

Autoxidation of Thiols with Cobalt (II) Phthalocyanine-Tetra-Sodium Sulfonate, Attached to Poly(Vinylamine)

1. pH and Viscometric Effects

W.M. Brouwer, P. Piet and A.L. German

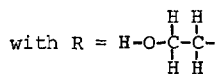
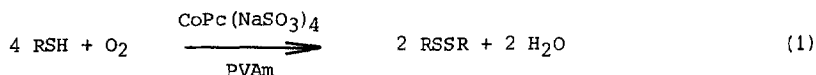
Laboratory of Polymer Chemistry, Eindhoven University of Technology,
Postbox 513, NL-5600 MB Eindhoven, The Netherlands

Summary

The oxidation of 2-mercaptoethanol with molecular oxygen in water with cobalt(II)phthalocyanine-tetra-sodium sulfonate attached to poly(vinylamine) has been investigated. Specially attention was paid to the effect of pH and chain dimensions on polymer activity. The polymer catalyst possesses a large conformational freedom at neutral pH, but at higher pH a shrinkage of the polymer coil occurs and diffusion limitations cannot be excluded. The catalyst shows an enzyme-like behaviour in the autoxidation of thiol. Overall activation energies appear to decrease with increasing pH. At pH = 7.4, $E_a = 61$ KJ mole⁻¹; at pH = 9.5, $E_a = 3$ KJ mole⁻¹. Electrostatic effects are of major importance in the chemical reactivity since they affect the local thiol-anion concentration in the close vicinity of the polymer attached oxidation sites.

Introduction

In our laboratory the autoxidation of 2-mercaptoethanol (RSH) with water soluble cobalt(II)phthalocyanine-tetra-sodium sulfonate (CoPc(NaSO₃)₄), attached to poly(vinylamine) (PVAm), has been investigated (SCHUTTEN and ZWART 1979; SCHUTTEN et al. 1979.).



The cobaltphthalocyanine is an organometallic compound, consisting of cobalt(II) incorporated in a porphyrin ring. The derivative used here (CoPc(NaSO₃)₄) carries four sulfonic groups, which makes it soluble in water. Thiol oxidation plays a role in biologic systems and is an important process in the desulfurization of oil and natural gas.

It was suggested that the enhanced activity of the polymeric system in comparison with the system CoPc(NaSO₃)₄/OH⁻ in the absence of PVAm mainly could be attributed to the high density of basic sites on the polymer, which increases the thiol-anion concentration, and to the polymeric coil structure, inhibiting the formation of binuclear oxo-adducts, which are, catalytically inactive (SCHUTTEN and ZWART 1979; SCHUTTEN et al. 1979.).

From these previous investigations it appeared that addition of base affected the catalytic activity. Therefore, we have examined the specific effect of pH on the catalytic activity and on the conformation of the polymeric catalyst. For the latter purpose viscometry was used. Moreover, overall activation energies have been determined. The results might elucidate some important aspects involved in the catalytic behaviour of the polymeric catalyst.

Experiments

Chemical reagents

All solutions were prepared with distilled water. PVAmHCl was purchased from Polysciences Inc. (Warrington U.S.A.), $M_w, PVAmHCl = 50,000-160,000$. Aqueous solutions of PVAm were obtained by eluting a 3% solution of PVAmHCl through an Amberlite IRA-401 ion-exchange column. The equivalent amine concentration (c_{-NH_2}) was determined by potentiometric titration with HCl solution (Merck, Titrisol ampoules) in the presence of 2 M NaCl. CoPc(NaSO₃)₄ was kindly provided by Dr. T.P.M. Beelen, and was synthesised analogous to the method by WEBER and BUSCH (1965), as described elsewhere (ZWART et al. 1977). 2-Mercaptoethanol (Merck) was distilled before use. It was stored in the dark at 5 °C for periods not exceeding two weeks. All salts, mentioned in the text were p.a.

Viscosity

Measurements on filtered solutions were carried out at $(25.00 \pm 0.05)^\circ\text{C}$ in a Hewlett Packard automatic solution viscometer of the Ubbelohde type. All measurements were performed under a nitrogen gas atmosphere to prevent absorption of oxygen and carbon dioxide. Samples were prepared using nitrogen purged, sealed ampoules and syringes. In those experiments where thiol was added, measurements were conducted twenty minutes after addition, since small time effects were observed.

Catalyst preparation

The catalyst was prepared by mixing aqueous solutions of PVAm and CoPc(NaSO₃)₄. First the solution of PVAm was added, the solution of CoPc(NaSO₃)₄ immediately afterwards. Then the desired pH was adjusted by addition of NaOH (0.3 N) or HCl-solution (0.01 N). The mixture was degassed twice and saturated with oxygen in twenty minutes, while stirring vigorously.

Catalytical activity measurements

Activity measurements were carried out in an all-glass double-walled, thermostated Warburg apparatus, equipped with a powerful mechanical glass-stirrer, at constant pressure (0.1 MPa). Stirring speed was 2300 r.p.m. Although vigorous stirring appeared imperative, this stirring speed was not within a critical range, since a somewhat higher or lower stirring speed did not affect the oxygen uptake rate. Since even small amounts of salt largely affect the conformation of the polymeric catalyst in solution (see text), no buffer solutions but instead, sodium hydroxide and hydrochloric acid were used to adjust the pH. The Warburg apparatus was equipped with a

pH-electrode (Radiometer Copenhagen GK 2401 B) and the pH was measured 15 seconds after addition of thiol. During the first minute of reaction the pH hardly varied at $\text{pH} \geq 8.3$, but a slight increase was observed at lower and intermediate values as a result of the conversion of thiol and the lower buffer capacity of the reaction system at these values.

Oxygen consumption rates were measured with a digital flow meter equipment (Inacom Veenendaal, The Netherlands).

The reaction was started by adding the substrate, 2-mercaptoethanol, to the reaction vessel with a syringe. Initial reaction rates were determined as the average O_2 consumption rate (normalized at 20 °C and 0.1 MPa) during the first minute. Such a fast measurement is advantageous since the influence of catalyst deactivation, which occurs as the reaction progresses (ROLLMAN 1975.), can be neglected; besides, pH and substrate concentration remain practically constant.

Results and discussion

Conformation of the polymer complex in the presence of 2-mercaptoethanol

The reduced viscosity of aqueous solutions of PVAm with and without thiol were determined as a function of deliberately imposed pH changes, in order to obtain a better insight in the conformation of the catalyst as a function of pH. HCl (0.01 N) and NaOH (0.3 N) were used to adjust the pH at the desired values. The results are presented in Figure 1. This figure shows

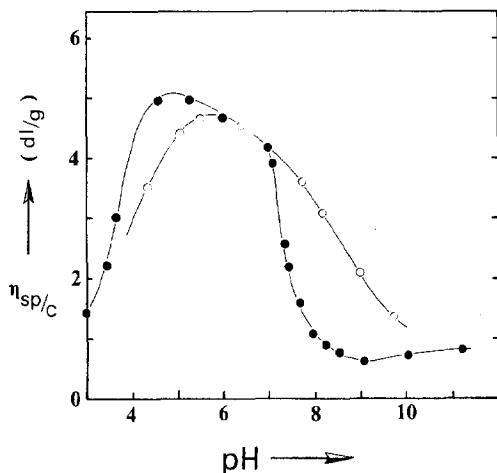


Figure 1.
Reduced viscosity of an aqueous solution of PVAm with (●) and without (○) thiol vs. pH. Polymer and thiol concentrations: $c_{\text{-NH}_2} = 1.7 \text{ mgreq dm}^{-3}$, $c_{\text{RSH}} = 0.186 \text{ mole dm}^{-3}$. Temperature: $(25.00 \pm 0.05) \text{ }^\circ\text{C}$. pH was adjusted by addition of HCl or NaOH solutions

that the conformation of pure PVAm is drastically influenced by the pH. A maximum in viscosity is reached at $\text{pH} = 6$. When thiol is present the maximum is shifted to lower pH and above $\text{pH} = 7$ the viscosity collapses in comparison with the behaviour of the PVAm solution without thiol. The viscosity increase upon neutralization of the basic PVAm solutions can be explained considering an increasing mutual repulsion of neighbouring charged groups with increasing polymer charge thus causing a more expanded conformation (TEYSSIE et al. 1965; BLOYS VAN TRESLONG 1978.). Although polymer charge increases continuously with lower pH (BLOYS VAN TRESLONG 1978.), polymer coil dimensions do not. The occurrence of a maximum in chain dimensions may be due to a very stiff structure at intermediate pH, a conformation stabilized by

hydrogen bonding between neighbouring ammonium and amine groups (LEWIS et al. 1981; RINALDI et al.1981.)

When thiol is added the viscosity of the system is somewhat higher at low pH and the maximum is shifted significantly to lower pH (Figure 1). Probably this is caused by a specific counter-ion effect. The collapse of viscosity above pH = 7 in comparison with the PVAm solution without thiol must be attributed to the increased salt concentration in the bulk (Na^+RS^-) under these conditions and is caused by the dissociation of the weakly acid RSH ($\text{pK}_a = 9.6$ (JOCELYN 1972.)). The latter effect will result in a shielding of the polymeric charges which in turn causes a sharp decrease in viscosity.

The slight increase in viscosity beyond pH = 9 in Figure 1 must be due to increasing salt and base concentrations, while the polymer charge is minimal. From the above it must be concluded that the polymer catalyst is most expanded at intermediate pH and in the absence of salt, but conformational freedom is lost upon addition of even small amounts of base.

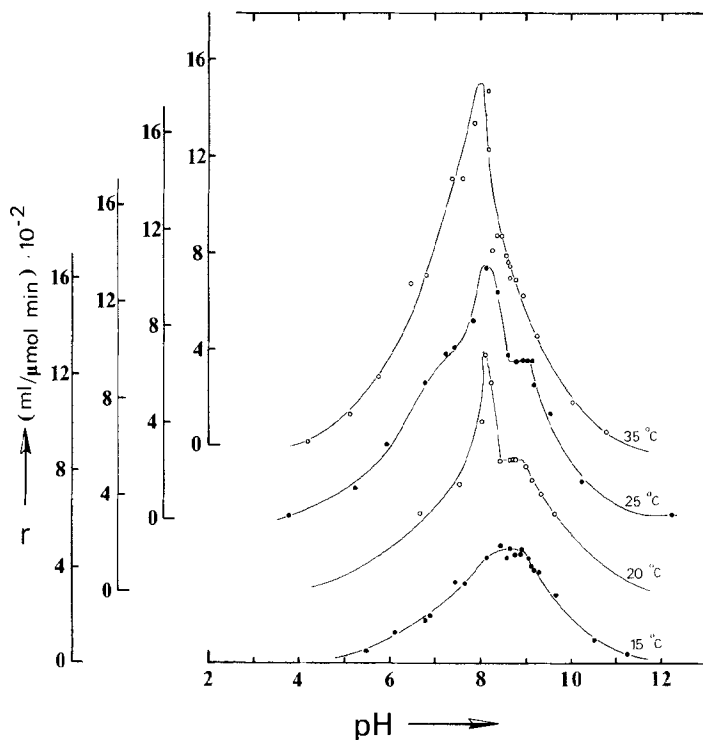


Figure 2.
Catalytic activity of polymeric systems at 15, 20, 25 and 35 °C vs. pH. $c_{-\text{NH}_2} = 1.7 \text{ mgreq dm}^{-3}$; $c_{\text{CoPc}(\text{NaSO}_3)_4} = 1.9 \cdot 10^{-7} \text{ mole dm}^{-3}$. Reaction volume = 101 ml. Added thiol: 18.5 mmole. r in ml $\text{O}_2/\mu\text{mole CoPc}(\text{NaSO}_3)_4 \text{ min}$

Catalytic activity experiments

Because the solubility of the polymeric catalyst is not restricted by the pH, we were able to investigate the effect of the pH on the catalytic activity. The effect of temperature on the activity-pH plots has been determined at 15, 20, 25 and 35 °C. This is shown in Figure 2. At each temperature level a maximum in reaction rate is observed at pH 8-9, depending on temperature. Such behaviour has often been observed in enzymatic reactions and generally is explained by assuming that acid as well as basic sites are playing a role in most enzyme-substrate interaction mechanisms (TANFORD 1961.). However, our polymeric catalyst carries only basic sites, and therefore this explanation does not hold for the present system. Here polymer charge and the presence of counter-ions other than RS^- are considered to be important. It was reported that the charge on the polymer chain decreases with increasing pH (BLOYS VAN TRESLONG 1978).

Below pH = 7.4, when HCl has been added to adjust the pH, more competing counter-ions are present (i.e. Cl^-) and the local thiol-anion concentration in the close vicinity of the polymer chain is supposed to decrease and so is the reaction rate. Beyond pH = 7.4 the thiol-anion concentration in the bulk increases considerably due to the weakly acid character of RSH.

A slight increase in pH above 7.4 does not necessarily mean that polymer charge decreases in the relevant catalytic systems, because ionic strength is increased by Na^+RS^- , which enhances polymer charge to some extent (BLOYS VAN TRESLONG 1978.). Thus at pH values slightly higher than 7.4 the local thiol-anion concentration near the polymer chain may be somewhat enhanced and so is the reaction rate. At still higher pH, polymer charge decreases and hydroxyl-ion concentration increases and a reduction of reaction rate must be expected, although the bulk thiol-anion concentration is still increasing.

The considerations above are summarized in Table 1.

Table 1.

Synopsis of some important parameters in the pH-dependent behaviour of the catalytic activity.

	Lower pH (<7.4)	Intermediate pH (7.4-8)	Higher pH (>8)
polymer charge	++++	+++	+
"strange" counter-anions other than RS^-	yes (Cl^-)	no	yes (OH^-)
c_{RS^-} in close vicinity of the polymer chain	+	+++	+
c_{RS^-} in the bulk	+	++	++++
catalytical activity, r	+	+++	+

From the above it seems that the course of the reaction rate curves can be explained in terms of a variation of the local thiol-anion concentration in the close vicinity of the polymer chain.

Further supporting evidence to this hypothesis, has been provided by the occurrence of a saturation effect in the relationship between reaction rate and thiol concentration and by the occurrence of a distinct fall in

activity upon addition of inert salt. The latter can be explained by a considerable decrease of thiol-anions in the near vicinity of the polymer chain because of repulsive forces between competitive anions (Cl^-) and shielding of the chain charge.

The observed temperature dependence of the reaction rate curves in Figure 2 was a motive to determine the activation energies accurately, by measurements performed in a range chosen from Figure 2, viz. 5-45 °C at pH = 7.4, 8.75 and 9.5. Activation energies, E_a , are given in Table 2.

Table 2.

Activation energies at different pH.

pH	E_a (KJ mole ⁻¹)
7.4	61 ± 7
8.75	19 ± 3
9.5	2.5 ± 2

In Figure 2 a shoulder appears between pH = 8.5 and 9 at lower temperatures. This peculiar behaviour may indicate that two mechanisms are operative with different activation energies and different pH optima. In earlier investigations the formation of considerable amounts of hydrogen peroxide at neutral pH was reported (SCHUTTEN and BEELEN 1980.). The concentration H_2O_2 decreased rapidly upon addition of small amounts of base which was attributed to a fast base catalysed reduction of the hydrogen peroxide by thiols. However, in the light of the present findings the occurrence of two pH-dependent mechanisms may be a more probable explanation. On the other hand, diffusion limitation may not be excluded, particularly at higher pH. In the presence of thiol, the polymer coil shrinks considerably upon addition of base (Figure 1). Therefore transport limitations of reactants or the product, which has larger dimensions, may be easily encountered. The apparent activation energy for diffusion of counter-ions and uncharged molecules in swollen resins amounts to about 20 KJ mole⁻¹ (MEARES 1968.), which is not in conflict with the present experimental observations. In order to elucidate the phenomenon of the pH dependent activation energies additional kinetic investigations are required.

Conclusions

Some final conclusions may be drawn. The polymeric catalyst exhibits an enzyme-like behaviour in the autoxidation of 2-mercaptoethanol, in contradistinction to the system with $\text{CoPc}(\text{NaSO}_3)_4$ as a catalyst in the absence of polymers (ZWART et al. 1977.).

The maximum rate is reached at pH = 8-9, depending on temperature. The polymeric catalyst possesses a large conformational freedom at neutral pH and electrostatic effects are of great importance in the catalytic activity, because these effects will influence the local thiol-anion concentration in the close vicinity of the oxidation sites.

The pH-dependence of activation energies may be explained by assuming two pH-dependent mechanisms with different activation energies to occur. On the other hand the polymer coil is considerably contracted at high pH values and the occurrence of diffusion controlled reactions cannot be excluded.

Acknowledgements

The authors are indebted to Mr. R. van der Wey, Mr. F. van der Put and Mr. D. François for their technical assistance.

References

- BLOYS VAN TRESLONG, C.J.: Recl. Trav. Chim. Pays-Bas 97 (1), 13 (1978)
HUGHES, A.R. and St. PIERRE, T.: Macromol. Synth. 6, 31 (1977)
JOCELYN, P.C.: Biochemistry of the SH-group, New York, Academic Press (1972)
LEWIS, E.A., BARKLEY, J., St PIERRE, T.: Macromolecules 14, 546 (1981)
MEARES, P. in Diffusion in Polymers, New York, Academic Press (1968)
RINALDI, P.L., CHIN YU and LEVY, G.C.: Macromolecules 14, 551 (1981)
ROLLMAN, L.D.: J. Am. Chem. Soc. 97, 2132 (1975)
SCHUTTEN, J.H. and ZWART, J.: J. Mol. Catal. 5, 9 (1979)
SCHUTTEN, J.H., PIET, P. and GERMAN, A.L.: Makromol. Chem. 180, 2341 (1979)
SCHUTTEN, J.H. and BEELEN, T.P.M.: J. Mol. Catal. 10, 85 (1980)
TANFORD, Ch., Physical chemistry of macromolecules, New York, John Wiley & Sons Inc. (1961)
TEYSSIE, Ph., DECOENE, C. and TEYSSIE, M.T.: Makromol. Chem. 84, 51 (1965)
WEBER, J.H. and BUSCH, P.H.: Inorg. Chem. 4, 469 (1965)
ZWART, J., WEIDE, H.C. v/d, BROKER, N., RUMMENS, C., SCHUIT, G.C.A. and GERMAN, A.L.: J. Mol. Catal. 3, 151 (1977-1978)

Received August 20, accepted August 28, 1982