mol dm⁻³ ionic strength. These pK_a values were obtained from the pK_a at zero ionic strength [7] and the Debye–Hückel equation [8] and were found to be: 8.2 for R⁺SH, 9.3 for R⁰SH, 10.2 for R⁻SH and 8.2 for cysteine (R⁺SH).

The obtained kinetic data were fitted to eqn. 1, using a non-linear least squares calculation procedure, where $\Sigma((v_{\text{calc}} - v_{\text{meas}})/v_{\text{meas}})^2$ was minimized.

TABLE 1
Effects of pH on kinetic parameters^{a,b}

pH	$10^{-5} k_1$	$10^{-2} k_{-1}$	$10^{-2} K_1$	$10^{-6} k_2^{\text{min}c}$	$10^{-3} K_2^{\text{min}c}$	$10^{-2} k_3$
7.9	3	50	0.6	13	14	9
8.3	3	40	0.8	7	7	10
8.85	1.1	6	2	3	3	10
9.5	5	7	7	3	3	10
10.5	2	1.4	14	2	3	9
11.5	1.3	1.1	12	1.9	3	8
12.3	1.3	0.6	20	1.7	3	5
13	4	1.2	30	1.6	5	3

^a 2,4-Ionene, thiol: 2-mercaptoethanol.

^b k_1 and k_2^{min} in $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$, k_{-1} and k_3 in s^{-1} , K_1 and K_2^{min} in $\text{dm}^3 \text{mol}^{-1}$.

^c $k_2^{\text{min}} = k_3/C_2 (k_{-2} \ll k_3)$, $K_2^{\text{min}} = 1/C_2 (k_{-2} \gg k_3)$.

With the knowledge on H_2O_2 accumulation obtained previously [1], it was possible to analyze complete oxygen uptake rate curves, deriving pairs of $[\text{RSH}]_t$ and uptake rate at time t , where $[\text{RSH}]_t$ was corrected for the amount of accumulated H_2O_2 .

In order to test the reliability of this method, the effect of small variations in $[\text{H}_2\text{O}_2]_t$ (and thus $[\text{RSH}]_t$) was studied. From the results, it appeared that only k_1 was significantly affected (see also Discussion). Relative errors in the calculated kinetic parameters were: $k_1 \pm 40\%$; k_{-1} , k_2^{min} and $K_2^{\text{min}} \pm 30\%$ (where k_2^{min} and K_2^{min} are defined as in Table 1); $k_3 \pm 10\%$.

Results

pH variation

pH effects on catalytic activity were measured for several oxygen and thiol concentrations, so that it was possible to determine how each kinetic parameter is affected by changing the pH (Table 1). The effect on the overall activity was also established, as illustrated in Fig. 1.

Keeping $[\text{RSH}]$ constant (Fig. 1a), the catalytic activity showed an optimum around pH 9.5. The activity increase up to a pH of 9.5 was due to the increasing degree of thiol dissociation, as is evident from the pH independence at constant $[\text{RS}^-]$ in this region (Fig. 1b). This effect is also reflected in the fact that k_1 is practically independent of pH (Table 1).

Above pH 9.5, activity decreases at both constant thiol and thiolate anion concentrations. This rate decrease is mainly due to a decreasing efficiency of the product formation step, *i.e.* to a decrease in rate constant k_3 (Table 1). The variation of kinetic parameters with pH will be further discussed below.

Ionene variation

Based on the results reported previously by Brouwer *et al.* [9], it was expected that variation of the ionene charge density would lead to a parallel

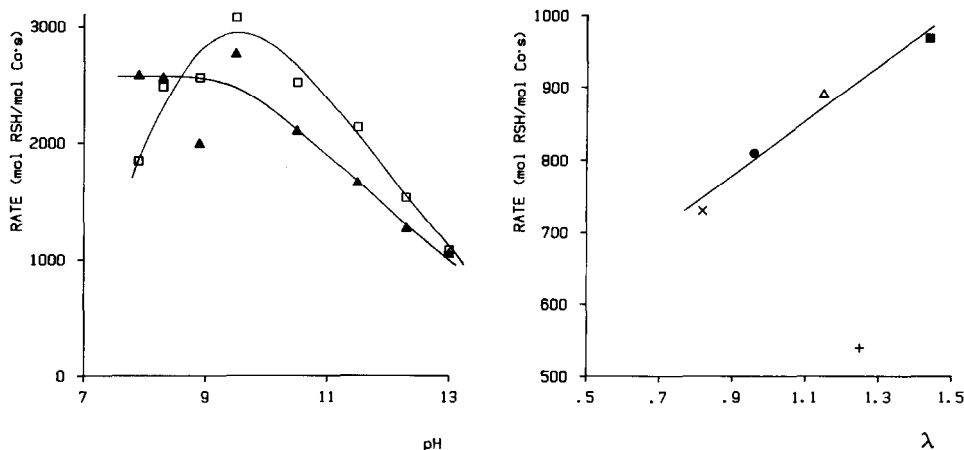


Fig. 1. Effect of pH on overall reaction rate at constant thiol concentration (□) $[\text{RSH}] = 0.14 \text{ mol dm}^{-3}$ and constant thiolate anion concentration (▲) $[\text{RS}^-] = 0.014 \text{ mol dm}^{-3}$. Other reaction conditions: $[\text{O}_2] = 0.0011 \text{ mol dm}^{-3}$, $[\text{N}^+] = 10^{-3} \text{ mol dm}^{-3}$; 2,4-ionene was used; thiol: 2-mercaptoethanol.

Fig. 2. Dependence of reaction rate on the linear charge density parameter, λ , of several ionenes: (■) 2,4-ionene, (△) 2,6-ionene, (●) 6,4-ionene, (×) 6,6-ionene, (+) 2,xyl-ionene. $[\text{O}_2] = 0.00055 \text{ mol dm}^{-3}$, $[\text{RSH}] = 0.017 \text{ mol dm}^{-3}$, $\text{pH} = 8.9$, $[\text{N}^+] = 10^{-3} \text{ mol dm}^{-3}$, thiol: 2-mercaptoethanol.

variation in overall activity, due to changes in local thiolate anion concentration.

Indeed, it was found that the activity increases with increasing charge density (Fig. 2, where the linear charge density parameter λ has been calculated according to [9]). Within the series of x,y -ionenes, where x and y were varied between 2 and 6, the observed relationship was linear. The 2,xyl-ionene, containing aromatic groups in the polymer backbone, showed an activity lower than expected on the basis of its calculated linear charge density. This is probably due to the fact that the 2,xyl-ionene chains have a longer persistence length and, thus, a lower coil density than the flexible x,y -ionene chains, leading to a lower electrostatic potential.

It was established which reaction rate constants are responsible for the observed variations in overall activity. As can be seen in Table 2, k_1 remained surprisingly constant within the x,y -ionene series. Since k_1 is in fact an apparent rate constant also accounting for differences in local $[\text{RS}^-]$, it must be concluded that the local thiolate anion concentration is not the determining factor in the different activities of these ionenes (presumably, variations in linear charge density are compensated by variations in coil dimensions). On the other hand, it was calculated that the decrease in activity on going from 2,4- to 6,6-ionene was predominantly caused by a (small) increase of C_2 (decrease of k_2 or K_2). For 2,xyl-ionene, the low value of k_1 and the high C_2 value appeared to contribute to its low activity. In all cases, the effects of k_1 and C_2 were partly compensated by changes in k_{-1} . These effects will be discussed in more detail below.

TABLE 2

Kinetic parameters for several ionenes^a

Ionene ^b	$10^{-5} k_1$	$10^{-2} k_{-1}$	$10^{-2} K_1$	$10^{-6} k_2^{\min}$	$10^{-3} K_2^{\min}$	$10^{-2} k_3$
2,4	1.1	6	2	3	3	10
2,6	1.3	2	7	1.4	1.4	10
6,4	1.5	2	8	1.0	1.1	9
6,6	1.1	1.3	8	1.0	1.1	9
2,xyl	0.6	0.2	30	0.8	0.8	10

^a Conditions: pH = 8.85, thiol: 2-mercaptoethanol.^b Linear charge density parameters: 2,4-ionene: 1.44; 2,6-ionene: 1.15; 6,4-ionene: 0.96; 6,6-ionene: 0.82; 2,xyl-ionene: 1.25.^c For dimensions and definitions of k_2^{\min} and K_2^{\min} ; see Table 1.*Thiol variation*

By varying the R-group of RSH, it is also possible to obtain mechanistic information. In particular, the charge on the R-group seemed an interesting parameter in our polyelectrolyte catalytic system. It was expected that thiols carrying a highly negative charge would be relatively more concentrated within the polymer coil domains and the oxidation of these thiols would therefore be enhanced. To verify this assumption, the following thiols were used in catalytic experiments and compared with the previously investigated mercaptoethanol ($R^0 = -CH_2CH_2OH$): mercaptoacetic acid ($R^- = -CH_2COO^-$), cysteine ($R^\pm = -CH_2CH(COO^-)NH_3^+$) and aminoethanethiol ($R^+ = -CH_2CH_2NH_3^+$).

Figure 3 shows the activities for these thiols at pH = 8.9 and constant oxygen concentration. It clearly shows, that, in contrast to our expectations,

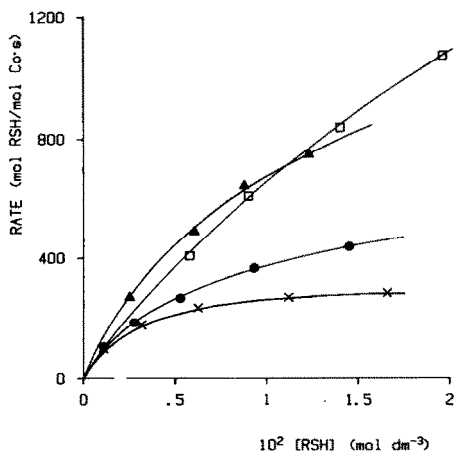


Fig. 3. Reaction rate versus thiol concentration for the oxidation of mercaptoethanol R^0SH (\square), aminoethanethiol R^+SH (\blacktriangle), cysteine $R^\pm SH$ (\bullet) and mercaptoacetic acid R^-SH (\times). $[O_2] = 0.00055 \text{ mol dm}^{-3}$, pH = 8.9, $[N^+] = 10^{-3} \text{ mol dm}^{-3}$, 2,4-ionene was used.

TABLE 3

Kinetic parameters for several thiols^a

Thiol ^b	$10^{-5} k_1$	$10^{-2} k_{-1}$	$10^{-2} K_1$	$10^{-6} k_2^{\min}$	$10^{-3} K_2^{\min}$	$10^{-2} k_3$
R ⁻ SH	11	3	30	0.8	8	1.0
R ⁰ SH	1.1	6	2	3	3	10
R [±] SH	0.5	1.5	3	1.4	7	2
R ⁺ SH	0.4	0.6	7	2	3	6

^a Conditions: 2,4-ionene, pH = 8.85 at which the degrees of thiol dissociation, $[RS^-]/[RSH]$, are 0.05 for R⁻SH, 0.26 for R⁰SH, 0.58 for R[±]SH and 0.86 for R⁺SH.

^b R⁻SH = mercaptoacetic acid, R⁰SH = mercaptoethanol, R[±]SH = cysteine, R⁺SH = aminoethanethiol.

^c For dimensions and definitions of k_2^{\min} and K_2^{\min} , see Table 1.

aminoethanethiol and mercaptoethanol are being oxidized at a higher rate than the thiols carrying negatively charged R-groups, although the values for k_1 (Table 3) indicated that the latter compounds are indeed more concentrated locally than the uncharged or positively charged thiols. The activity differences are mainly caused by different k_3 values (Table 3) and will be further discussed below.

Discussion

The reaction mechanism of the ionene-promoted catalytic thiol oxidation was evaluated in detail with the aid of the dependences of the kinetic parameters on pH (Table 1), ionene charge density (Table 2) and type of thiol (Table 3). These dependences are summarized in Table 4.

TABLE 4

Summary of effects of reaction conditions on kinetic parameters and overall reaction rate^a

	k_1	k_{-1}	K_1	k_2 or K_2	k_3	Rate ^b
pH						
7.9 → 10	0	-	+	-	0	+ ^c
10 → 13	0	0	0	0	□	-
ionene						
2,xy1 → x,y	⊕	+	-	+	0	+
6,6 → 2,4	0	+	-	⊕	0	+
R(RSH)						
R ⁻ → R ⁰	-	+ ^d	- ^d	+	⊕	+
R ⁰ → R ⁺	□	- ^d	+ ^d	-/0	□	-

^a - = Decrease, + = increase, 0 = constant; the symbols ⊕ and □ denote the rate constants contributing most to the observed differences in overall reaction rate.

^b Keeping all other conditions constant.

^c $[RSH]$ is constant; if $[RS^-]$ is constant, then the rate is also constant.

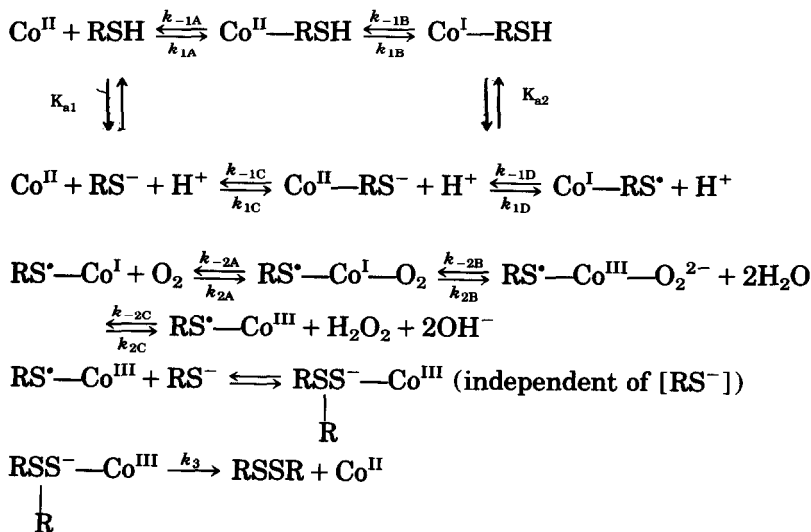
^d At constant pH; expected at constant $[RSH]/[RS^-]$: $k_{-1} + K_1 -$.

The model of Scheme 1 formed the basis of this evaluation. However, it was taken into account that this scheme is only a simplified representation of the process, because each presented reaction step in reality consists of more than one step, *viz.* coordination and electron transfer (redox) steps.

Furthermore, an alternative mechanism was considered, in which the first kinetically perceptible reaction step is the interaction of oxygen with the RS^- -Co complex. Formation of that complex was then regarded as a saturated pre-equilibrium, whereas the addition of the second thiolate anion (necessary to form RSSR) was assumed to be responsible for the observed Michaelis-Menten kinetics in thiol. In the mechanism of Scheme 1, the rate of the addition of the second thiolate anion is assumed to be independent of thiol concentration. Both these mechanisms are in agreement with the observation that the catalytic thiol oxidation does not show second-order kinetics in thiol.

A third possible mechanism, in which the first reaction is the addition of oxygen to $\text{CoPc}(\text{NaSO}_3)_4$, was rejected since it has been demonstrated spectroscopically that no interaction occurs between oxygen and the ionene-bound metal complex [10].

On the basis of all kinetic data obtained, the mechanism of Scheme 1 appeared to be the most probable reaction pathway. In Scheme 2, a more detailed description is given, which we propose as the mechanism for the ionene-promoted process. Further argumentation for the choice of this mechanism, based on various experimental observations, follows below.



Scheme 2.

pH effects

The value of k_1 appeared to be very sensitive to small changes in thiol concentration caused by small variations in H_2O_2 accumulation (see

Experimental), and therefore k_1 could not be determined very accurately. Nevertheless, it could be concluded that this rate constant does not change significantly within the pH-range investigated (7.9–13) and has a value of $2.6 \pm 1.4 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The constancy of k_1 is in good agreement with the fact that the reactivity of the thiol molecule is negligible as compared to that of the thiolate anion [9] ($k_{1A}, k_{1B} \ll k_{1C}, k_{1D}$), which was implemented in our kinetic equation (1).

The largest pH effect was found for k_{-1} , although its effect on the overall reaction rate was calculated to be rather small. It was found that k_{-1} decreases on going from pH 7.9 to about 10, while at still higher pH values k_{-1} remained constant. This suggests the involvement of an acid/base equilibrium in this reaction step, with a $\text{pK}_a \sim 9$. Since mercaptoethanol has a pK_a of 9.3 under reaction conditions, this thiol, coupled to the catalyst, seemed a likely candidate for this equilibrium. Therefore, we have tried to describe the pH dependence of k_{-1} by assuming two parallel Co–thiol dissociation routes for both the protonated and unprotonated thiol forms, as presented in Scheme 2. The following set of equations corresponds to this model:

$$k_{-1} = (1 - \alpha)k_{-1}^{\text{RSH}} + \alpha k_{-1}^{\text{RS}^-} \quad (2)$$

$$\alpha = 1/(10^{\text{pK}_{a2} - \text{pH}} + 1) \quad (3)$$

where k_{-1}^{RSH} (a combination of k_{-1A} and k_{-1B}) and $k_{-1}^{\text{RS}^-}$ (k_{-1C} and k_{-1D}) are the rate constants for the dissociation of the Co–RSH complex and the Co–RS[−] complex, respectively, and K_{a2} is the apparent acid dissociation constant of the Co–RSH complex (either in the Co^{II} or the Co^I state). With $k_{-1}^{\text{RSH}} = 6 \times 10^3 \text{ s}^{-1}$, $k_{-1}^{\text{RS}^-} = 10^2 \text{ s}^{-1}$ and $\text{pK}_{a2} = 8.4$, a good fit of the experimentally determined k_{-1} values was obtained, as can be seen in Fig. 4.

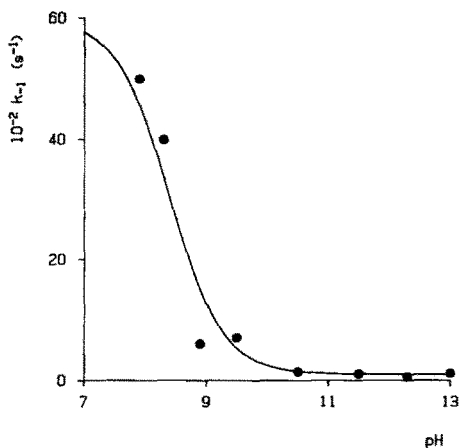


Fig. 4. Rate constant k_{-1} as a function of pH. Data points obtained from fitting the kinetic results to eqn. 1, drawn curve calculated according to eqns. 2 and 3, assuming $k_{-1}^{\text{RSH}} = 6000 \text{ s}^{-1}$, $k_{-1}^{\text{RS}^-} = 100 \text{ s}^{-1}$ and $\text{pK}_{a2} = 8.4$.

Apparently, the acidity of the thiol is increased upon its binding to the phthalocyanine complex. The fact that the RSH complex reacts at a much faster rate than the deprotonated form probably is due to the electron-withdrawing property of RSH, which will cause weakening of the Co—RSH bond.

Concerning oxygen addition to the $\text{Co}^{\text{I}}\text{—RS}^-$ complex, also a small pH dependence was observed. However, it is difficult to draw conclusions from this, because k_{-2} cannot be determined and therefore it remains unknown whether a kinetic effect is measured (if $k_{-2} \ll k_3$ then $k_2 = k_3/C_2$, see eqn. (1)) or a thermodynamic effect (if $k_{-2} \gg k_3$ then $K_2 = 1/C_2$). Thus, either k_2 or K_2 decreases with increasing pH until $\text{pH} \approx 8.5$, after which constant values are reached ($k_2 = 2.2 \pm 0.6 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $K_2 = 3.3 \pm 0.8 \times 10^3 \text{ dm}^3 \text{ mol}^{-1}$). Presumably, the acid dissociation of water plays a role in this pH dependence since the effect is largest around pH 7. Moreover, it seems very likely that the presence of OH^- hinders the formation of peroxide as shown in Scheme 2.

Finally, the rate constant of the product formation step, k_3 , appeared to be constant for $7.9 \leq \text{pH} \leq 11$. At high pH, however, k_3 was observed to decrease. This may be due to one of the following effects: (1) OH^- stabilizes (inactivates) the ternary reaction intermediate or (2) large amounts of hydroxyl ions induce the formation of (small amounts of) the inactive μ -peroxo Co complex [10, 11], thus lowering the efficiency of the catalyst.

Varying the type of ionene; conformational and structural effects

Before discussing the dependence of the kinetic parameters on the type of ionene, the effects of varying the ionene structure on chain conformation and catalyst structure must be considered. As the alkyl and xyl segments were regarded as chemically inert, the direct effects of ionene structural elements on reaction kinetics have not been taken into account.

With respect to chain conformation, it is clear that 2,xyl-ionene differs considerably from the x,y-ionenes, since the latter compounds consist of flexible chains, whereas 2,xyl-ionene contains aromatic groups in the polymer backbone, keeping the $\text{N}^+\text{—N}^+$ distances more or less fixed. Therefore, the x,y-ionenes will exhibit higher coil densities than the 2,xyl-ionene, accompanied by higher electrostatic potentials, leading to stronger enhancement of the thiolate anion concentration within the polymer coil domains ($[\text{RS}^-]_{\text{local}}$). This will be shown to affect thiol oxidation kinetics.

Within the x,y-ionene series, differences in electrostatic potential will probably be rather small, since the variation in linear charge density will be (at least partly) compensated by changes in coil dimensions: while the 2,4-ionene chains will be largely expanded due to repulsion between the closely spaced positive charges, the chains of e.g. 6,6-ionene may be more contracted since the repulsion will be less along the longer alkyl segments. Therefore, only minor differences in $[\text{RS}^-]_{\text{local}}$ within this ionene series are expected.

Apart from the effect on thiolate enrichment within the polymer domains, the ionene charge density or, more precisely, the electrostatic

potential may also affect another quantity, *viz.* the degree of aggregation of the cobalt catalyst. The importance of the latter phenomenon has been discussed in a previous article [3], in which it was demonstrated that the aggregated phthalocyanine complex is far more active in the catalytic thiol autoxidation than its monomeric form.

For the ionenes discussed here, the degree of aggregation was spectroscopically studied, revealing that the 2,xyl-ionene system contains only dimers (unreduced: $\lambda_{\max} = 628$ nm, reduced: $\lambda_{\max} = 460$ and 690 nm), whereas the *x,y*-ionenes contain higher aggregates ($\lambda_{\max} = 622$ nm and $\lambda_{\max} = 452$ and 686 nm, respectively). It is most likely that formation of higher aggregates in the 2,xyl-ionene system is prevented by a too large separation of neighbouring $\text{CoPc}(\text{SO}_3)_4^{4-}$ anions along the xylyl segments ($\text{N}^+ - \text{N}^+$ distance approx. 8 Å).

In the next section, it will be demonstrated that the degree of phthalocyanine aggregation is an important factor influencing reaction kinetics. It would have been interesting to include 2,10-ionene in these kinetic investigations, since this ionene stabilizes the catalyst complex in its monomeric form [3]. However, the activity of this system was too low to allow determination of the kinetic parameters with sufficient accuracy. Moreover, the kinetic behaviour of this system was observed to be complicated by a deviation from first-order kinetics in Co [3].

Effects of the type of ionene on kinetic parameters

Looking at Table 2, it is evident that k_1 is not very sensitive to charge density changes. Between the *x,y*-ionenes ($k_1 = 1.3 \pm 0.2 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and 2,xyl-ionene the observed difference in this rate constant is only a factor of 2. Nevertheless, this relatively small decrease in k_1 was calculated to be the most important factor determining the lower overall activity of the 2,xyl-ionene. The lowering of k_1 is probably a result of the lowered local thiolate anion concentration due to the decreased charge density. Within the *x,y*-ionene series, k_1 , and thus $[\text{RS}^-]_{\text{local}}$, appears to be constant, indicating that differences in linear charge density are indeed (at least partly) being compensated by coil dimensions, as was discussed above.

The value of k_{-1} varies considerably (Table 2); even within the *x,y*-ionene series the observed variation is significant. If this variation is caused by a shift in electrostatic potential leading to a shift in the K_{a2} equilibrium, one would expect an increase of k_{-1} with decreasing charge density: as was stated in the discussion on pH effects, $k_{-1}^{\text{RSH}} \gg k_{-1}^{\text{RS}^-}$ and a system with low charge density, where $[\text{RSH}]_{\text{local}}$ is relatively high, should therefore exhibit a high value for k_{-1} . Instead, it was found that k_{-1} strongly decreases on going from 2,4- to 2,xyl-ionene (by a factor of 30!).

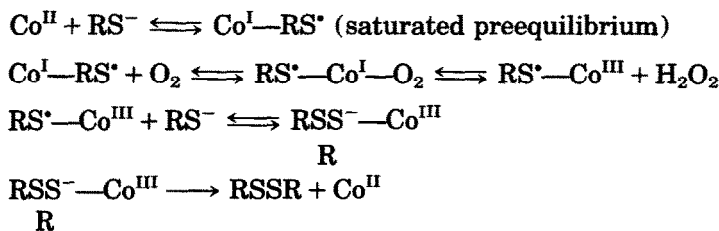
A possible explanation for this phenomenon can be found in the variation of the degree of cobalt aggregation on varying the type of ionene. In the 2,xyl-ionene system only dimers occur, while the *x,y*-ionenes stabilize higher aggregates. If transfer of electrons from Co^{I} to RS^{\cdot} is facilitated by an increase in the degree of aggregation, this would account for the observed variation in k_{-1} . It would also be in good agreement with the results of Nevin

et al. [12], who found that tetranuclear phthalocyanine complexes are more efficient reductors than the analogous mononuclear or binuclear complexes. It must be noted that this argument implies a variation of the degree of aggregation even within the *x,y*-ionene series, which appeared impossible to prove spectroscopically. Nevertheless, it is postulated that the observed charge density effect on k_{-1} is a result of the dependency of k_{-1B} and/or k_{-1D} on the degree of aggregation of the cobalt catalyst.

Based on the foregoing, it is obvious that reaction step 2B (Scheme 2) must also show a dependence of reaction rate on charge density, because an analogous electron transfer is involved as was discussed above. Indeed, an increase in C_2 (decrease in k_2 or K_2) with decreasing charge density was recorded, but the effect was very small. This may be due to one of the following reasons: (1) the redox step (2B) is much faster than the coordination of oxygen to the catalyst complex (2A), so that the rate of the latter step determines the observed k_2 value; (2) if $k_3 \ll k_{-2}$ only a thermodynamic effect is measured and a change in charge density probably affects k_{2B} and k_{-2B} equally. On the basis of the present results it is impossible to discriminate between these possibilities.

The rate constant for product formation, k_3 , was found to be constant for all ionenes investigated. This implies that neither local concentration effects nor aggregate-facilitated Co oxidation play a role during this step. This is consistent with the proposed mechanism of Scheme 2, where peroxide formation takes place in step 2 and the second thiolate anion addition is assumed to be kinetically undetectable.

The constancy of k_3 was also the main reason why the alternative mechanism, mentioned at the beginning of this section, was rejected. If, according to that mechanism, peroxide formation would take place before the formation of disulfide, its scheme would become:



Scheme 3.

This scheme corresponds to a so-called ping-pong mechanism [13], which is described by a kinetic expression of the form of eqn. (4):

$$v = \frac{a[\text{Co}]}{1 + b/[\text{O}_2] + c/[\text{RS}^-]} \quad (4)$$

However, the obtained kinetic data presented in this report cannot be fitted to this equation satisfactorily. Thus, it can be concluded that Scheme 3 does not provide an appropriate representation of the catalytic process.

Effects of varying the type of thiol

Variation of the R-group of RSH leads to large variations in overall reaction rate and kinetic parameters (especially k_1 and k_3), as was demonstrated in Fig. 3 and Table 3. The value of k_1 increases with increasing negative charge on the thiolate anion. This is in accordance with expectation, since negatively charged species will be attracted more by the positively charged ionene than species carrying no net charge and will thus be more concentrated within the polymer domains (in the vicinity of the polymer-bound catalyst complex).

The behaviour of k_{-1} is much more complicated; this rate constant increases in the order: $R^+SH < R^\pm SH < R^-SH < R^0SH$. Probably, this is due to different degrees of thiol dissociation at the applied pH. Considering the pH effects, it was discussed above that $k_{-1}^{RS^-} \ll k_{-1}^{RSH}$. Therefore, the obtained value of k_{-1} for aminoethanethiol will be relatively small ($\approx k_{-1}^{RS^-}$), because this thiol is dissociated to a large extent at pH 8.9. On the other hand, the thiol group of mercaptoacetic acid is hardly dissociated at this pH and thus, k_{-1} will be relatively large ($\approx k_{-1}^{RSH}$). On these grounds, we estimate that, at a constant $[RSH]/[RS^-]$ ratio, k_{-1} will increase in the following order: $R^-SH \ll R^\pm SH \leq R^0SH \leq R^+SH$. This order was expected and can be easily understood, since electron transfer to RS^* (k_{-1B} or k_{-1D}) will be more difficult when the R-group is negatively charged (electron-donating).

The effect of changing the type of thiol on $C_2(k_2$ or $K_2)$ is rather small, leading to the conclusion that electron-donating or -withdrawing properties of the thiols are not very important in this reaction step. This means that the electron transfer step (k_{2B}) is not the determining factor in the observed rate effect. Therefore, either a thermodynamic effect is being measured or k_{2A} is determining the value of k_2 , which was also concluded on the basis of the charge density effects (*vide supra*).

Finally, k_3 appeared to depend strongly on the type of thiol. Very low values were found for mercaptoacetic acid and cysteine (10 and 5 times lower than for mercaptoethanol, respectively). This may be due to the position of the (saturated) equilibrium preceding the product formation step 3. Since the Co-bound thiol ligands in question are already carrying negatively charged groups ($R^-S^-Co^{III}$), it is likely that addition of a second thiolate anion will be relatively unfavourable because of repulsion. On the other hand, a positively charged R-group may exert an electron-withdrawing effect and thus retard the electron transfer from RSS^-R to Co^{III} , lowering k_3 . This explains the observed order of increase for k_3 : $R^-SH < R^\pm SH \ll R^+SH < R^0SH$.

Conclusions

Summarizing all kinetic data (see Table 4) and the discussion above, it can be concluded that:

—the efficient oxidation of thiols requires a high thiolate anion

concentration in the vicinity of the cobalt catalyst ($[\text{RS}^-]_{\text{local}}$), since $k_1^{\text{RSH}} \ll k_1^{\text{RS}^-}$. The local thiolate concentration can be increased by increasing the pH and the negative charge on the R-group of the thiol. Furthermore, $[\text{RS}^-]_{\text{local}}$ is enhanced by a high electrostatic potential on the ionene, which is, however, not directly related to the linear charge density of the polymer. Therefore, the differences in activity of the x,y -ionenes cannot be explained on the basis of differences in thiolate enrichment.

— a low charge density of the ionene, leading to a low degree of phthalocyanine aggregation, gives rise to decreasing efficiency for electron transfer from Co to substrates. Presumably, the degree of aggregation varies even within the x,y -ionene series, accounting for the different activities observed.

— the dissociation of the $\text{Co}^{\text{I}}\text{—RS}^*$ complex (k_{-1}) appears to be affected by the above mentioned aggregation effect. This reaction step is acid-catalyzed, as became evident from the dependence of k_{-1} on pH and $\text{pK}_a(\text{thiol})$.

— the overall reaction rate is largely dependent on k_3 ; this rate constant decreases upon increasing the pH above 11, or when the R-group of the thiol is more negatively charged.

The observed dependencies of the kinetic parameters on pH, the type of ionene and the type of thiol, can be combined with the general kinetic characteristics of the polymer-promoted catalytic system (two-substrate Michaelis–Menten model) to give a reaction mechanism of the form of Scheme 2.

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