THE OXIDATIVE COUPLING OF PHENOLS CATALYZED BY SOLUBLE COPPER–POLYMER COMPLEXES.
THE ACTIVE ROLE OF THE POLYMER CHAIN DURING ACTIVATION OF THE SUBSTRATE–CATALYST COMPLEXES

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Summary

The kinetics of the oxidative coupling of 2,6-dimethylphenol and 2,6-diphenylphenol was studied using a catalyst consisting of copper(II) chloride and polystyrene partially substituted with dimethylaminomethyl ligand groups. The polymers were not covalently crosslinked and were completely soluble in the reaction mixture. At an amino-nitrogen to copper ratio of 1 the reaction rate depended on the degree of substitution, \( \alpha \), of the polystyrenes. This effect was explained in terms of activation parameters obtained from the temperature dependence of the rate constant for the electron transfer step. It appeared that the polymer chain plays an active role in the activation process merely by increasing the entropy of activation with \( \alpha \). The formation of diphenoquinone appeared to be dependent on the reaction temperature and was almost independent of \( \alpha \).

Introduction

Following the discovery by Hay [1] that copper complexes of amines can catalyze the oxidative coupling of 2,6-substituted phenols, yielding aromatic polyethers, much work has been done to clarify the mechanism of the reaction [2]. Radical formation by the action of the copper catalyst, is now accepted [3], but still unexplained is the reason for C–C or C–O coupling [4–6]. For instance, the conditions favouring C–O coupling for 2,6-dimethylphenol result in C–C coupling for 2,6-diphenylphenol and vice versa. [7–9].

We studied the oxidative coupling of 2,6-substituted phenols as a model reaction for polymer catalysis [10, 11]. Using a soluble, non-crosslinked polymer as a polymeric ligand for the copper allows one to study the action of the catalyst and the special effects of introducing polymer ligands in a catalyst.
We found that polystyrene, which had been partially substituted by dimethylaminomethyl groups, yields, at an amino-nitrogen to copper ratio of 1, a more active catalyst for the oxidative coupling of 2,6-dimethylphenol than does the copper complex with the low molecular analogue, \( N,N \)-dimethylbenzylamine (DMBA). Moreover, the activity of the polymeric catalyst appeared to depend on the degree of substitution of the polystyrène. This dependence of the rate on the degree of loading of the polymer with catalytic sites is the subject of the present study. The steady state kinetics of the reaction can be described by the Michaelis–Menten equations [10, 13]:

\[
\frac{1}{R} = \frac{1}{V_s} + \frac{K_s}{V_s [\text{phenol}]} \tag{1}
\]

\[
V_s = k_2 [\text{Cu–L}_x]_0 \tag{2}
\]

where

\( R \) is the initial rate in mol dm\(^{-3} \) s\(^{-1} \),

\( V_s \) the limiting rate for \([\text{phenol}]=\alpha\),

\( K_s \) is the Michaelis constant in mol dm\(^{-3} \),

\( k_2 \) the rate constant for the e-transfer step in s\(^{-1} \), and

\([\text{Cu–L}_x]_0 \) the initial concentration of CuCl\(_2\) in mol dm\(^{-3} \) (if all the Cu is active at the same time).

From the temperature dependence of \( K_s^{-1} \) and \( k_2 \) we calculated the thermodynamic parameters of the complex formation and the e-transfer step for 4 polymers with different degrees of substitution. In this study we applied both 2,6-dimethylphenol and 2,6-diphenylphenol as substrates. Under the experimental conditions used, the main reaction products were the diphenoquinones 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dimethyl-2,5-cyclohexadien-1-one and the corresponding tetraphenylidiphenoquinone according to the following reaction scheme:

\[
\begin{align*}
L_2Cu^{II}Cl_2 + \text{Ph} & \xrightleftharpoons[k_1]{k_2} L_2Cu^{II}Cl_{\text{Ph}} + \text{HCl} \\
\text{L(PhCl)} + \text{L} + \text{Cu}^{I}Cl & \xrightarrow{k_2} \text{2Cu}^{I}Cl + \text{Ph} + \text{HCl} \\
\text{2Cu}^{I}Cl + \text{2HCl} + \frac{1}{2}O_2 & \rightarrow \text{2Cu}^{II}Cl_2 + \text{H}_2\text{O}
\end{align*}
\]
A + B $\xrightarrow{\text{further ox}}$ polymer
2B $\xrightarrow{\text{further ox}}$ diphenquinone
L = tertiary amine ligand.

Probably the initial complex, $L_2Cu^{II}Cl_2$, is binuclear [11]:

![Diagram of binuclear complex]

At present it is not clear whether this binuclear complex remains binuclear during the reaction or dissociates into two mononuclear complexes.

Experimental

*Partially dimethylaminomethylated polystyrenes*

The polystyrene samples used were the commercial product, Dow Styron 666, and a low molecular weight product obtained by precipitation polymerization in ethanol. These polymers were purified and chemically modified as described previously [10].

At-PS-X was chloromethylated by the method of Galeazzi [14] using 500 cm$^3$ of methylal, 280 cm$^3$ of thionylchloride, 50 g of Dow Styron 666 and 15 g of ZnCl$_2$. The reaction temperature was 34 °C and the reaction time 1 h. The chloromethylation reactions were stopped by adding aqueous dioxane and the polymer was precipitated in methanol. After purification of the polymer by dissolving in chloroform and precipitating in methanol, i.r. spectra were recorded on a Perkin-Elmer 457 infrared spectrophotometer. New peaks showed up at 670 cm$^{-1}$ (C–Cl), 820 and 1265 cm$^{-1}$ (para-substitution). There was no indication of ortho- or meta-substitution, which is in accordance with the findings of Brown and Nelson [12]. The amination of chloromethylated polystyrenes was performed in dioxane solution with a large excess of dimethylamine (30 vol% in ethanol) at room temperature over a period of 1 week. The polymer solution was then poured into an excess of methanol or methanol/water. In cases of high degrees of substitution, flocculation of the polymer did not occur and NaCl was added. After filtration and drying, the polymer was purified by reprecipitation from chloroform in methanol and dried over P$_2$O$_5$ under vacuum.

I.r. spectra showed absorption bands of tertiary amines at 2 810, 2 760 and 2 700 cm$^{-1}$, whereas the C–Cl absorption at 670 cm$^{-1}$ was absent. Elemental analyses of the samples gave nitrogen contents as listed in Table 1. Traces of Zn or Cl remained within a few parts per ten thousand.

We obtained soluble, non-crosslinked polymers of the type:
2,6-diphenylphenol, 2,6-dimethylphenol, solvents and CuCl$_2$·2H$_2$O

2,6-diphenylphenol was kindly provided by Dr. H. M. van Dort of AKZO Research Laboratories, Arnhem. 2,6-dimethylphenol was purified by sublimation. Analytically pure CuCl$_2$·2H$_2$O, 1,2-dichlorobenzene, and methanol from Merck were used without further purification. N,N-dimethylbenzylamine was from Schuchardt and was at least 98% pure. It was stored on molecular sives.

Oxidative coupling

The reactions were carried out in dry 1,2-dichlorobenzene/methanol mixtures (6.5 : 1 v/v) at constant temperatures between 15 and 35 °C, [CuCl$_2$] = 3.3 × 10$^{-3}$ mol dm$^{-3}$, and an overall ratio N/Cu = 1, unless otherwise indicated. The total reaction volume was always 15 cm$^3$, and the reaction mixture was shaken in a 150 cm$^3$ reaction vessel connected with an automatic gas burette for measuring the oxygen consumption at constant oxygen pressure of 98 kPa (1 atm). The oxygen consumption rate is a good measure of the rate of the e-transfer step in apolar solvents, as was pointed out by Tsuchida [13; 15].

Product analysis

The amount of diphenoquinone was determined by u.v. spectroscopy of an aliquot of the reaction mixture at 100% oxygen consumption using an Optica CR-4 double-beam spectrophotometer. The relevant extinction coefficients are:

for tetramethyldiphenoquinone: $\epsilon_{430} = 61 000$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$,
and for tetraphenyldiphenoquinone: $\epsilon_{480} = 47 500$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$.

Results

Our previous results showed that the catalytic systems we applied have some peculiar properties [10, 11]. At the polymer concentrations usually used by us, one may consider the coils to be separate, and complex forma-
tion between copper and amine ligands results in intrachain crosslinking and contraction of the coils. At higher polymer concentrations where the coils overlap each other, interchain crosslinking occurs yielding a gel.

Because of the high local amine concentration, complex formation between copper and amine groups within the coils is almost complete. So, at an overall ratio N/Cu = 1 we have about 50% 'unbound' copper in solution and 50% copper in active complexes, with N/Cu = 2, within the coils [11]. This system was catalytically most active [10] and was chosen for the present study.

In Fig. 1 is plotted the stationary oxygen consumption rate as a function of the degree of substitution, α, of polystyrenes for both substrates at N/Cu = 1. The rate increases with α and levels off at α = 0.3. As the concentrations of all the reactants are constant, we obtain a higher rate simply by concentrating the catalytic sites in a smaller number of polymeric domains. This effect was investigated further by varying the phenol concentration and the reaction temperature.

For each α, the dependence of the rate on the phenol concentration has been measured at 5 different temperatures between 15 and 35 °C. By plotting the reciprocal initial rates against the reciprocal substrate concentration according to eqn. (1), we constructed Lineweaver–Burk plots for each polymeric catalyst at different temperatures. Figure 2 shows such a graph for one polymeric catalyst and 2,6-diphenylphenol as substrate. This whole program has also been carried out for 2,6-dimethylphenol. For comparison, the low molecular analogue DMBA was also used as a ligand, but with N/Cu = 2,
Fig. 2. Lineweaver–Burk plot for the oxidation of 2,6-diphenylphenol catalyzed by a copper complex of partially dimethylaminomethylated polystyrene at 5 different temperatures. Degree of substitution = 12%; \([\text{CuCl}_2]\) = \(3.3 \times 10^{-3}\) mol dm\(^{-3}\); N/Cu = 1; solvent, 1,2-dichlorobenzene/methanol (6.5:1 v/v).

since N/Cu = 1 produced a very low rate independent of the phenol concentration. The intercepts and the slopes of the lines were calculated with a Hewlet-Packard-25 calculator, using a linear least-square-fit program. From the intercepts, \(1/V_s\), we calculated \(k_2\) according to eqns. (1) and (2). The slopes \(K_s/V_s\) allowed calculation of the Michaelis constants, \(K_s\).

From the temperature dependence of \(K_s^{-1}\) and \(k_2\) we derived the thermodynamic parameters of \(K_s^{-1}\) and the e-transfer step in the catalytic cycle for each polymeric catalyst. The values are shown in Tables 2 and 3 for the oxidative coupling of 2,6-diphenylphenol and 2,6-dimethylphenol, respectively.

Product analysis

For each phenol we measured the diphenoquinone formation at two temperatures after 100% oxygen uptake. The results are shown in Table 4. It is obvious that both C–C and C–O coupling occurred in most cases. As previously published by others for low molecular ligands [9], here, too, the tendency for C–C coupling decreases for 2,6-dimethylphenol on lowering the temperature, whereas it increases for 2,6-diphenylphenol. It is also seen from Table 4 that the degree of substitution, \(\alpha\), of the polymeric ligands hardly affects the fraction of C–C coupling.
### TABLE 2
Thermodynamic parameters at 25 °C of $k_2$ and $K_s^{-1}$ for the oxidative coupling of 2,6-diphenylphenol catalyzed by copper complexes of different aminated polystyrenes at N/Cu = 1

<table>
<thead>
<tr>
<th>$\alpha$ (%)</th>
<th>$k_2 \times 10^3$ (s$^{-1}$)</th>
<th>$K_s^{-1}$ (dm$^3$ mol$^{-1}$)</th>
<th>$\Delta H_s$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_s$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta H_2^+$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_2^+$ (J K$^{-1}$ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>2</td>
<td>4.2</td>
<td>35.6</td>
<td>129.7</td>
<td>27.2</td>
<td>-209</td>
</tr>
<tr>
<td>12</td>
<td>7</td>
<td>3.1</td>
<td>13.8</td>
<td>54.4</td>
<td>43.9</td>
<td>-138</td>
</tr>
<tr>
<td>18</td>
<td>19</td>
<td>1.5</td>
<td>-22.6</td>
<td>-73.2</td>
<td>73.2</td>
<td>-33</td>
</tr>
<tr>
<td>39</td>
<td>32</td>
<td>0.8</td>
<td>-28.9</td>
<td>-97.1</td>
<td>86.6</td>
<td>+ 21</td>
</tr>
</tbody>
</table>

### TABLE 3
Thermodynamic parameters at 25 °C of $k_2$ and $K_s^{-1}$ for the oxidative coupling of 2,6-dimethylphenol catalyzed by copper complexes of different aminated polystyrenes and $N,N$-dimethylbenzylamine at N/Cu = 1 (2 for DMBA)

<table>
<thead>
<tr>
<th>$\alpha$ (%)</th>
<th>$k_2 \times 10^3$ (s$^{-1}$)</th>
<th>$K_s^{-1}$ (dm$^3$ mol$^{-1}$)</th>
<th>$\Delta H_s$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_s$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>$\Delta H_2^+$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_2^+$ (J K$^{-1}$ mol$^{-1}$)</th>
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<tr>
<td>6.5</td>
<td>3.1</td>
<td>11.4</td>
<td>31.0</td>
<td>121.3</td>
<td>10.5</td>
<td>-259.4</td>
</tr>
<tr>
<td>10.3</td>
<td>12.6</td>
<td>4.5</td>
<td>24.9</td>
<td>96.2</td>
<td>23.9</td>
<td>-196.6</td>
</tr>
<tr>
<td>18</td>
<td>39.5</td>
<td>1.7</td>
<td>8.8</td>
<td>33.5</td>
<td>36.4</td>
<td>-150.6</td>
</tr>
<tr>
<td>39</td>
<td>88.3</td>
<td>1.1</td>
<td>4.2</td>
<td>16.7</td>
<td>51.9</td>
<td>-96.2</td>
</tr>
<tr>
<td>DM-</td>
<td>2.5</td>
<td>32.3</td>
<td>26.1</td>
<td>114.2</td>
<td>20.1</td>
<td>-228.1</td>
</tr>
<tr>
<td>BA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>

### TABLE 4
The amount of diphenooquinone, formed by copper complexes of partially dimethylamino-methylated polystyrenes during oxidation of 2,6-dimethylphenol and 2,6-diphenylphenol after 100% oxygen uptake

Solvent 1,2-dichlorobenzene/methanol (6.5:1 v/v), $[\text{CuCl}_2]_0 = 3.3 \times 10^{-3}$ mol dm$^{-3}$, $[\text{Phenol}]_0 = 5.98 \times 10^{-2}$ mol dm$^{-3}$ and N/Cu = 1

<table>
<thead>
<tr>
<th>Phenol</th>
<th>$T(K)$</th>
<th>$\alpha$ (%)</th>
<th>Diphenooquinone (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-Dimethylphenol</td>
<td>288</td>
<td>6.5</td>
<td>34.0</td>
</tr>
<tr>
<td></td>
<td>288</td>
<td>39.3</td>
<td>36.3</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6.5</td>
<td>65.6</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>39.3</td>
<td>68.9</td>
</tr>
<tr>
<td>2,6-Diphenylphenol</td>
<td>293</td>
<td>12.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>39.3</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>39.3</td>
<td>24.0</td>
</tr>
</tbody>
</table>
Discussion

The rate constant $k_2$

From Tables 2 and 3, it follows that $k_2$ as well as $\Delta H^\ddagger_2$ increase by using polymeric ligands with a higher degree of substitution, $\alpha$. So, the reason for the increase of $k_2$ with increasing $\alpha$ is the over-compensating effect of the increasing activation entropy, $\Delta S^\ddagger_2$. This was found for each of the phenols which we used.

We shall first discuss the possible reason for this increasing $\Delta S^\ddagger_2$. During the activation of the copper-substrate complex one must consider those parts of the polymer chain situated between amine ligands in the same complex. The activation of the complex can be considered to involve a primary deformation of the copper complex, as required for subsequent e-transfer by the Franck-Condon principle [13]; in this case, probably a deformation into a configuration which resembles, more or less, a tetrahedron. The activation entropy of this process should be dependent on the degree of substitution, $\alpha$, of the polymer if one considers that parts of the polymer chain must take up some definite conformation to attain this specific configuration around the copper ion. It seems reasonable to suppose that the entropy of a polymeric complex decreases with decreasing chain length, i.e., with increasing degree of substitution. This leads to a smaller loss of entropy during activation and explains the increase of $\Delta S^\ddagger_2$ with $\alpha$, as demonstrated in Tables 2 and 3. The activation energy necessary for the above-mentioned deformation appeared to increase with increasing degree of substitution. From Table 3 we see that $\Delta H^\ddagger_2$ for the catalyst with the low molecular ligand, DMBA, is about the same as for polymeric catalysts with low values of $\alpha$. By increasing $\alpha$ we introduce more intramolecular crosslinks into the polymer coils, which means that the crosslink density increases. From the rubber elasticity theory it is known that the force required to deform a polymer network increases with increasing crosslink density. Thus, the work necessary to attain a suitable deformation for e-transfer will also increase, which implies an increase of the activation enthalpy $\Delta H^\ddagger_2$.

It is clear from the foregoing that the polymer chains should not be considered as inert species in this type of catalyst. Therefore, the attachment of metal complexes to polymer ligands must lead to changed properties of the complexes.

The Michaelis constant $K_s$

From results such as those in Fig. 2, it is obvious that the kinetics of our catalytic reaction can be described by the simple form of the Michaelis-Menten kinetic scheme. Then $K_s$, known as the Michaelis constant, is some reciprocal measure for the affinity of the catalyst for the corresponding substrate:

$$K_s = \frac{k_{-1} + k_2}{k_1}.$$  \hspace{1cm} (3)
$K_s$ represents the equilibrium constant for the dissociation of the catalyst-substrate complex only if $k_2$ is much smaller than $k_{-1}$, as was pointed out by Tsuchida et al. [13]. Only in that case do the calculated values of $\Delta S_s$ and $\Delta H_s$ for $K_s^{-1}$ equal the changes in entropy, $\Delta S_e$, and enthalpy, $\Delta H_e$, for coordination of the phenols to the copper complex. However, by comparing all values in Tables 2 and 3 we noted that the sums of $\Delta H_s$ and $\Delta H_2^+$ and of $\Delta S_s$ and $\Delta S_2^+$ remain nearly constant for all the polymeric catalysts tested. This fact can only be explained by assuming that $k_2$ cannot be neglected in eqn. (3) for $K_s$. Therefore, we derived the relationships between $\Delta H_s$ and $\Delta H_2^+$, and between $\Delta S_s$ and $\Delta S_2^+$, starting from eqn. (3):

\[
\Delta H_s = \Delta H_1^+ - \frac{k_{-1}}{k_{-1} + k_2} \Delta H_{1-1}^+ - \frac{k_2}{k_{-1} + k_2} \Delta H_2^+ \tag{4}
\]

or

\[
\Delta H_s + \beta \Delta H_2^+ = \Delta H_e + \beta \Delta H_{1-1}^+ \tag{5}
\]

with

\[
\beta = \frac{k_2}{k_{-1} + k_2} \quad (0 < \beta < 1) \quad \text{and} \quad \Delta H_e = \Delta H_1^+ - \Delta H_{1-1}^+.
\]

Using the transition state theory, a similar relationship can be derived for the entropies from eqn. (4):

\[
\Delta S_s + \beta \Delta S_2^+ = \Delta S_e + \beta \Delta S_{1-1}^+ + \beta R \ln \frac{k_2}{k_{-1}} - R \ln \left(1 + \frac{k_2}{k_{-1}}\right).
\]

The difference between the last two terms approaches zero for $\beta \to 0$ or $\beta \to 1$ and reaches an extreme value of $-6$ Joule K$^{-1}$ mol$^{-1}$ for $\beta = 0.5$, when $k_2 = k_{-1}$. This value can be neglected in respect of the values of $\Delta S_s$ and $\Delta S_2^+$, and the resulting eqn. (6) for the entropies becomes analogous to eqn. (5) for the enthalpies:

\[
\Delta S_s + \beta \Delta S_2^+ = \Delta S_e + \beta \Delta S_{1-1}^+. \tag{6}
\]

From eqns. (4) - (6) it is evident that the experimental values of $\Delta H_s$ and $\Delta S_s$ are composites of the different enthalpy and entropy changes relating to the rate constants in eqn. (3) for $K_s$. Moreover, it is clear that the values of $\Delta H_s$ and $\Delta S_s$ are determined by $\Delta H_2^+$ and $\Delta S_2^+$. Consequently, the positive values of $\Delta S_s$ found may be due to the strongly negative $\Delta S_2^+$, and do not necessarily mean that the binuclear copper complex dissociates on entering the substrate.

Conclusions

From our results it is obvious that a polymeric ligand can play an active role in the catalysis of the oxidative coupling of phenols. The copper ion,
which is anchored to the polymer by at least two ligand groups, 'feels' the polymer chain situated between these ligand groups. This finds expression in the activation of the copper substrate complex. The activation entropy increases with increasing degree of substitution of the polymeric ligand because of a more favourable configuration of the complex for e-transfer, but, at the same time, the activation enthalpy increases, since it will require more work to deform a polymer chain bearing more crosslinks.

It will be evident, from the derived eqns. (5) and (6) for $\Delta H_s$ and $\Delta S_s$, that conclusions concerning the coordination step of phenols to the copper-polymer complex cannot be drawn as long as separate values of $k_{-1}$ or $k_1$ are not known.

References