Autoxidation of mercaptans promoted by a bifunctional catalyst

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AUTOXIDATION OF MERCAPTANS PROMOTED BY A BIFUNCTIONAL CATALYST

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Summary

A new bifunctional catalyst of cobalt–phthaloxyanine (CoPc) has been developed in which an efficient co-operation between oxidation catalyst and basic sites has been attained. Investigation of this bifunctional catalyst has led to the following interesting observations. (1) A significant enhancement in specific activity is observed for the bifunctional system compared with the corresponding NaOH/CoPc system (factor 50); the polymeric character of the base appears to be essential. (2) The amount of basic groups incorporated in the polymer, necessary to get this high activity, is less than the amount of NaOH used in the corresponding NaOH/CoPc system by about a factor of 100 - 1 000. From the reaction products, being disulfide and \( \text{H}_2\text{O}_2 \), the accumulated \( \text{H}_2\text{O}_2 \) is probably responsible for the formation of traces of sulfur acids, which may occupy and thus deactivate the basic sites of the polymer in subsequent runs. The high activity of the bifunctional catalyst may be ascribed to a fundamental change in the mechanism of oxidation, which also can be inferred from the notably reduced value of the apparent activation energy observed for the bifunctional catalyst compared with its NaOH/CoPc counterpart (8 and 12.7 kcal/mole), respectively.

1. Introduction

Multifunctionality seems to be one of the main characteristics of enzymes. This presumably is connected with their high activity and selectivity. Model systems can be useful to elucidate the factors governing the cooperative interaction between various catalytic sites. Polymers generally have been used in the preparation of model systems, since they offer an opportunity to introduce a variety of chemical modifications.

For hydrolysis reactions, remarkable results were already obtained using multifunctional polymers — incorporating imidazole groups — as catalyst [1, 2]. Very reactive oxidation catalysts can be obtained by complex formation [3] of modified polymers with metal ions [4 - 6].
The purpose of this work is to synthesize bifunctional catalysts composed of cobalt–phthalocyanine (CoPc) and a variety of polymeric bases, the catalyst obtained being tested for the oxidation of mercaptan in aqueous media. Earlier experiments in this laboratory [7] have shown polymer attached CoPc to be much more active than their homogeneous counterpart. However, the presence of additional base (NaOH) appeared to be necessary.

Other experiments carried out in organic media by Rollman [8] point to the possibility of cooperation between polymeric base and CoPc.

2. Experimental

2.1 Supporting materials

Poly(ethylene imine): PEI
Polymin F (50% Sol. in H₂O), N = 16% by wt.; Fluka Cross-linked PEI: glutardialdehyde used as agent. Product washed with cold water and Soxhlet-extraction (designated PEI-X).

Poly(vinylamine): PVAm
Prepared according to method given by Bloys van Treslong [9]. Anal. PVAm.HCl: C/N-ratio = 2.03, N/Cl ratio = 1.02. Desalting of PVAM.HCl by use of DOWEX 2 (Fluka).

Poly(acrylamide) modified by amine groups: PAA–NH₂
Poly(acrylamide) (=PAA) obtained by polymerization of acrylamide (recryst. from chloroform) in ethanol as solvent; initiator AIBN, T = 63 °C, N₂ atmosphere. Yield 98%; [α] = 0.335 5 ~ Mᵥ = 30.000 [10]. Introduction of amine groups according to Inman and Dintzis [11] (eqn. 1).

\[
\begin{align*}
\text{PAA} & \quad \text{(Bis-(3-aminopropyl)-amine)} \\
\end{align*}
\]

Silica modified by amine groups: Silica–NH₂
Silica: Davison Grade 950 (Koch-Light); sieve fraction 0.125 mm < d < 0.16 mm, pore volume 0.4 ml/g, spec. surf. area 500 m²/g.
Dried and coupled with γ-amino-propyl-triethoxy-silan according to Horner and Schumacher [12].

2.2. Analysis of base content (Table 1)
The soluble polymers (PEI and PAA–NH₂) were titrated with 0.1 N HCl. Titration of PAA–NH₂ shows the successive neutralization of primary amines (pKₐ = 9.6) and sec. amines (pKₐ = 7.2), ratio 1/1 according to product formation as given in eqn. (1).
TABLE 1

Resulting basic carriers

<table>
<thead>
<tr>
<th>Material</th>
<th>Base (μ-equiv./mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>17.3</td>
</tr>
<tr>
<td>PEI-X</td>
<td>17.2</td>
</tr>
<tr>
<td>PVAm</td>
<td>18.0</td>
</tr>
<tr>
<td>PAA-NH$_2$(1)</td>
<td>2.54</td>
</tr>
<tr>
<td>PAA-NH$_2$(2)</td>
<td>1.58</td>
</tr>
<tr>
<td>Silica-NH$_2$</td>
<td>0.40</td>
</tr>
</tbody>
</table>

The base content of PVAm was calculated from the nitrogen content of the corresponding PVAm.HCl (N = 15.2%). The insoluble supports were analyzed according to the method usually applied to weak-base ion exchangers.

2.3 Cobalt(II) 4, 4', 4'', 4'''-tetrasulfo-phthalocyanine: CoTSPc

Prepared according to Weber and Busch [13]; recryst. by cooling an aqueous sol. and addition of ethanol. The precipitate was washed with ethanol and refluxed for 4 h in abs. ethanol, product dried under vacuum over P$_2$O$_5$; yield 75%. Anal.: C$_{32}$H$_{12}$N$_8$O$_{12}$S$_4$Na$_4$CO$.7H_2O$. Calcd.: C = 34.75, H = 2.17, N = 10.13, Na = 8.33, Co = 5.34. Found: C = 34.68, H = 2.06, N = 10.31, Na = 8.1, Co = 5.1%.

2.4 Catalyst preparation

Method 1

A CoTSPc solution in methanol was added to the carrier, causing decolorization of the solution. The carrier/CoTSPc complex was washed with methanol and dried under vacuum.

Method 2

In situ preparation of the polymeric catalyst, i.e., polymer as well as CoTSPc were added separately to the reaction liquid.

No substantial differences in activity were noticed between the products of the two. Only the silica system was prepared according to method 1.

2.5 Oxidation conditions

The oxidation was carried out in all-glass Warburg apparatus provided with a magnetic stirring device. The temperature of the reaction liquid was maintained constant by a thermostating jacket. The rate of oxidation was determined by measuring the amount of oxygen consumed (ml/min) at constant oxygen pressure ("initial rate" was calculated for consumption of first 20 ml of oxygen). A representative experiment was carried out in 130 ml H$_2$O
TABLE 2
Maximal rates observed

<table>
<thead>
<tr>
<th>System</th>
<th>Basic agent</th>
<th>Base (µequiv.)</th>
<th>CoTSPc (mole)</th>
<th>v-specific (ml/min µmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>homogeneous</td>
<td>NaOH</td>
<td>6 000</td>
<td>200</td>
<td>22</td>
</tr>
<tr>
<td>non-polymeric</td>
<td>BAA-*</td>
<td>60</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>homogeneous</td>
<td>PAA-NH₂(2)</td>
<td>163</td>
<td>10</td>
<td>740</td>
</tr>
<tr>
<td>polymeric</td>
<td>PEI</td>
<td>35</td>
<td>10</td>
<td>235</td>
</tr>
<tr>
<td>non-soluble</td>
<td>PVAm</td>
<td>100</td>
<td>5</td>
<td>930</td>
</tr>
<tr>
<td>supports</td>
<td>Silica-NH₂</td>
<td>53.6</td>
<td>50</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Imac-A27**</td>
<td>640</td>
<td>10</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>PEI-X</td>
<td>76</td>
<td>10</td>
<td>31</td>
</tr>
</tbody>
</table>

*BAA = Bis-(aminopropyl)-amine
**Imac-A27: A weak base ion-exchanger with epoxy amine matrix (AKZO)

oxidizing 1 ml (=14.25 mmol) of mercapto-ethanol (ME) with vigorous stirring; \( P(O_2) = 1 \text{ atm.}, \, T = 24 \, ^\circ\text{C} \). The amount of catalyst was chosen in such a way that an appropriate rate of oxygen consumption resulted (0.5 - 5 ml/min).

\( \text{H}_2\text{O}_2 \) was quantitatively analyzed at the end of the oxidation according to a spectrophotometric method using \( \text{TiCl}_3-\text{H}_2\text{O}_2 \) as reagent [14].

2.6 Oxidation reaction

The oxidation of mercaptan (RSH) resulted in the formation of disulfide (RSSR) together with a non-stoichiometric amount of \( \text{H}_2\text{O}_2 \). The overall reaction can be represented by eqn. (4), being a combination of eqns. (2) and (3).

\[
\begin{align*}
4\text{RSH} + \text{O}_2 & \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O} \quad \chi(1-a) \\
4\text{RSH} + 2\text{O}_2 & \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O}_2 \quad \chi(a) \\
4\text{RSH} + (1 + a)\text{O}_2 & \rightarrow 2\text{RSSR} + 2(1-a)\text{H}_2\text{O} + 2a\text{H}_2\text{O}_2
\end{align*}
\]

3. Results

It is well established [15] that the catalytic autoxidation of mercaptans (RSH) is appreciably accelerated by addition of a base, such as alkaline hydroxide, the thiolate anion (RS⁻) being the species susceptible to reaction with oxygen.

\[
\begin{align*}
2\text{RSH} + 2\text{OH}^- & \rightarrow 2\text{RS}^- + 2\text{H}_2\text{O} \quad \text{catalyst} \\
2\text{RS}^- + 2\text{H}_2\text{O} + \text{O}_2 & \rightarrow \text{RSSR} + \text{H}_2\text{O}_2 + 2\text{OH}^-.
\end{align*}
\]
TABLE 3
Influence of basic groups on specific activity (10 nanomoles of CoTSPc applied)

<table>
<thead>
<tr>
<th>No.</th>
<th>Support*</th>
<th>Basic groups (µequiv.)</th>
<th>NaOH (µequiv.)</th>
<th>$u$-specific (ml/min µmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAA–NH$_2$(1)</td>
<td>10.8</td>
<td>—</td>
<td>165</td>
</tr>
<tr>
<td>2</td>
<td>PAA–NH$_2$·HCl—**</td>
<td>—</td>
<td>—</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>PAA</td>
<td>—</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>PAA–NH$_2$(1)</td>
<td>10.8</td>
<td>6 000</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>—</td>
<td>—</td>
<td>6 000</td>
<td>22</td>
</tr>
</tbody>
</table>

*If applied here: 4.25 mg.

**A stoichiometric amount of HCl (11 µequiv.) added.

An ideal catalyst, therefore, should be bifunctional, *i.e.*, possess oxidation sites and basic sites in cooperative interaction. Therefore it was attempted to bind cobalt–phthalocyanine covalently onto a carrier which contains basic groups. This led us to the observation that also without covalent bonding a very reactive catalyst system was obtainable.

Adding a polymeric base, or an inorganic carrier modified with amine groups, was sufficient to improve the catalytic activity of an aqueous solution of CoTSPc. Soluble polymers are particularly effective in raising the reaction rate (Table 2). It is noteworthy that a significant enhancement in specific rate was observed with very low amounts of basic groups, amounts that were a factor of 100 less than required in the NaOH/CoTSPc system. Moreover, the low value found for the specific rate when using a non-polymeric amine, *i.e.*,...
TABLE 4
Variation of the amount of bifunctional catalyst (applied: PAA-NH₂(1))

<table>
<thead>
<tr>
<th>Basic groups (µequiv.)</th>
<th>CoTSPc (nmole)</th>
<th>base ( \frac{\text{CoTSPc}}{\times 10^{-3}} )</th>
<th>( \nu )-specific (ml/min µmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8</td>
<td>10</td>
<td>1</td>
<td>155</td>
</tr>
<tr>
<td>21.6</td>
<td>20</td>
<td>1</td>
<td>223</td>
</tr>
<tr>
<td>10.7</td>
<td>5</td>
<td>2</td>
<td>144</td>
</tr>
<tr>
<td>21.3</td>
<td>10</td>
<td>2</td>
<td>261</td>
</tr>
<tr>
<td>21.6</td>
<td>5</td>
<td>4</td>
<td>200</td>
</tr>
<tr>
<td>42.8</td>
<td>10</td>
<td>4</td>
<td>306</td>
</tr>
</tbody>
</table>

bis-(aminopropyl)-amine (BAA), shows that the polymeric character of the base is essential for obtaining high activities.

3.1 Influence of additional base or acid

To evaluate the role of the amine groups of the polymers a stoichiometric amount of HCl was added to the system sufficient to neutralize the amine groups. Alternatively, poly-(acrylamide) without incorporated basic groups was used. From the results given in Table 3 the essential role of the amine groups becomes evident.

On the other hand, addition of the normal amount of NaOH results in significant loss of activity. Actually, a comparison of the results of exp. 5 and 6 shows the polymeric base in this case does not contribute to the activity. In this context, the observation that addition of an NaOH solution to a preformed polymer/CoTSPc complex resulted in decoloration of the polymer, is of significance. The bond of CoTSPc with the polymer was broken apparently by the addition of NaOH.

3.2 Kinetic measurements

The rate as function of the amount of polymeric base (PAA-NH₂) increases up to a maximal value. A Michaelis–Menten description of the kinetics fits rather well as can be inferred from the Lineweaver–Burk plot (Fig. 1). The base/CoTSPc ratio seems not to be a very important factor, rather the amount of polymeric base dictates the specific activity of the catalytic system (Table 4).

3.3 Stability of the catalytic system

During the catalytic oxidation, using PAA-NH₂ or Silica-NH₂ as basic material, a significant amount of \( \text{H}_2\text{O}_2 \) is formed, giving rise to an increase in the volume of oxygen required for total conversion of 1 ml of ME. A typical plot of oxygen absorption vs. time is shown in Fig. 2.

After completion of oxygen absorption, measurement of the amount of \( \text{H}_2\text{O}_2 \) and the total oxygen absorption allows the fractional conversion of RSH into RSSR to be calculated. From the values in Table 5 it is clear that
TABLE 5
H₂O₂ accumulation
(PAA-NH₂(1): 4.2 mg ~10.7 μequiv. of base;
Silica-NH₂: 136 mg ~53.9 μequiv. of base)

<table>
<thead>
<tr>
<th>No.</th>
<th>Base</th>
<th>CoTSPc (nmole)</th>
<th>Rate (ml/min)</th>
<th>V₀₂ (total) (ml)</th>
<th>N₂H₂O₂ (mmole)</th>
<th>η*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAA-NH₂(1)</td>
<td>20</td>
<td>3.4</td>
<td>119</td>
<td>2.52</td>
<td>0.99</td>
</tr>
<tr>
<td>2</td>
<td>PAA-NH₂(1)</td>
<td>40</td>
<td>4.5</td>
<td>128</td>
<td>3.44</td>
<td>0.95</td>
</tr>
<tr>
<td>3</td>
<td>PAA-NH₂(1)</td>
<td>80</td>
<td>6.1</td>
<td>128</td>
<td>3.62</td>
<td>0.93</td>
</tr>
<tr>
<td>4</td>
<td>PAA-NH₂(1)</td>
<td>160</td>
<td>3.7</td>
<td>115</td>
<td>3.30</td>
<td>0.82</td>
</tr>
<tr>
<td>5</td>
<td>Silica-NH₂</td>
<td>50</td>
<td>2.0</td>
<td>116</td>
<td>2.15</td>
<td>0.99</td>
</tr>
</tbody>
</table>

*η = fractional conversion of RSH into RSSR.

TABLE 6
Activity in successive runs*
(PAA-NH₂(1): 8.5 mg ~21.5 μequiv. base;
Silica-NH₂: 135.8 mg ~53.9 μequiv. base)

<table>
<thead>
<tr>
<th>No.</th>
<th>Base</th>
<th>CoTSPc</th>
<th>V₀₂ (total) (ml)</th>
<th>Rate (ml/min)</th>
<th>η**</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAA-NH₂(1)</td>
<td>33</td>
<td>120</td>
<td>7.4</td>
<td>0.85</td>
</tr>
<tr>
<td>1(a)</td>
<td></td>
<td>85</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1(b)</td>
<td></td>
<td>—***</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Silica-NH₂</td>
<td>50</td>
<td>116</td>
<td>2.0</td>
<td>0.99</td>
</tr>
<tr>
<td>2(a)</td>
<td></td>
<td>84</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(b)</td>
<td></td>
<td>81</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2(c)†</td>
<td></td>
<td>22</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*At the end of each run a subsequent 1 ml portion of mercapto ethanol was added.
**η = fractional conversion, determined after the absorption of oxygen stopped.
***Not measured.
†Measured after storing overnight.

Complete conversion has not been obtained in all cases. Apparently, the catalyst becomes gradually deactivated during the course of the reaction. However, it is possible to recover catalytic activity, at least in part, by adding an additional 1 ml portion of ME (Table 6). Repetition of this cycle, however, gives rise to a decrease in initial rate, particularly if the previous reaction mixture has been stored overnight (exp 2(c)).

Catalytic systems using heterogeneous bases allow an alternative way of determining their stability, namely, by separation of the heterogeneous base from the reaction liquid and re-use of it in a fresh aqueous solution of ME (1 ml) without further addition of CoTSPc. By doing so, only the fractional amount of CoTSPc fixed to the matrix will be regained. From measurement of the activity of the next run an estimate can be made of this fraction of
Fig. 2. Oxygen absorption during a catalytic run (20 nmole of CoTSPc, 4.26 mg PAA-NH₂(1), 1 ml ME, 130 ml H₂O; P(O₂) = 1 atm, T = 23 °C).

**TABLE 7**

<table>
<thead>
<tr>
<th>No.</th>
<th>Silica-NH₂ (mg)</th>
<th>CoTSPc (μequiv.)</th>
<th>rate (ml/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>135.7</td>
<td>53.9</td>
<td>50</td>
</tr>
<tr>
<td>1(a)</td>
<td>135.7</td>
<td>53.9</td>
<td>1.1*</td>
</tr>
<tr>
<td>1(b)</td>
<td>135.7</td>
<td>53.9</td>
<td>0.8*</td>
</tr>
<tr>
<td>1(c)</td>
<td>135.7</td>
<td>53.9</td>
<td>0.7*</td>
</tr>
</tbody>
</table>

*After 15 min of reaction time for the previous run, the activated silica was separated from the liquid, washed with double dist. H₂O, and re-used in a freshly prepared H₂O/ME solution.

CoTSPc situated on the carrier during the catalytic oxidation. From the results of Table 7, combined with those reported in Table 6, it can be calculated that about 75% of the total amount of CoTSPc, present in the first run, will remain fixed onto the silica surface during the reaction.

**4. Discussion**

4.1 Bifunctionality

From the results obtained it can be concluded that a *bifunctional* catalyst can be created by combining a polymeric base with cobalt-tetrasulfo-phthalocyanine (CoTSPc). Investigation of this catalyst in the autoxidation...
process of mercapto-ethanol has led to the following remarkable observations.

1. A significant enhancement in specific activity is observed for the bi-functional system compared with the conventional NaOH/CoTSPc system (factor 50).

2. The amount of basic groups incorporated in the polymer, required for such a high activity, is less than the amount of NaOH used in the corresponding NaOH/CoTSPc system by about a factor of 100 - 1000.

3. Soluble polymers give rise to the most active systems, but also micro-gels or solid carriers can be used, as, for instance, cross-linked polymeric bases or inorganic materials, such as silica modified with amino-groups.

4. The polymeric bases are much more effective in raising the activity of the catalytic system than their monomeric counterpart.

5. The catalytic system obeys Michaelis–Menten kinetics with respect to the amount of polymeric base.

The Michaelis–Menten kinetics observed indicate the formation of a complex between the polymeric base and CoTSPc in equilibrium with its free components, while this complex acts as the actual catalyst. A particularly effective cooperation between CoTSPc and the polymeric basic groups has to be assumed within such a complex, considering the high catalytic activity using relatively low amounts of polymeric base.

4.2 Characterization of the catalytic active complex

In order to elucidate the mode of binding in the catalytic complex, we should ascertain the influence of the thiol (RSH) in modifying the basic carrier.

\[
\text{\underline{2}}\text{NH}_2 + \text{RSH} \rightleftharpoons \text{\underline{2}}\text{NH}_2^+ \cdot \text{SR.} \quad (7)
\]

Under reaction conditions, using 0.1 M ME (pK_a = 9.6), the aqueous solution will be slightly acidic (pH ~5.3). Under these circumstances, equilibrium (7) will be strongly shifted to the right; the approximate ratio of RNH_2 / RNH_3^+ (pK_a = 9.6) then will be 10^{-4.3}. Hence, the amount of non-protonated amine can be neglected.

Complex formation between CoTSPc and the modified carrier will most probably occur by a coordinative interaction between the matrix-bound mercaptide anions and the cobalt nucleus of CoTSPc as shown in Fig. 3(a). Similar, non-polymeric, mercaptide complexes of Fe(II)-Porphyrins have been shown to exist and were studied as a model for Cytochrome P-450 [16]. From these studies it became apparent that the sulfur in the mercaptide anion is a strong \(\pi\)-electron donor, giving rise to the high affinity for oxygen, as exhibited by these complexes.

It should be noted here that a complex between CoTSPc and the amine carrier could also be obtained in the absence of RSH using methanol as the solvent for CoTSPc (see 2.3). In this case, complex formation can be accomplished by a coordinative bond between the non-protonated amine groups and the cobalt nucleus (Fig. 3(b)).
Such a mode of interaction seems to be conceivable, considering the high affinity of low molecular N-bases for the central metal atom, due to their strong \( \sigma \)-donor properties, as observed earlier for analogous planar metal complexes \([17, 18]\). As stated before, such a direct N/Co-interaction does not seem to be very likely under catalytic conditions.

4.3 Mechanistic interpretation

Optical measurements carried out by us during the oxidation of RSH in the NaOH/CoTSPc system give evidence for the existence of an intermediate binuclear dioxygen adduct. Presumably this is formed from oxygenation and subsequent dimerization, the dioxygen adduct being the main species present during this particular reaction \([19]\).

For the matrix bound CoTSPc an analogous oxygenation reaction may be expected. However, the dimerization step may be partially or completely inhibited as a result of binding the CoTSPc to a polymer or inorganic carrier, as, e.g., silica. These considerations have led to a suggested reaction sequence as given in Scheme 1.

Scheme 1

The internal electron transfer in (II) from coordinated \( \text{RS}^- \) to \( \text{O}_2^- \), resulting in (III), seems to be a very attractive one because formation of the
peroxo-complex will be thermodynamically strongly favored over the super-
oxo-complex, as can be inferred from the high standard potential for the
reaction \( \text{HO}_2^- + \text{H}^+ + e^- = \text{H}_2\text{O}_2 \) \( (E^o = 1.17 \text{ V} [20]) \) combined with the low
value of the \( \text{RS}^-/\text{RS}^- \) couple being \( E^o \sim -0.3 \text{ V} [21] \). The subsequent reac-
tion with another molecule of \( \text{RSH} \) may then give rise to product formation
(\( \text{RSSR} \) and \( \text{H}_2\text{O}_2 \)).

Although the proposed mechanism is a tentative one demanding further
experimental evidence, the crucial point in this mechanism leading to a
strongly enhanced reaction rate should be the separation of the catalytic
units from each other, thus avoiding dimerization reactions, normally occur-
rning in the \( \text{NaOH}/\text{CoTSPc} \) system.

In the following, two major effects of the presence of a polymer carrier
will be discussed, \( \text{viz.} \), (1) shielding and (2) diffusion controlled dimeriza-
tion.

(1) Shielding

In the relevant, very diluted, solutions (\( e.g., 4 \text{ mg polymer per 130 ml}
\text{H}_2\text{O} \)) in a good solvent, the polymer molecules will be present as separate,
relatively extended coils, which certainly do not fill all the space. Under the
above conditions it then can be calculated for a typical experiment (no. 1 in
Table 3), that the number of coils per \( \text{Co-unit} \) amounts to about 15, which
means that in first approximation there are no \( \text{coils containing more than}
\text{one CoTSPc unit} \). As it may be expected that the polymer bound \( \text{RS}^- \)
coordinatively interact with the \( \text{Co-nucleus} \) in \( \text{CoTSPc} \), the catalyst will
preferably be surrounded by polymer segments. The latter shielding effect
will be enhanced by the high local concentration of coordinative sites within
the polymeric coil, due to the non-homogeneous features of dilute polymer
solutions. As a result, the \( \text{CoTSPc} \) will be shielded by the polymeric environ-
ment against dimerization reactions, which readily occur without the use of
specifically interacting polymers.

(2) Diffusion controlled dimerization

Dimerization of polymer bound \( \text{CoTSPc} \) involves the reaction of two large
polymeric species, while the competing reaction only involves electron
transfer within the complex. A reasonable estimation of the upper limit of
the apparent rate constant of this dimerization reaction seems to be the rate
constant of the (diffusion controlled) termination in radical polymerizations,
\( i.e., 10^7 \text{ M}^{-1} \text{ s}^{-1} \). Since the dimerization in \( \text{NaOH}/\text{CoTSPc} \) systems appears to
be an intrinsically fast reaction (approx. order of \( 10^8 \)), it becomes evident
that the dimerization of polymer bound \( \text{CoTSPc} \) will be diffusion controlled
to such an extent as to favor the competing fast electron transfer reaction.

Further supporting evidence for such a fundamental change in the mecha-
nism of oxidation in the presence of specific polymers has been obtained by
measurements of the observed overall activation energy, being 7.8 kcal/mole
for the \( \text{PAA-NH}_2/\text{CoTSPc} \) system and 12.7 kcal/mole for the \( \text{NaOH}/\text{CoTSPc}
\) system. For the \( \text{heterogeneous} \) silica–\( \text{NH}_2/\text{CoTSPc} \) system even a lower value
of 3.4 kcal/mole was obtained. However, this may be attributed to substrate limitation due to diffusion within the narrow pores of the matrix ($d = 32 \text{ Å}$).

It may be expected that above a certain concentration of CoTSPc, dimerization reactions of the catalyst can no longer be avoided by the polymer coil segments.

A study of the specific activity as a function of the amount of CoTSPc bound to the polymer will serve to shed light on this question. Figure 4 shows the specific activity to be independent of the total amount of CoTSPc, if used at low concentration. At higher concentration levels, however, the specific activity diminishes with further addition of CoTSPc, which is ascribed to dimerization processes now becoming operative. One should note that at too high a CoTSPc level even a decrease in absolute rate can be effected by an additional amount of CoTSPc.

The proposed equilibrium between free CoTSPc and CoTSPc bound to the matrix (Scheme 1) can account for the deactivation of the catalyst on addition of NaOH or HCl. Since additional NaOH generates free RS$^-$-species in the solution, which will compete with the polymer bound RS$^-$ for CoTSPc ligation, the catalyst will move away out of the polymeric environment. On the other hand, a strong acid will occupy the amine groups, thus preventing the thiolate groups from coordinating to the polymeric base.

The latter phenomenon may also be the reason for the loss in activity observed in subsequent runs: by the action of the accumulated $\text{H}_2\text{O}_2$, traces of sulfur-acids may be generated [22] poisoning the catalyst. An additional amount of RSH initially will be able to partly drive out these strong acidic species, but as the accumulation of strong acids grows this recovery of active sites will diminish.

The bifunctional catalyst is now under continued investigation in order to elucidate the details of binding of the complexes and the mechanism of oxidation. Improvement of the stability of the catalyst during the oxidation,
as well as during regeneration with alkaline solutions, will be pursued by means of fixation of the catalyst to the carrier by a covalent bond.

References