

Short Communication

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

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Kjäll, P., Blomquist, J., Sheng, T.-C. and Larsson, R., 1994. Mössbauer Investigation on the Kinetics of the Pyrolysis of Iron(III) Tetraphenylporphyrin Chloride. – Acta Chem. Scand. 48: 526–529 © Acta Chemica Scandinavica 1994.

The pyrolysis of MN_4 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.¹ 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.^{2,3} 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.⁴ 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) tetraphenylporphyrin chloride, Fe(III)TPPCL, 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.⁵ 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

Table 1. Weight loss of FeTPPCL caused by pyrolysis at 773 K.^a

Time, t/min	Weight loss (%)	Weight, W (arb. units)	$\frac{(W - W_x)}{W_0 - W_x}$	$\frac{-1n(1-x)/t}{k/\text{min}^{-1}}$
0	0	100	1	0
5	6.0	94.0	0.672	0.08
15	17.3	82.7	0.055	0.19
30	17.7	82.3	0.033	0.11
240	18.3	0		

$k = 0.13 \pm 0.05$

^aIn columns 4 and 5 the rate constant for the weight loss is estimated, denoting the degree of transformation as x . The molecular weight of FeTPPCL is 704.0.

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.⁶

Results

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

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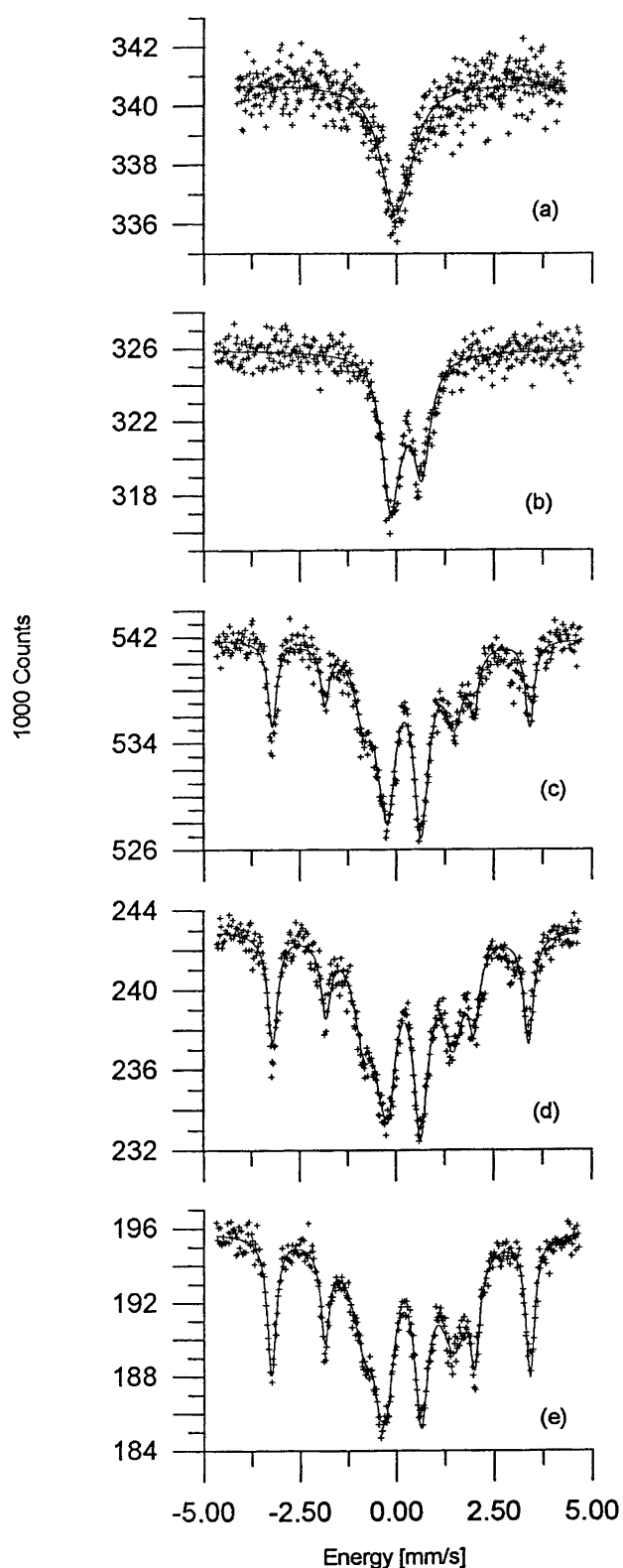


Fig. 1. Mössbauer spectra of samples measured after increasing times of pyrolysis: (a) $t=0$, (b) $t=5$; (c) $t=15$, (d) $t=30$ and (e) $t=240$ min.

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 Tsin⁷ 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 ($H=20.7 \text{ T}$). These findings agree quite well with our previous investigation⁴ in which the two first sites were related to FeN₄-type structures with the porphyrin skeleton more or less intact, and the third site was tentatively suggested to be an iron carbide related structure.⁹ 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

Table 2. Mössbauer parameters for the observed spectra.

Species	Heating time /min	Abundance	IS / mm s^{-1}	QS / mm s^{-1}
0	0	100	0.00	0.30
	5	14.4 ± 3.1	0.00	0.30
	15	0	—	—
1	5	85.7 ± 2.7	0.233	0.820
	15	46.0 ± 0.9	0.211	0.886
	30	37.2 ± 0.8	0.214	0.882
	240	28.0 ± 0.7	0.195	0.943
2	5	0	—	—
	15	24.4 ± 1.2	0.312	2.335
	30	29.5 ± 1.1	0.319	2.286
	240	34.9 ± 1.0	0.334	2.294
3	5	0	—	—
	15	29.6 ± 1.2	0.08	0.03
	30	33.9 ± 1.1	0.10	0.00
	240	37.1 ± 0.7	0.09	0.02

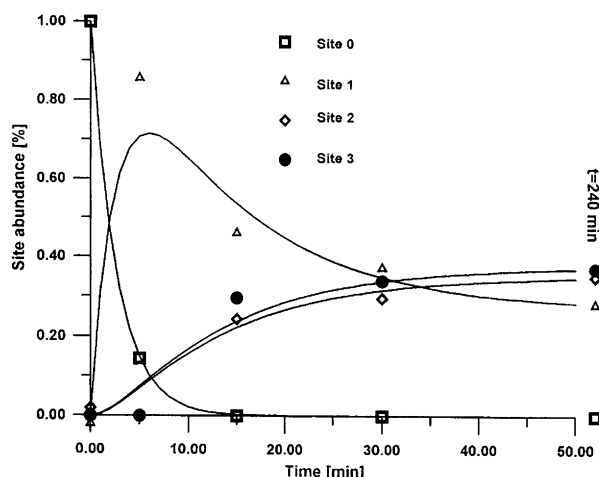


Fig. 2. The variation with time of the abundance of the different spectroscopic sites. The full lines represent the solution of the kinetic model and are drawn using the rate constants resulting from the analysis.

to the loss of chlorine as suggested in a previous paper.¹⁰ Thus $\text{Fe(III)N}_4\text{Cl} \rightarrow \text{Fe(II)N}_4 + \text{Cl}$. As the molecular weight of FeTPPCl is 704.0, one can calculate that the loss of only Cl corresponds to 5.0%; the loss of Cl and one benzene unit corresponds to 16.1%; the loss of Cl and $\text{C}_6\text{H}_5\text{-CH}$ corresponds to 17.8%.

To get a better measure of the rate of weight loss we can model it with the process $W_0 \rightarrow W_\infty$, where W_0 denotes the mass of the original substance and W_∞ denotes the mass of the product. If x is the degree of transformation it follows that the mass W at time t is

$$W = (1 - x)W_0 + xW_\infty \quad (1)$$

Assuming a first-order transformation, $\ln[1/(1-x)] = kt$, or

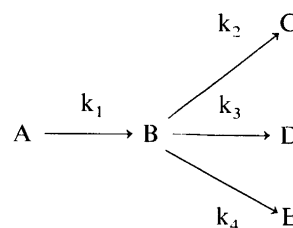
$$\ln(W_0 - W_\infty)/(W - W_\infty) = kt \quad (2)$$

The data in Table 1 give a mean value $k = 0.13 \pm 0.05 \text{ min}^{-1}$.

Secondly, one notes from Table 2 that the ratio of the abundance of site 2 to that of site 3 is almost constant (0.9 ± 0.05) during the time measured. This probably indicates that the decomposition of site 1 proceeds via two parallel reactions, one leading to site 2, the other one leading to site 3. However, if site 1 is gradually transformed into sites 2 and 3 as the pyrolysis continues, one might expect that the site 1 would vanish when the formation of the other two sites was complete. Fig. 2 indicates that this is not so. On the contrary, one can observe that the curve of site 1 levels off at about the same time as those of the other two sites. We cannot explain this observation other than by assuming that there must be a transformation of site 1 into something that we might call site 1a. From the spectroscopic point of view it is not

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 = $\text{A}[\text{Fe(III)TPPCl}]$, site 1 = $\text{B} + \text{C}[\text{Fe(II)N}_4(S=0; S=1)]$, site 2 = $\text{D}[\text{Fe(III)N}_4(S=1/2)]$ and site 3 = $\text{E}(\text{Fe}_x\text{C}_y)$.



Scheme 1.

We now apply the following kinetic model for this scheme

$$dA(t)/dt = -k_1 A(t) \quad (3)$$

$$dB(t)/dt = k_1 A(t) - k_2 B(t) - k_3 B(t) - k_4 B(t) \quad (4)$$

$$dC(t)/dt = k_2 B(t) \quad (5)$$

$$dD(t)/dt = k_3 B(t) \quad (6)$$

$$dE(t)/dt = k_4 B(t) \quad (7)$$

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

$$A(t) = A_0 e^{-k_1 t} \quad (8)$$

$$B(t) = k_1 (k_2 + k_3 + k_4 - k_1)^{-1} \times A_0 (e^{-k_1 t} - e^{-(k_2 + k_3 + k_4)t}) \quad (9)$$

$$C(t) = k_1 k_2 (k_2 + k_3 + k_4 - k_1)^{-1} A_0 ((1 - e^{-k_1 t}) k_1^{-1} - (1 - e^{-(k_2 + k_3 + k_4)t}) (k_2 + k_3 + k_4)^{-1}) \quad (10)$$

$$D(t) = k_3 k_2^{-1} C(t) \quad (11)$$

$$E(t) = k_4 k_2^{-1} C(t) \quad (12)$$

Fitting the data of Table 2 to these relations we get $k_1 \approx 0.38 \text{ min}^{-1}$, $k_2 \approx 0.022 \text{ min}^{-1}$, $k_3 \approx 0.029 \text{ min}^{-1}$ and $k_4 \approx 0.031 \text{ min}^{-1}$.

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).

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Received November 8, 1993.