Short Communication

Mössbauer Investigation on the Kinetics of the Pyrolysis of Iron(III) Tetrphenylporphyrin Chloride

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The pyrolysis of MN₄ macrocyclic complexes has been found to yield products with increased catalytic activity and increased lifetime, when these products are used as catalysts for the electrochemical reduction of oxygen. However, there has been some controversy about the very nature of the products formed, e.g. one problem concerns the possible influence of the carbon support on which the macrocyclic complexes often are deposited. Are the same products formed in the presence as in the absence of carbon? This question has been addressed by us in a previous publication. Another, even more intricate question is: Is it possible to describe the pyrolysis products as distinct chemical species or are they amorphous decomposition products of no reproducible composition? Only if one can answer such questions is it possible to discuss, and hopefully understand, the catalytic properties of the products that are formed.

In the present paper we have pyrolysed iron(III) tetrphenylporphyrin chloride, Fe(III)TPPCI, at one constant temperature but for a different timespan for each of the investigated specimens. The decomposition was measured by recording the ⁵⁷Fe Mössbauer spectrum for these samples, but also in terms of weight loss.

Experimental

Preparation and pyrolysis. The complex was prepared following literature descriptions. The sample was purged in a quartz tube with argon for 30 min at room temperature. Pyrolysis was performed so that the sample tube was introduced in an oven that had been brought to the desired temperature (773 K). After a preset time the sample was taken out and cooled to room temperature in a stream of argon. The experiment was repeated with a new sample and the heating was performed for a different length of time. The samples were weighed before and after the heat treatment. The weight losses are given in Table 1.

Mössbauer measurements. The samples were transferred to the Mössbauer laboratory in well sealed tubes. They were put in cylindrical plastic containers (ca. 150 mg cm⁻² powder per container). A spectrometer of the constant acceleration type was used with a Co source in a Rh matrix. Data were collected in transmission geometry at room temperature, and the subsequent least-squares fitting to Lorentzian functions was done with the CERN program MINUIT.

Results

The Mössbauer spectra for samples heated at 0, 5, 15, 30 and 240 min are reproduced in Fig. 1. The curves have

Table 1. Weight loss of FeTPPCI caused by pyrolysis at 773 K.¹

<table>
<thead>
<tr>
<th>Time, t/min</th>
<th>Weight loss, W (arb. units)</th>
<th>W₀–Wₓ</th>
<th>1–(1–x)/t k/min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>94.0</td>
<td>0.672</td>
</tr>
<tr>
<td>15</td>
<td>17.3</td>
<td>82.7</td>
<td>0.055</td>
</tr>
<tr>
<td>30</td>
<td>17.7</td>
<td>82.3</td>
<td>0.033</td>
</tr>
<tr>
<td>240</td>
<td>18.3</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

k=0.13±0.05

¹In columns 4 and 5 the rate constant for the weight loss is estimated, denoting the degree of transformation as x. The molecular weight of FeTPPCI is 704.0.

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been analysed as representing four different iron sites, corresponding to four distinctly different species. The Mössbauer parameters of these sites are reported in Table 2. The spectrum of Fe(III)TPPCl was remeasured, giving a small isomer shift (0.00 mm s$^{-1}$) and a likewise small quadrupole splitting (0.30 mm s$^{-1}$). These data are in fair agreement with those given by Sams and Bik Tsin$^7$ and Maeda.$^8$

The spectrum of the starting material, i.e. Fe(III)TPPCl, is observable after pyrolysis only for the 5 min treatment. Thus one can conclude that after 5 min exposure to a temperature of 773 K not much is left of the original complex. Almost 85%, of the material is found in a form with a distinctly measurable isomer shift (site 1, Table 2), which is probably an iron(II) low-spin ($S = 0$), or possibly intermediate spin ($S = 1$), species. After prolonged heating, cf. Table 2, two other spectroscopic sites appear. Site 2 shows characteristics of an iron(III) low-spin species ($S = 1/2$). Site 3 exhibits a magnetic hyperfine interaction ($H = 20.7$ T). These findings agree quite well with our previous investigation$^4$ in which the two first sites were related to FeN$_x$-type structures with the porphyrin skeleton more or less intact, and the third site was tentatively suggested to be an iron carbide related structure.$^8$ The relative abundance of the four species observed in the present investigation is reported graphically in Fig. 2.

Some observations can now be made in more detail than in Ref. 4. First one can observe that the constancy in weight after some 10 min must indicate that the conditions of pyrolysis were such that no sublimation took place. One also notes that the decrease of weight is faster than the rise of components 2 and 3. The half-time of the weight loss is not much greater than 5 min, i.e. the time lapsed when almost all of the material has transformed to site 1. This might indicate that the loss of weight is related

![Figure 1. Mössbauer spectra of samples measured after increasing times of pyrolysis: (a) t=0, (b) t=5, (c) t=15, (d) t=30 and (e) t=240 min.](image)

<table>
<thead>
<tr>
<th>Species</th>
<th>Heating time /min</th>
<th>Abundance</th>
<th>IS /mm s$^{-1}$</th>
<th>QS /mm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>100</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>14.4±3.1</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>86.7±2.7</td>
<td>0.233</td>
<td>0.820</td>
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<tr>
<td></td>
<td>15</td>
<td>48.0±0.9</td>
<td>0.211</td>
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<td>37.2±0.8</td>
<td>0.214</td>
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<td>240</td>
<td>28.0±0.7</td>
<td>0.195</td>
<td>0.943</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>24.4±1.2</td>
<td>0.312</td>
<td>2.335</td>
</tr>
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<td></td>
<td>30</td>
<td>29.5±1.1</td>
<td>0.319</td>
<td>2.286</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>34.9±1.0</td>
<td>0.334</td>
<td>2.294</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>29.6±1.2</td>
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<td>0.03</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>33.9±1.1</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>37.1±0.7</td>
<td>0.09</td>
<td>0.02</td>
</tr>
</tbody>
</table>
possible to discriminate this new site 1a from site 1. One should note, however, a slight variation in the quadrupole splitting of site 1.

We can therefore suggest a decomposition scheme as shown in Scheme 1, where site 0 = A[Fe(III)TPPCl], site 1 = B + C[Fe(II)N₄(S = 0, S = 1)], site 2 = D[Fe(II)N₄(S = 1/2)] and site 3 = E(Fe₅C₅).

![Scheme 1](image)

**Scheme 1.**

We now apply the following kinetic model for this scheme

\[
\frac{dA(t)}{dt} = -k_A A(t)
\]

\[
\frac{dB(t)}{dt} = k_A A(t) - k_B B(t) - k_C B(t) - k_D B(t)
\]

\[
\frac{dC(t)}{dt} = k_B B(t)
\]

\[
\frac{dD(t)}{dt} = k_C B(t)
\]

\[
\frac{dE(t)}{dt} = k_D B(t)
\]

Assuming, as we do above, that \(B(t = 0) = 0\) one obtains the solution of this system:

\[
A(t) = A_0 e^{-k_A t}
\]

\[
B(t) = k_A (k_B + k_C + k_D - k_A)^{-1}
\]

\[
C(t) = k_B k_C (k_B + k_C + k_D - k_A)^{-1} A_0 (1 - e^{-k_B t}) k_A^{-1}
\]

\[
D(t) = k_C k_D^{-1} C(t)
\]

**Conclusions**

The results indicate the appearance of distinct chemical species during the pyrolysis of Fe(III)TPPCl. According to the Mössbauer data the first species that appears is most likely an iron(II) species with low spin, probably
Fe(II)TPP. This species is then gradually transformed into three other species. It seems reasonable that more than one reaction might take place in parallel after the formation of the first degradation species. As we do not know the exact stoichiometry of these reactions it is not possible to compare the numerical values of the rate constants, i.e. we cannot say if they all run with the same rate, depending on each other.

One of these reactions, forming species C, results in a slight shift of the properties of the Fe(II)TPP mother compound, perhaps by the loss of one or more of the phenyl rings. It may be relevant here to point to the results from weight loss measurements (Table 1) indicating that the weight loss is not complete when the formation of species B from species A is completed. The next reaction producing species D (site 2) is probably a low-spin Fe(III) compound; the reoxidation is probably caused by the reduction in the parallel step forming the iron carbide-like species E (site 3).

References


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