

# The hydrolysis of $\text{Me}_2\text{Sn}^{\text{IV}}$ and $\text{Me}_3\text{Sn}^{\text{IV}}$ moieties monitored through $^{119}\text{Sn}$ Mössbauer spectroscopy

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## Abstract

The  $^{119}\text{Sn}$  Mössbauer parameters  $\delta$ , isomer shift, and  $\Delta E$ , nuclear quadrupole splitting, have been determined in frozen aqueous solutions of  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $\text{Me}_3\text{Sn}^{\text{IV}}$  moieties at varying pH. The resulting functions  $\bar{n}$  versus pH (where  $\bar{n}$  is the average number of protons released per mole of the organotin aquocation) agree satisfactorily with functions from potentiometry. The structures of the aquocations, as well as of the hydroxides, and of the mono-hydroxo complex  $[\text{Me}_2\text{Sn}(\text{OH})(\text{OH}_2)_n]^+$ , are correlated to the  $\Delta E_{\text{exp}}$  data by point-charge model calculations.

## Introduction

The environment of the metal atom in organotin(IV) moieties interacting with biological molecules, or inserted into biological systems, has often been studied by  $^{119}\text{Sn}$  Mössbauer spectroscopy. In fact, organotins in cell membranes [1, 2] and walls [3], bound to hemoglobin [4–6] and possibly to native DNA [7–9], as well as organotin compounds, in aqueous systems, tested as antitumour drugs [10], have been investigated by the technique. In this context, Mössbauer parameters of frozen aqueous solutions of  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $\text{Me}_3\text{Sn}^{\text{IV}}$ , at highly acidic, and at neutral and basic pH values, have been determined and discussed [5, 6], in order to possibly infer, at a given pH, the presence of hydrolyzed organotins and/or organotin moieties associated to biological constituents. It then seemed advisable to determine the functions: Mössbauer parameters versus pH, in aqueous (frozen) solutions of  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $\text{Me}_3\text{Sn}^{\text{IV}}$  in the pH range 1–10, and the results obtained are reported in the present paper. The data are treated and discussed in the light of the ample literature on hydrolysis constants of  $\text{Me}_2\text{Sn}^{\text{IV}}$  [11–13] and  $\text{Me}_3\text{Sn}^{\text{IV}}$  [14, 15], mainly following the procedures outlined by R. Stuart Tobias and his school.

## Materials and methods

The compounds  $\text{Me}_2\text{SnCl}_2$  and  $\text{Me}_3\text{SnCl}$  were gifts from Schering A.G., Bergkamen (F.R.G.), and other

chemicals were from C. Erba, Milan (Italy). Solutions of  $\text{Me}_2\text{Sn}(\text{ClO}_4)_2$  were prepared according to Tobias *et al.* [11]. The values of pH were adjusted by addition of diluted  $\text{HClO}_4$  (to  $\text{Me}_2\text{Sn}(\text{ClO}_4)_2$  in  $\text{H}_2\text{O}$ ) and  $\text{HCl}$ , as well as  $\text{NaOH}$ , and measured with a Crison 2000 pH meter. The absorber samples of frozen aqueous solutions submitted to  $^{119}\text{Sn}$  Mössbauer spectroscopy were obtained according to the literature [5, 6]. The Mössbauer spectrometer, the conditions of operation, and the data reduction procedures, were as reported earlier [5, 6]. The results are given in Table 1.

## Treatment of data

The Mössbauer parameters isomer shift,  $\delta$ , and nuclear quadrupole splitting,  $\Delta E$ , of complexes  $\text{SnL}_n$  in frozen aqueous solution, are correlated to  $\bar{n}$ , the average number of ligands L per mole of complex, by the relationship [16]

$$p = p_0 + \bar{n}(p_N - p_0)/N \quad (1)$$

where  $p$  are values of  $\delta$ , as well as of  $\Delta E$ , at a given  $\bar{n}$ , and  $p_0$  and  $p_N$  are inherent to the free cation  $\text{Sn}^{n+}$  and to the saturated complex  $\text{SnL}_N$ , respectively [16]. Equation (1) is in line with the treatment generally employed in studies of complex formation in solution by spectroscopic methods, as well as by any technique monitoring the variation of physical properties as function of complex formation [17]; in this context, NMR parameters have been, for example, amply employed in the study of equilibria,

TABLE 1.  $^{119}\text{Sn}$  Mössbauer parameters of  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $\text{Me}_3\text{Sn}^{\text{IV}}$  in aqueous solution, frozen at 77.3 K, as function of the pH values<sup>a</sup>

pH	$\delta^b$ (mm s <sup>-1</sup> )	$\Delta E^c$ (mm s <sup>-1</sup> )	$\Gamma_1^d$ (mm s <sup>-1</sup> )	$\Gamma_2^d$ (mm s <sup>-1</sup> )
<b>(A) <math>\text{Me}_2\text{Sn}^{\text{IV}}</math></b>				
0.95	1.34	4.64	0.83	0.86
1.60	1.35	4.62	0.90	0.89
3.23	1.32	4.01	1.02	0.92
4.13	1.29	3.82	1.04	1.09
5.06 <sup>e</sup>	1.22	3.13	0.94	0.77
5.25 <sup>e</sup>	1.17	2.96	0.95	0.75
6.05	1.06	2.74	1.33	1.08
7.36 <sup>f</sup>	0.96	2.35	0.89	0.66
7.37 <sup>g</sup>	1.00	2.27	0.82	0.83
8.13	0.97	2.41	1.12	1.41
9.70 <sup>f</sup>	0.98	2.33	0.93	0.72
10.74	0.97	2.37	0.96	0.74
<b>(B) <math>\text{Me}_3\text{Sn}^{\text{IV}}</math></b>				
1.70	1.47	3.84	0.92	0.82
3.10 <sup>h</sup>	1.47	3.82	0.92	0.79
3.73 <sup>h</sup>	1.52	3.92	0.80	1.00
4.54	1.43	3.72	1.03	0.97
5.03	1.37	3.71	1.28	0.82
5.48	1.38	3.54	1.01	0.64
6.05	1.29	3.38	0.95	0.88
6.50	1.26	3.00	1.01	0.89
7.03 <sup>h</sup>	1.25	2.91	1.06	0.75
7.30 <sup>h</sup>	1.23	2.77	0.72	0.71
7.50	1.25	2.80	0.84	0.80
8.80 <sup>h</sup>	1.26	2.90	0.87	0.88
9.63 <sup>h</sup>	1.24	2.76	0.67	0.72
10.70	1.24	2.76	1.04	1.18

<sup>a</sup>20 mM  $\text{Me}_2\text{Sn}(\text{ClO}_4)_2$  and  $\text{Me}_3\text{SnCl}$  unless otherwise stated. See 'Materials and methods'. The % resonant effect of the quadrupole split components were in the range 1–2% ( $\text{Me}_2\text{Sn}^{\text{IV}}$ ) and 0.5–1.4% ( $\text{Me}_3\text{Sn}^{\text{IV}}$ ) for 20 mM samples, and around 0.5% ( $\text{Me}_2\text{Sn}^{\text{IV}}$ ) and 0.2–0.8% ( $\text{Me}_3\text{Sn}^{\text{IV}}$ ) for 10 mM. <sup>b</sup>Isomer shift with respect to r.t. Ca  $^{119}\text{SnO}_3$ ,  $\pm 0.02$  mm s<sup>-1</sup> (standard deviation). <sup>c</sup>Nuclear quadrupole splitting,  $\pm 0.02$  mm s<sup>-1</sup>. <sup>d</sup>Full width at half height of the resonant peaks at lesser and larger velocity than the spectrum centroid, respectively. <sup>e</sup>20 mM  $\text{Me}_2\text{SnCl}_2$  in  $\text{H}_2\text{O}$ . <sup>f</sup>10 mM  $\text{Me}_2\text{SnCl}_2$  in  $\text{H}_2\text{O}$ . <sup>g</sup>10 mM  $\text{Me}_2\text{Sn}(\text{ClO}_4)_2$  in  $\text{H}_2\text{O}$ . <sup>h</sup>10 mM  $\text{Me}_3\text{SnCl}$  in  $\text{H}_2\text{O}$ .

involving also organometals, by equations of type (1) [18]. Taking into account that Mössbauer parameters of organotin may either increase [7] or decrease [5, 6, 19] upon formation of complexes, from eqn. (1) is obtained

$$\bar{n} = \pm(p - p_0) / \pm(p_n - p_0) / N \quad (2)$$

In the present work, functions  $\bar{n}$  versus pH have been estimated by eqn. (2),  $\bar{n}$  being the average number of protons released per mole of  $[\text{Me}_n\text{Sn}(\text{OH}_2)_m]^{(4-n)+}$  ( $n=2$  and 3) at the pH value corresponding to the given parameter  $p$ ; the values

$N=2$  for  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $N=1$  for  $\text{Me}_3\text{Sn}^{\text{IV}}$  have been employed, which correspond to the saturated hydroxo complexes  $\text{Me}_2\text{Sn}(\text{OH})_2$  and  $\text{Me}_3\text{SnOH}$  [11–15]. The following sets of data have been employed:

(A)  $\text{Me}_2\text{Sn}^{\text{IV}}$ .  $\bar{n}(\delta, \Delta E) = (p_0 - p) / (p_0 - p_2) / 2$ . Data from Table 1(A).

(1)  $p_x = \delta$ , isomer shift;  $p_0 = 1.34(5)$ , average of  $\delta$  values at pH 0.95 and 1.60;  $p_2 = 0.97(6)$ ,  $\delta_{av}$  in the pH range 7.36–10.74.

(2)  $p_x = \Delta E$ , nuclear quadrupole splitting;  $p_0 = 4.64 = \Delta E$  at pH = 0.95;  $p_2 = 2.34(6)$ ,  $\Delta E_{av}$  in the pH range 7.36–10.74.

(B)  $\text{Me}_3\text{Sn}^{\text{IV}}$ .  $\bar{n}(\delta, \Delta E) = (p_0 - p) / (p_0 - p_1)$ . Data from Table 1(B).

(1)  $p_x = \delta$ ;  $p_0 = 1.48(7)$ ,  $\delta_{av}$  in the pH range 1.70–3.73;  $p_1 = 1.24(4)$ ,  $\delta_{av}$  in the pH range 7.30–10.70.

(2)  $p_x = \Delta E$ ;  $p_0 = 3.86$ ,  $\Delta E_{av}$  in the pH range 1.70–3.73;  $p_1 = 2.79(8)$ ,  $\Delta E_{av}$  in the pH range 7.80–10.70.

The functions  $\bar{n}$  versus pH thus obtained are reported in Fig. 1(A) and (B).

## Results and discussion

The data points  $\delta$  and  $\Delta E$  of Table 1, plotted versus pH, describe well-shaped sigmoid functions (as evidenced in the derived plots  $\bar{n}$  versus pH of Fig. 1) which correspond to the trends detected in a series of complex systems investigated by a number of techniques [17]. The observed function seems particularly remarkable for sets  $\delta$  versus pH, considering the limited variation shown by the parameter  $\delta$ . The eventual occurrence of outlier points has been observed for  $\text{Me}_2\text{SnCl}_2$  adjusted to pH < 3.0 (e.g. pH = 2.6,  $\delta = 1.52$ ,  $\Delta E = 4.20$ , mm s<sup>-1</sup>); no effects of this type have been observed at pH > 5. Outliers occur also for  $\text{Me}_3\text{Sn}^{\text{IV}}$  (e.g. pH = 1.0,  $\delta = 1.39$ ,  $\Delta E = 3.61$ , mm s<sup>-1</sup>). We are tempted to ascribe these effects to the formation of the covalent species  $(\text{Me}_2\text{SnCl})^+$  and  $(\text{Me}_3\text{SnCl})$ , respectively, although eventually formed in quite low amounts due to the related stability constants [20, 21].

The experimental functions  $\bar{n}$  versus pH, Fig. 1, satisfactorily agree with the functions pertaining to the following potentiometric values of hydrolysis constants: (a)  $\text{Me}_2\text{Sn}^{\text{IV}}$ :  $\log^* \beta_{11} = -3.245$ ,  $\log^* \beta_{21} = -8.516$  [11]; (b)  $\text{Me}_3\text{Sn}^{\text{IV}}$ :  $\log^* \beta_{11} = -6.600$  [14]. The observed agreement is noticeable in view of the peculiar conditions inherent to the determination of the Mössbauer data in Table 1. In fact, these have been measured on aqueous  $\text{Me}_2\text{Sn}(\text{ClO}_4)_2$  and  $\text{Me}_3\text{SnCl}$  (as in the potentiometric studies [11–15]); on the other hand, no electrolyte has been added to yield a constant ionic strength, in order

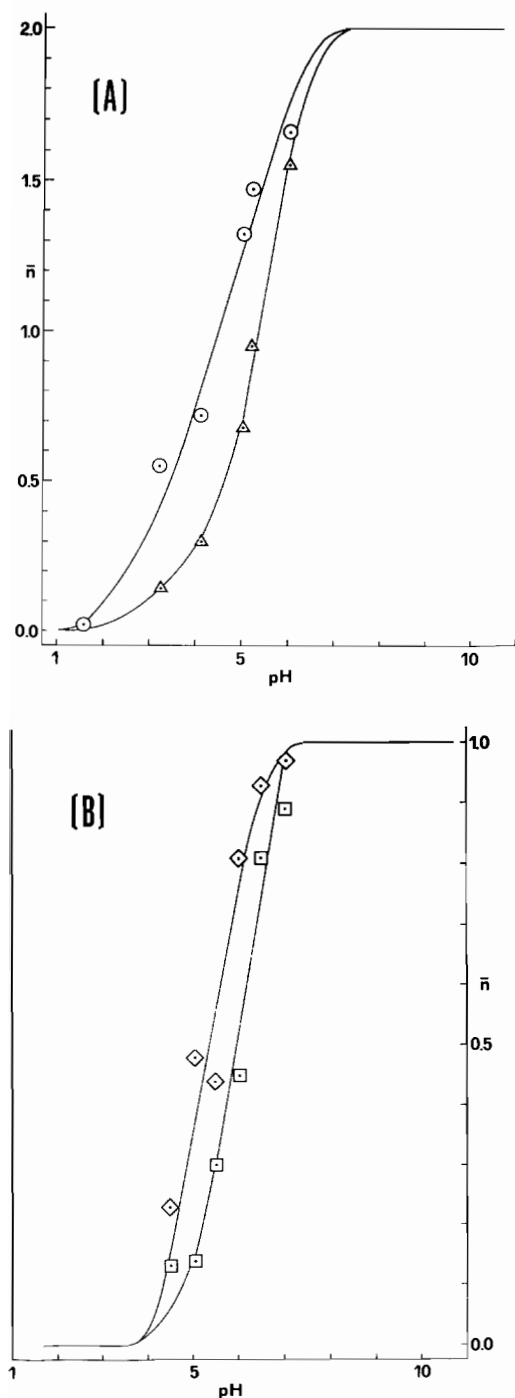


Fig. 1. The average number of OH<sup>(-)</sup> bound per organotin(IV),  $\bar{n}$ , as function of pH. Data calculated from parameters  $\delta$  and  $\Delta E$  of Table 1 (see text). (A) Me<sub>2</sub>Sn<sup>IV</sup>:  $\Delta$   $\bar{n}$  ( $\delta$ );  $\circ$   $\bar{n}$  ( $\Delta E$ ). (B) Me<sub>3</sub>Sn<sup>IV</sup>:  $\diamond$   $\bar{n}$  ( $\delta$ );  $\square$   $\bar{n}$  ( $\Delta E$ ).

not to favour the formation of crystalline environments of the metal ion upon freezing to 77 K, which would yield Mössbauer absorbers unrelated to the parent aqueous solutions [22]. It seems worth mentioning also that significant effects on  $\delta$  and  $\Delta E$  due

to the concentration of Me<sub>2</sub>Sn<sup>IV</sup> have not been detected in the systems here investigated, so that polynuclear species [11–14] cannot be taken into account.

The <sup>119</sup>Sn Mössbauer parameters of Me<sub>2</sub>Sn<sup>IV</sup> and Me<sub>3</sub>Sn<sup>IV</sup> moieties vary as a function of the configuration of C<sub>2</sub>Sn and C<sub>3</sub>Sn fragments. In fact,  $\delta$ s decrease from, for example, *trans*-Me<sub>2</sub>- to *cis*-Me<sub>2</sub>-octahedral, as well as from *trans*-Me<sub>2</sub>-octahedral to tetrahedral, species, following the decrease of s-electron density at the tin nucleus; a parallel diminution of  $\Delta E$  takes place, which reflects the correlation of the electric field gradient tensor at Sn with the angle CSnC [23–29]. Analogous trends have been detected for Me<sub>3</sub>Sn<sup>IV</sup> [23–29]. In the present context,  $\Delta E$  values at acid pH have been attributed to [Me<sub>2</sub>Sn(OH<sub>2</sub>)<sub>n</sub>]<sup>2+</sup>, with linear CSnC skeleton, as well as of [Me<sub>3</sub>Sn(OH<sub>2</sub>)<sub>n</sub>]<sup>+</sup>, where a trigonal planar C<sub>3</sub>Sn fragment would occur [5, 6]. The hydroxides Me<sub>2</sub>Sn(OH)<sub>2</sub> and Me<sub>3</sub>Sn(OH)(OH<sub>2</sub>) assume instead a tetrahedral [5] and a heavily distorted trigonal bipyramidal [6] structure, respectively. The structural variations parallel to the increase of pH are reported in Fig. 2, as interpreted by point-charge model calculations of  $\Delta E$  by the conventional approach [25–27] as well as by considering Sn–C bond electrons only [28, 29] (see caption to Fig. 2). It is observed that the species [Me<sub>2</sub>Sn(OH)(OH<sub>2</sub>)<sub>n</sub>]<sup>+</sup> is likely to assume the *tbp* structure (II) (according to the rule of the axial location of electronegative ligands [30]) rather than the (distorted) octahedral structure (III), considering the perfect agreement between the estimated angle CSnC and  $\Delta E_{\text{calc}}$  obtained for structure II, Fig. 2. This is in line also with the thermodynamic study by Arena *et al.* [13], with the assumption of structure II in place of a *cis*-octahedral species.

The results reported in the present paper are applicable to the determination of the organotin species present in aqueous solution as well as in biological environments. For example, in the aqueous system Me<sub>2</sub>Sn<sup>IV</sup>–L-cysteine, the value  $\Delta E \approx 3.0$  is measured at pH = 4.3 [19], which excludes the formation of the hydrolysis product [Me<sub>2</sub>Sn(OH)(OH<sub>2</sub>)<sub>n</sub>]<sup>+</sup> (II, Fig. 2) and strengthens the assumed formation [19] of [Me<sub>2</sub>Sn(SCH<sub>2</sub>CH(NH<sub>2</sub>)COO)(OH<sub>2</sub>)<sub>2</sub>] and related species. Applications of the present results to studies in biological systems [2] are underway.

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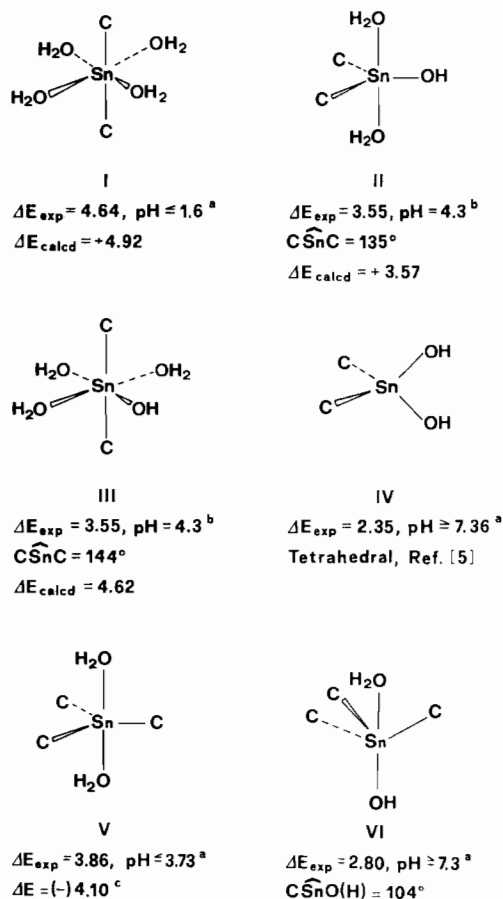


Fig. 2. Point-charge model estimates of the possible structures of  $\text{Me}_2\text{Sn}^{\text{IV}}$  and  $\text{Me}_3\text{Sn}^{\text{IV}}$  species as function of the extent of hydrolysis: (I)  $\rightarrow$  [(II) or (III)]  $\rightarrow$  (IV); (V)  $\rightarrow$  (VI). The angles  $\text{CSnC}$  and  $\text{CSnO}$  have been estimated by correlations  $\Delta E$ -angle from the partial nuclear quadrupole splittings due to Sn-C bonds only [28, 29]. The data  $\Delta E_{\text{calc}}$  ( $\text{mm s}^{-1}$ ) refer to calculations by the conventional point-charge model referred to regular structures [25-27]; the *p.q.s.* values employed are tabulated in ref. 5. <sup>a</sup>Data from Table 1. <sup>b</sup>Obtained from Fig. 1(A), for  $\bar{n} = 1$ , and a plot  $\Delta E_{\text{exp}}$  vs.  $\text{pH}$  drawn with the data in Table 1. <sup>c</sup>Value estimator of *p.q.s.* for  $\text{H}_2\text{O}$  tba, ref. 27. (a, b) See 'Treatment of data'.

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