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

# CHING-CHU TSAI, YAO-JUNG CHEN and JYH-HORUNG CHEN\*

Department of Chemistry, National Chunghsing University, Taichung, Taiwan 40227, R.O.C.

and

## LIAN-PIN HWANG

Department of Chemistry, National Taiwan University and Institute of Atomic and Molecular Science, Academia Sinica, Taipei, Taiwan, R.O.C.

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Abstract—The hydrolysis of a new compound, dimethoxo(tetra-*p*-tolylporphyrinato)tin (IV), Sn(tptp)(OMe)<sub>2</sub>, was studied by NMR spectroscopy. The use of a limited amount of water in CDCl<sub>3</sub> allowed the hydrolysis intermediate, hydroxomethoxo(tetra-*p*-tolylporphyrinato)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  $k_1 = (6.63 \pm 0.66) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$  and that of the second step  $k_2 = (3.55 \pm 0.35) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$  at  $28 \pm 2^{\circ}$ C.

<sup>1</sup>H NMR spectroscopy provides a convenient means of identifying and quantifying reaction intermediates. Previous workers have reported the difficulty in detecting dimethoxo(tetraphenylporphyrinato)tin(IV),  $Sn(tpp)(OMe)_2$  (tpp = 5,10,15, 20-tetraphenylporphyrinato), by <sup>1</sup>H NMR spectroscopy due to its rapid hydrolysis to dihydroxo (tetraphenylporphyrinato)tin(IV), Sn (tpp)(OMe)<sub>2</sub>, unless CDCl<sub>3</sub> is specially dried.<sup>1,2</sup> Recently, we reported the two-step hydrolysis of dimethoxo (tetraphenylporphyrinato)tin(IV), Sn(tpp)(OMe)<sub>2</sub>, by <sup>1</sup>H NMR spectroscopy.<sup>3</sup> In the previous paper,<sup>3</sup> the absolute values of two consecutive rate constants  $k_1$  and  $k_2$  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  $k_1/k_2$ . The new compound described in this paper, dimethoxo (tetra-p-tolylporphyrinato)tin(IV), Sn(tptp)(OMe)<sub>2</sub>, was synthesized and used in the hydrolysis investigation. With the aid of <sup>119</sup>Sn and <sup>117</sup>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 <sup>1</sup>H 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)<sub>2</sub> to  $Sn(tptp)(OH)_2$ . With the aid of known water concentration determined by proton NMR intensity, the graphical-integration time-variable transformtion method was used to evaluate the absolute values for both rate constants.

### **EXPERIMENTAL**

# Preparation of Sn(tptp)(OMe)<sub>2</sub>

 $Sn(tptp)(OMe)_2$  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.<sup>1,3,4</sup>

<sup>\*</sup>Author to whom correspondence should be addressed.



Fig. 1. Structure of Sn(tptp)XY complexes.

#### NMR sample preparation

Deuterated chloroform (99.8% from Aldrich) was dried with CaCl<sub>2</sub>. The trace amount of residual water in CDCl<sub>3</sub> was quantified by an NMR method after the sample solution was prepared. The sample was prepared by dissolving Sn(tptp)(OMe)<sub>2</sub> in CDCl<sub>3</sub> to give a concentration of  $2.53 \times 10^{-2}$  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  $28 \pm 2^{\circ}$ C.

### NMR spectra

<sup>1</sup>H and <sup>13</sup>C 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 secondorder reaction. Let  $A = H_2O$ ,  $B = Sn(tptp)(OMe)_2$ , C = Sn(tptp)(OMe)(OH),  $D = Sn(tptp)(OH)_2$  and E = MeOH. The chemical equations for the hydrolysis of B are

$$A + B \xrightarrow{k_1} C + E \text{ (step 1)}$$
 (1)

$$A+C \xrightarrow{\kappa_2} D+E \text{ (step 2)}$$
 (2)

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

$$\frac{\mathbf{d}[\mathbf{B}]}{\mathbf{d}t} = -k_1[\mathbf{A}][\mathbf{B}] \tag{3}$$

$$\frac{\mathrm{d}[\mathbf{C}]}{\mathrm{d}t} = k_1[\mathbf{A}][\mathbf{B}] - k_2[\mathbf{A}][\mathbf{C}]$$
(4)

$$\frac{\mathrm{d}[\mathbf{D}]}{\mathrm{d}t} = k_2[\mathbf{A}][\mathbf{C}]. \tag{5}$$

From the principle of material balance, they read

$$[B] + [C] + [D] = [B]_0 + [C]_0 + [D]_0$$
(6)

and

$$[A]+[B]+[C]+[D]+[E]$$
  
= [A]<sub>0</sub>+[B]<sub>0</sub>+[C]<sub>0</sub>+[D]<sub>0</sub>+[E]<sub>0</sub> (7)

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<sup>5-10</sup>  $\theta = \int_0^t [H_2O] dt$ . On integration, we obtain

$$[\mathbf{B}] = [\mathbf{B}]_0 e^{-k_1 \theta} \tag{8}$$

$$[C] = [C]_0 e^{-k_2 \theta} + \frac{k_1}{k_2 - k_1} [B]_0 (e^{-k_1 \theta} - e^{-k_2 \theta})$$
(9)

$$[D] = [D]_0 + [C]_0 (1 - e^{-k_2 \theta})$$

+[**B**]<sub>0</sub>
$$\left(1-\frac{k_2}{k_2-k_1}e^{-k_1\theta}+\frac{k_1}{k_2-k_1}e^{-k_2\theta}\right)$$
. (10)

The relationship between  $\theta$  and t is readily established by plotting [H<sub>2</sub>O] against t and integrating graphically. The data giving [H<sub>2</sub>O] 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)(O-Me)(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  $H_2O$  are shown in Fig. 4.



Fig. 2. NMR spectrum for Sn(tptp)(OMe)<sub>2</sub> hydrolysis after a reaction time of 20 min. The spectral resonances used to measure the concentrations of compounds B–D, MeOH and H<sub>2</sub>O are shown. The proton assignments are: (a) H<sub>β</sub> (pyrrole); (b) phenyl H (*ortho*); (c) phenyl H (*meta*); (d) CHCl<sub>3</sub>; (e) methyl group of methanol; (f) p-CH<sub>3</sub>; (g) hydroxy group of water; (h) methanol OH group; (i) tetramethyl silane; (j) methoxy group of Sn(tptp)(OMe)<sub>2</sub>; (l) methoxy group of Sn(tptp)(OMe)(OH); (n) hydroxy group of Sn(tptp)(OH)<sub>2</sub>.

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)<sub>2</sub> 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)<sub>2</sub> 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  $28 \pm 2^{\circ}$ C. The solid curves were obtained by computer-fitting with eqs (8)–(10). This yields  $k_1 = (6.63 \pm 0.66) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ ;  $k_2 = (3.55 \pm 0.35) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ ;  $K = 0.54 \pm 0.11$ .

	Pyrrole H		DIALIT	DI 111		Sn-	ОН	Sn—OMe	
Compound	δ	J(Sn—H)	ortho)	Phenyl H ( <i>meta</i> )	<i>p</i> -Me	δ	J(Sn-H)	δ	J(Sn-H)
В	9.12		8.19 (d <sup><i>d</i></sup> )	7.60 (d)	2.73		—	-2.16	70.0 ( <sup>119</sup> Sn) 66.8 ( <sup>117</sup> Sn)
С	9.13	—	8.21	7.61	2.73	-7.50	35.6 ( <sup>119</sup> Sn) 34.0 ( <sup>117</sup> Sn)	-2.15	71.4 ( <sup>119</sup> Sn) 68.2 ( <sup>117</sup> Sn)
D	9.15	10.6	8.22 (d)	7.62 (d)	2.73	-7.48	37.0 ( <sup>119</sup> Sn) 35.6 ( <sup>117</sup> Sn)	_	
$\mathbf{D}^{\prime\prime}$	9.13	12.2	8.21	7.62 (d)	2.73	- 7.49	36.1		—
$\mathbf{D}^{c}$	9.14	10.3	8.21	7.61		-7.46 (br)		_	_

Table 1. <sup>1</sup>H NMR chemical shifts ( $\delta$  in ppm)<sup>*a*</sup> and <sup>1</sup>H-<sup>117,119</sup>Sn coupling constants (J in Hz) for compounds B-D

"Chemical shifts in ppm relative to TMS.

<sup>*h*</sup> From ref. 11.

<sup>c</sup> From ref. 2.

 $^{d}$ d = doublet.

Compound	C-α	С-β	C-meso	C-1′	C-2′	C-3′	C-4′	C(p-Me) <sup>b</sup>	C(OMe)
В	147.3	132.3	121.6	138.6	135.1	127.6	137.8	21.5	44.6
С	147.0	132.4	121.4	138.6	135.0	127.7	137.9	21.5	44.6
D	146.7	132.6	121.2	138.4	135.0	127.7	137.9	21.5	

Table 2. <sup>13</sup>C NMR chemical shifts ( $\delta$  in ppm)<sup>*a*</sup> for compounds B–D

<sup>a</sup> Chemical shifts relative to the centre line of the CDCl<sub>3</sub> triplet at 77.0 ppm.

<sup>b</sup> 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  $[H_2O]$  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  $28 \pm 2^{\circ}$ C. They give  $k_1 = (6.63 \pm 0.66) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ ,  $k_2 = (3.55 \pm 0.35) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$  and  $K = k_2/k_1 = 0.54 \pm$ 0.11. This K value is comparable with K = 0.43obtained from the hydrolysis of a similar compound, Sn(tpp)(OMe)<sub>2</sub>.<sup>3</sup>

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

In this work a controlled trace amount of water has been involved in the study of the hydrolysis of Sn(tptp)(OMe)<sub>2</sub> to Sn(tptp)(OH)<sub>2</sub>. 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  $k_1 = (6.63 \pm 0.66) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$ and that of the second step is  $k_2 = (3.55 \pm 0.35) \times 10^{-3} \text{ s}^{-1} \text{ M}^{-1}$  at  $28 \pm 2^{\circ}$ 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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