THE KINETICS OF COMPETITIVE CONSECUTIVE SECOND-ORDER REACTIONS: THE TWO-STEP HYDROLYSIS OF DIMETHOXO(TETRA-p-TOLYPORPHYRINATO)TIN(IV)

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Abstract—The hydrolysis of a new compound, dimethoxo(tetra-p-tolyporphyrinato)tin (IV), Sn(tptp)(OMe)₂, was studied by NMR spectroscopy. The use of a limited amount of water in CDCl₃ allowed the hydrolysis intermediate, hydroxomethoxo(tetra-p-tolyporphyrinato)tin(IV), to be identified. The results show that the hydrolysis is a two-step competitive consecutive second-order reaction, with an absolute rate constant of the first step \( k₁ = (6.63 \pm 0.66) \times 10^{-3} \text{s}^{-1} \text{M}^{-1} \) and that of the second step \( k₂ = (3.55 \pm 0.35) \times 10^{-3} \text{s}^{-1} \text{M}^{-1} \) at 28°C.

\(^1\text{H} \text{NMR spectroscopy provides a convenient means of identifying and quantifying reaction intermediates. Previous workers have reported the difficulty in detecting dimethoxo(tetraphenylporphyrinato)tin(IV), Sn(tpp)(OMe)₂, by \(^1\text{H} \text{NMR spectroscopy due to its rapid hydrolysis to dihydroxo(tetraphenylporphyrinato)tin(IV), Sn(tpp)(OH)₂, unless CDCl₃ is specially dried.}^{1,2} \text{Recently, we reported the two-step hydrolysis of dimethoxo(tetraphenylporphyrinato)tin(IV), Sn(tpp)(OMe)₂, by \(^1\text{H} \text{NMR spectroscopy.}^{3} \text{In the previous paper, the absolute values of two consecutive rate constants \( k₁ \) and \( k₂ \) could not be determined since the precise concentration of water was not measured. However, an analysis of data led to an estimate of 2.3 for the ratio \( k₁/k₂ \). The new compound described in this paper, dimethoxo(tetra-p-tolylporphyrinato)tin(IV), Sn(tptp)(OMe)₂, was synthesized and used in the hydrolysis investigation. With the aid of \(^{119}\text{Sn} \text{and} \(^{117}\text{Sn couplings, the stoichiometry of the species Sn(tptp)(OMe)₂ (B), hydroxomethoxo(tetra-p-tolylporphyrinato)tin(IV), Sn(tptp)(OMe)(OH) (C), and dihydroxo(tetra-p-tolylporphyrinato)tin(IV), Sn(tptp)(OH)₂ (D) (shown in Fig. 1), was determined from the relative intensities of the \(^1\text{H} \text{signals of the hydroxy and methoxy groups. The results indicate that there is a two-step competitive consecutive second-order process involved in the hydrolysis of Sn(tptp)(OMe)₂ to Sn(tptp)(OH)₂. With the aid of known water concentration determined by proton NMR intensity, the graphical-integration time-variable transformation method was used to evaluate the absolute constants for both rate constants.}

**EXPERIMENTAL**

**Preparation of Sn(tptp)(OMe)₂**

Sn(tptp)(OMe)₂ was prepared by substituting meso-tetraphenylporphyrinato, tpp, with meso-tetra-(p-tolyl)porphyrin, tptp, in the preparation of Sn(tptp)(OMe)₂ as described elsewhere.¹,³,⁴
**Fig. 1**. Structure of Sn(tptp)XY complexes.

**NMR sample preparation**

Deuterated chloroform (99.8% from Aldrich) was dried with CaCl₂. The trace amount of residual water in CDCl₃ was quantified by an NMR method after the sample solution was prepared. The sample was prepared by dissolving Sn(tptp)(OMe)₂ in CDCl₃ to give a concentration of 2.53 x 10⁻² M. Immediately after the freshly prepared solution was poured into a 5 mm NMR tube, the tube was sealed with a plastic cap, wrapped with parafilm and measured at 28 ± 2°C.

**NMR spectra**

¹H and ¹³C NMR spectra were recorded at 300 and 75.46 MHz, respectively, on a Varian VXR-300 spectrometer.

**RESULTS AND DISCUSSION**

The hydrolysis of Sn(tptp)(OMe)₂ may be expressed as a two-step competitive consecutive second-order reaction. Let A = H₂O, B = Sn(tptp)(OMe)₂, C = Sn(tptp)(OMe)(OH), D = Sn(tptp)(OH)₂ and E = MeOH. The chemical equations for the hydrolysis of B are

\[
\begin{align*}
A + B & \; \xrightarrow{k_1} \; C + E \quad \text{(step 1)} \\
A + C & \; \xrightarrow{k_2} \; D + E \quad \text{(step 2)}
\end{align*}
\]

where \( k_1 \) and \( k_2 \) are the rate constants for steps 1 and 2, respectively.

For eqs (1) and (2), the pertinent rate equations are

\[
\begin{align*}
\frac{d[B]}{dt} &= -k_1[A][B] \\
\frac{d[C]}{dt} &= k_1[A][B] - k_2[A][C] \\
\frac{d[D]}{dt} &= k_2[A][C].
\end{align*}
\]

From the principle of material balance, they read

\[
[B]_0 + [C]_0 + [D]_0 = [B]_0 + [C]_0 + [D]_0 + [E]_0
\]

and

\[
[A]_0 + [B]_0 + [C]_0 + [D]_0 + [E]_0
\]

where the subscripts 0 represent the initial concentrations of the respective chemical species.

It is apparent that eqs (3–5) may be readily converted to equations of first-order type by introduction of the parameter \( \theta = \int_0^t [H₂O] \, dt \). On integration, we obtain

\[
\begin{align*}
[B] &= [B]_0 e^{-k_1 \theta} \\
[C] &= [C]_0 e^{-k_1 \theta} + \frac{k_1}{k_2 - k_1} [B]_0 (e^{-k_1 \theta} - e^{-k_2 \theta}) \\
[D] &= [D]_0 + [C]_0 (1 - e^{-k_2 \theta}) + [B]_0 \left( \frac{k_2}{k_2 - k_1} e^{-k_2 \theta} + \frac{k_1}{k_2 - k_1} e^{-k_1 \theta} \right).
\end{align*}
\]

The relationship between \( \theta \) and \( t \) is readily established by plotting [H₂O] against \( t \) and integrating graphically. The data giving [H₂O] as a function of \( t \) are then converted to the \( \theta \) basis and subsequently handled as a first-order process.

NMR spectra of Sn(tptp)(OMe)₂ at various stages of hydrolysis are displayed in Figs 2 and 3. The proton NMR spectrum from the hydrolysis of Sn(tptp)(OMe)₂ at reaction time \( t = 20 \) min is shown in Fig. 2. The peaks corresponding to the three compounds B–D at various times are shown in Fig. 3. Figure 3a is the NMR spectrum obtained 3 min after dissolution; it is dominated by the Sn(tptp)(OMe)₂ resonance j, with a smaller resonance l for Sn(tptp)(OMe)(OH) and an almost negligible Sn(tptp)(OH)₂ resonance m. Figure 3b–d shows increasing production of Sn(tptp)(OMe)(OH) and Sn(tptp)(OH)₂ with reaction time \( t \).

The time-dependent concentrations of the five species Sn(tptp)(OMe)₂, Sn(tptp)(OMe)(OH), Sn (tptp)(OH)₂, MeOH and H₂O are shown in Fig. 4.
Fig. 2. NMR spectrum for Sn(tptp)(OMe)$_2$ hydrolysis after a reaction time of 20 min. The spectral resonances used to measure the concentrations of compounds B–D, MeOH and H$_2$O are shown. The proton assignments are: (a) H$_A$ (pyrrole); (b) phenyl H (ortho); (c) phenyl H (meta); (d) CHCl$_3$; (e) methyl group of methanol; (f) p-CH$_3$; (g) hydroxy group of water; (h) methanol OH group; (i) tetramethyl silane; (j) methoxy group of Sn(tptp)(OMe)$_2$; (l) methoxy group of Sn(tptp)(OMe)(OH); (l') hydroxy group of Sn(tptp)(OMe)(OH)$_2$; (m) hydroxy group of Sn(tptp)(OH)$_2$.

The initial build-up and subsequent decay of Sn(tptp)(OMe)(OH) are clearly evident for $k_2 < k_1$. Further experiments indicate that more than 95% of the initial concentration of Sn(tptp)(OMe)$_2$ is consumed within 3 h. Thus the reactions with water are essentially irreversible. The initial water concentration was quantified by the NMR integration method with respect to the known Sn(tptp)(OMe)$_2$ concentration of $2.53 \times 10^{-2}$ M. As the reaction proceeds, the increase of methanol concentration and the decrease of water concentration as expressed in eqs (1) and (2) were monitored by integration of the peaks e and g shown in Fig. 2 and comparison with the known Sn(tptp)(OMe)$_2$ concentration at peak j. The result is also shown in Fig. 4. The value of the new time variable, $\theta$, at any time was

Fig. 3. NMR spectra for Sn(tptp)(OMe)$_2$ hydrolysis after reaction times of 3 min (a), 20 min (b), 50 min (c) and 90 min (d).
Fig. 4. A plot showing the concentration of compounds A–E with respect to reaction time. The concentrations of these five compounds are obtained by normalizing with eq. (7). The solid curves are graphed to guide the eye.

Fig. 5. A plot showing the concentration of compounds B–D with respect to $\theta$ (see Fig. 4) at 28 ± 2°C. The solid curves were obtained by computer-fitting with eqs (8)–(10). This yields $k_1 = (6.63 \pm 0.66) \times 10^{-3}$ s$^{-1}$ M$^{-1}$; $k_2 = (3.55 \pm 0.35) \times 10^{-3}$ s$^{-1}$ M$^{-1}$; $K = 0.54 \pm 0.11$.

Table 1. $^1$H NMR chemical shifts (δ in ppm)$^a$ and $^1$H–$^{117,119}$Sn coupling constants (J in Hz) for compounds B–D

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pyrrole H δ</th>
<th>J(Sn–H) (ortho)</th>
<th>Phenyl H δ</th>
<th>Phenyl H J (meta)</th>
<th>p-Me J</th>
<th>Sn−OH δ</th>
<th>J(Sn–H)</th>
<th>Sn−OMe δ</th>
<th>J(Sn–H)</th>
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<tbody>
<tr>
<td>B</td>
<td>9.12</td>
<td>—</td>
<td>8.19 (d$^a$)</td>
<td>7.60 (d)</td>
<td>2.73</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C</td>
<td>9.13</td>
<td>—</td>
<td>8.21</td>
<td>7.61</td>
<td>2.73</td>
<td>−7.50</td>
<td>35.6 (119Sn)</td>
<td>34.0 (119Sn)</td>
<td>2.15</td>
</tr>
<tr>
<td>D</td>
<td>9.15</td>
<td>10.6</td>
<td>8.22 (d)</td>
<td>7.62 (d)</td>
<td>2.73</td>
<td>−7.48</td>
<td>37.0 (119Sn)</td>
<td>35.6 (119Sn)</td>
<td>—</td>
</tr>
<tr>
<td>D$'$</td>
<td>9.13</td>
<td>12.2</td>
<td>8.21</td>
<td>7.62 (d)</td>
<td>2.73</td>
<td>−7.49</td>
<td>36.1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>D''</td>
<td>9.14</td>
<td>10.3</td>
<td>8.21</td>
<td>7.61</td>
<td>—</td>
<td>−7.46 (br)</td>
<td>—</td>
<td>—</td>
<td>—</td>
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*Chemical shifts in ppm relative to TMS.
$^a$ From ref. 11.
$^b$ From ref. 2.
$^d$ = doublet.
Kinetics of competitive consecutive second-order reactions

Table 2. $^{13}$C NMR chemical shifts ($\delta$ in ppm) for compounds B–D

<table>
<thead>
<tr>
<th>Compound</th>
<th>C-α</th>
<th>C-β</th>
<th>C-meso</th>
<th>C-1'</th>
<th>C-2'</th>
<th>C-3'</th>
<th>C-4'</th>
<th>C(p-Me)$^b$</th>
<th>C(OMe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>147.3</td>
<td>132.3</td>
<td>121.6</td>
<td>138.6</td>
<td>135.1</td>
<td>127.6</td>
<td>137.8</td>
<td>21.5</td>
<td>44.6</td>
</tr>
<tr>
<td>C</td>
<td>147.0</td>
<td>132.4</td>
<td>121.4</td>
<td>138.6</td>
<td>135.0</td>
<td>127.7</td>
<td>137.9</td>
<td>21.5</td>
<td>44.6</td>
</tr>
<tr>
<td>D</td>
<td>146.7</td>
<td>132.6</td>
<td>121.2</td>
<td>138.4</td>
<td>135.0</td>
<td>127.7</td>
<td>137.9</td>
<td>21.5</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$Chemical shifts relative to the centre line of the CDCl$_3$ triplet at 77.0 ppm.

$^b$p-Me is the methyl group at the para position.

determined by graphical integration of $\int_0^t [H_2O] dt$ and thereby the relationship between [H$_2$O] and $\theta$ established. The $t$-dependence for compounds B–D shown in Fig. 4 was then transformed to $\theta$-dependence as shown in Fig. 5. The solid curves were computer-fitted with eqs (8)–(10) at 28 ± 2°C. They give $k_1 = (6.63 \pm 0.66) \times 10^{-3}$ s$^{-1}$ M$^{-1}$, $k_2 = (3.55 \pm 0.35) \times 10^{-3}$ s$^{-1}$ M$^{-1}$ and $K = k_2/k_1 = 0.54 \pm 0.11$. This $K$ value is comparable with $K = 0.43$ obtained from the hydrolysis of a similar compound, Sn(tpp)(OMe)$_2$.

The $^1$H NMR data for compounds B–D are displayed in Table 1, together with relevant literature data.$^{2,11}$ $^{13}$C chemical shifts for compounds B–D are given in Table 2. $^{13}$C shifts were assigned with the aid of published data of a similar compound.$^3$

In this work a controlled trace amount of water has been involved in the study of the hydrolysis of Sn(tptp)(OMe)$_2$ to Sn(tptp)(OH)$_2$. A two-step competitive consecutive second-order process with Sn(tptp)(OMe)(OH) as an intermediate has been found. The exact solution for the rate constant of the first step is $k_1 = (6.63 \pm 0.66) \times 10^{-3}$ s$^{-1}$ M$^{-1}$ and that of the second step is $k_2 = (3.55 \pm 0.35) \times 10^{-3}$ s$^{-1}$ M$^{-1}$ at 28 ± 2°C. The graphical-integration time variable transformation method developed in this work may be applied to the study of the kinetics of general competitive consecutive second-order reactions.

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REFERENCES