Formation and Stability Constants of Dimethyltin(IV) Complexes with Citrate, Tripolyphosphate, and Nitrilotriacetate in Aqueous Solution

Giuseppe Arena
Istituto di Chimica Analitica, Università di Messina, 98010 Messina, Italy
Annalinda Contino, Salvatore Musumeci, and Roberto Purrello
Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy

The complex formation of $[SnMe_2]^{2+}$ with citrate, tripolyphosphate, and nitrilotriacetate has been investigated potentiometrically at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3); the protonation constants for all three ligands have also been determined under the same experimental conditions. The species formed, together with their stability constants, have been determined by analysing a large number of data points. The results are compared critically to literature data obtained under analogous experimental conditions. The possible implications of the interaction of dimethyltin(IV) with the same ligands are also outlined.

Organometallic species, in general, and organotin compounds, in particular, may be found in the natural environment either because they are introduced or because they are formed there. As a result of the wide range of industrial applications [*e.g.*, poly(vinyl chloride) (pvc) stabilizers, glass-coating operations, waste burial, *etc.*] organotin compounds enter the environment through a variety of direct or indirect pathways. Since organotin compounds are most widely used as pvc stabilizers, the main indirect routes are (*i*) leaching/weathering, (*ii*) land burial, and (*iii*) incineration of waste material.[1] Direct introduction is mainly through biocidal uses.

However, organotin compounds may also be formed in the natural environment from inorganic precursors through chemical or biological processes. Both environmental[2–4] methylation and biomethylation[5] have been shown to occur. Routes of environmental methylation have been reviewed recently by Wood and co-workers[6–9] and Craig[10–12] and various mechanisms have been proposed. The formation of methyltin compounds in sediments has also been described.[2–4]

Regardless of the mechanism through which methyltin compounds are generated, however, methyltin derivatives are the most commonly encountered organotin compounds.[13] Hence a reliable *in vitro* speciation for methyltin derivatives is highly desirable.

Further interest in the *in vitro* speciation of organotin compounds is a result of the evidence that di- and tri-alkyltin compounds, complexed to a variety of ligands, are effective against P-388 leukemia[14,15] and the implication of organotin compounds in cancer prophylaxis and other physiological processes.[16,17]

Moreover tin-labelled technetium complexes have been used as imaging agents for tumour localization.[18] Alkyltin compounds have been tested in various tumour systems[19] and, interestingly, the most pronounced activity is shown by diorganotin derivatives.

The need to study organotin compounds in solution 'especially in aqueous media' has been pointed out recently[20] and the importance of chemical speciation has also been stressed.[21]

With the above in mind, continuing our studies on the species distribution[22,23] of dialkyltin(IV) ions that are of interest either from an environmental or bioinorganic point of view, here we report on the complex formation of dimethyltin(IV) ($[SnMe_2]^{2+}$) with citrate (cit^{3-}), tripolyphosphate (tpp^{5-}), and nitrilotriacetate (nta^{3-}). The choice of these ligands is not fortuitous. In fact, citrate has been recently considered as a possible substitute for polyphosphates added to solid detergents. Tripolyphosphate was until not long ago the most widely used detergent and continues to be used in various sectors (*e.g.*, dispersing agent for oil drilling muds, curing of meats such as ham); this ligand was also included because of the interest in tripolyphosphate esters, such as adenosine 5′-triphosphate, in biochemical reactions.

Nitrilotriacetate has been used mostly as a detergent builder; in addition, it is also used for cleaning boilers.[24] In the latter application it has the advantage, over ethylenediaminetetraacetate for example, of being more thermally (hydrolytically) stable in aqueous solution, thus proving more adept as a high pressure, high temperature cleaner for boilers.

The speciation for the above systems was obtained by potentiometric measurements performed at $T = 25$ °C and $I = 0.1$ mol dm^{-3} (KNO_3).

Experimental

Chemicals.—Nitrilotriacetic acid (H_3nta) (C. Erba RPE) was used without further purification. Citric acid (H_3cit) (C. Erba RPE-ACS) was recrystallized from twice-distilled water. Pentasodium tripolyphosphate [$Na_5(tpp)$] (Sigma) was purified further by repeated crystallizations from water–ethanol mixtures, according to a procedure described in the literature.[25] The purity of the above ligands, checked by alkalimetric titrations, was always >99.5%.

Dimethyltin(IV) ($[SnMe_2]^{2+}$) nitrate was obtained using dimethyltin oxide (ICN Biomedical Inc.) as the starting material. The oxide was purified to remove chloride ions and converted to the nitrate according to the procedure described previously.[22] The purity of the dimethyltin(IV) nitrate solution was checked potentiometrically by using the computer program SUPERQUAD (see Calculations). The coincidence between stoicheiometrically calculated and observed excesses of nitric acid, added to dimethyltin oxide to make up the dimethyltin nitrate solution, indicated that the purity was >99.5%.

Stock solutions of HNO_3 and KOH were prepared by diluting concentrated ampoules (Merck). The ionic strength of all solutions was adjusted to 0.1 mol dm^{-3} by adding KNO_3 (Merck).

Twice-distilled water and Grade A glassware were used throughout.

Table 1. Experimental conditions of potentiometric measurements at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)*

c^0_M/mmol dm^{-3} $[SnMe_2]^{2+}$	C^0_L/mmol dm^{-3}			Titrant, KOH/mol dm^{-3}	pH range	No. of points
	cit^{3-}	nta^{3-}	tpp^{5-}			
	6.051			0.100 95	2.7—6.5	48
	6.051			0.100 91	2.7—6.5	47
		6.003		0.100 13	2.2—9.9	44
		6.003		0.100 08	2.2—9.9	43
		6.049		0.100 13	2.2—9.9	43
		6.049		0.100 08	2.2—9.9	42
			3.001	0.100 00	2.4—8.6	41
			3.001	0.999 90	2.4—8.6	40
			3.004	0.101 13	2.4—8.6	41
			3.004	0.087 96	2.4—8.6	46
			4.781	0.100 00	2.4—8.6	44
			4.847	0.101 13	2.4—8.7	45
4.001	8.003			0.100 95	2.3—6.5	46
4.001	8.003			0.100 95	2.3—6.5	45
3.006	8.054			0.100 00	2.3—6.5	53
3.006	8.054			0.099 97	2.3—6.5	53
6.001	6.024			0.100 00	2.3—6.5	49
6.001	6.024			0.099 97	2.3—6.5	49
6.009	6.642			0.100 13	2.5—6.6	42
6.009	6.642			0.100 08	2.5—6.5	41
6.004	5.553			0.099 94	2.3—6.5	46
6.012	9.090			0.099 94	2.2—6.4	47
6.006		6.030		0.100 73	2.3—6.3	23
6.006		6.030		0.099 94	2.3—6.4	23
4.023		6.021		0.100 78	2.3—6.4	27
4.023		6.021		0.100 44	2.3—6.4	28
3.004		6.012		0.100 78	2.3—6.3	29
3.004		6.012		0.100 78	2.3—6.3	29
4.009		6.018		0.100 78	2.5—6.3	30
5.022		5.006		0.100 78	2.5—6.4	43
5.022		5.006		0.100 44	2.5—6.4	42
6.021		6.014		0.100 78	2.5—6.4	47
6.021		6.014		0.100 44	2.5—6.4	46
5.000			5.000	0.101 60	3.1—8.8	45
5.029			5.034	0.100 17	3.1—8.8	40
3.014			6.002	0.101 60	3.1—8.8	51
3.014			6.002	0.088 41	3.1—8.9	50
4.022			6.046	0.101 60	3.1—8.8	47
4.022			6.046	0.101 60	3.1—8.8	47
4.085			6.075	0.101 60	3.1—8.7	47

* The volume of the solution to be titrated was 20 cm^3 in all cases.

E.M.F. Measurements.—The potentiometric measurements were carried out by means of four fully automated sets of apparatus. These made use of Metrohm equipment (burette, E 665; meter, E 654; glass electrodes, EA 109; calomel electrodes, EA 404) and were controlled by an IBM computer or IBM compatible PC. Each computer was able to control two potentiometric set ups simultaneously by using a program written in our laboratory. Values of $E^{\ominus}$ and the nernstian slope of the electrode system were determined by titrating 20 cm^3 of HNO_3 with CO_2-free KOH. All experiments were carried out at 25.0 ± 0.1 °C using 25-cm^3 thermostatted cells. The solutions were kept in an atmosphere of CO_2- and O_2-free nitrogen, previously bubbled through 0.1 mol dm^{-3} KNO_3 solutions. To avoid systematic errors and to check for reproducibility, each experiment was run simultaneously in at least two of the four different sets of potentiometric apparatus. The readings of these 'parallel' experiments were taken at different time intervals to confirm that there were no kinetic problems. In addition, checks on the initial pH of each solution to be titrated showed no detectable drift over a period of 90 min.

Experimental details for the potentiometric titrations are reported in Table 1. Other details were as described previously.[26]

Calculations.—The calculations concerning the calibration of the electrode system ($E^{\ominus}$, slope, and E_j) were performed using the computer program ACBA[27] which refines the parameters of an acid–base titration by using a non-linear least-squares method minimizing the function $U = \Sigma(V_{\text{exptl},i} - V_{\text{calc},i})^2$, where V is the volume of titrant added. SUPERQUAD[28] was used to handle all the data for the evaluation of stability constants. MINIQUAD 76A[29] was also employed for the computation of stability constants to double check the validity of the selected model.

The above programs minimize the error square sum based on measured electrode potentials and concentrations, respectively. For the analysis of residuals, the procedure recommended by Vacca *et al.*[30] was followed.

The distribution diagrams were obtained by means of the computer program DISDI.[31]

Results and Discussion

Dimethyltin(IV) is a hard acid[32] cation and hydrolyses according to equation (1). The hydrolytic species existing in the pH

Table 2. Stability constants of dimethyltin(IV)–hydroxo complexes at 25 °C and $I = 0.1$ mol dm^{-3} (KNO$_3$)

Reaction	log β*
$[SnMe_2]^{2+} + H_2O \rightleftharpoons [SnMe_2(OH)]^+ + H^+$	−3.124
$2[SnMe_2]^{2+} + 2H_2O \rightleftharpoons [(SnMe_2)_2(OH)_2]^{2+} + 2H^+$	−5.05
$2[SnMe_2]^{2+} + 3H_2O \rightleftharpoons [(SnMe_2)_2(OH)_3]^+ + 3H^+$	−9.74
$[SnMe_2]^{2+} + 2H_2O \rightleftharpoons SnMe_2(OH)_2 + 2H^+$	−8.428
$[SnMe_2]^{2+} + 3H_2O \rightleftharpoons [SnMe_2(OH)_3]^- + 3H^+$	−19.450

* Ref. 22.

Table 3. Stability constants of citrate (cit^{3-}) (L^{3-}) complexes together with protonation constants at 25 °C and $I = 0.1$ mol dm^{-3} (KNO$_3$)

Reaction	log β[a]
$L^{3-} + H^+ \rightleftharpoons HL^{2-}$	5.69(2)[b]
	5.66[c]
	5.61[d]
$L^{3-} + 2H^+ \rightleftharpoons H_2L^-$	10.04(3)[b]
	10.00[c]
	9.91[d]
$L^{3-} + 3H^+ \rightleftharpoons H_3L$	12.94(6)[b]
	12.90[c]
	12.78[d]
$[SnMe_2]^{2+} + L^{3-} + H^+ \rightleftharpoons SnMe_2LH$	10.83(1)[b]
$[SnMe_2]^{2+} + L^{3-} \rightleftharpoons [SnMe_2L]^-$	6.55(2)[b]
$[SnMe_2]^{2+} + L^{3-} + H_2O \rightleftharpoons [SnMe_2LH_{-1}]^{2-} + H^+$	0.99(6)[b]
$2[SnMe_2]^{2+} + L^{3-} + H_2O \rightleftharpoons (SnMe_2)_2LH_{-1} + H^+$	6.65(9)[b]
$2[SnMe_2]^{2+} + L^{3-} + 2H_2O \rightleftharpoons [(SnMe_2)_2LH_{-2}]^- + 2H^+$	2.38(6)[b]

[a] 3σ are given in parentheses. [b] This work. [c] Recommended values (ref. 33; $I = 0.1$ mol dm^{-3} and $T = 25$ °C). [d] Ref. 34; $I = 0.1$ mol dm^{-3} (KNO$_3$) and $T = 25$ °C.

$$x[SnMe_2]^{2+} + yH_2O \longrightarrow [(SnMe_2)_x(OH)_y]^{2x-y} + yH^+ \quad (1)$$

range investigated in the present study as well as their stability constants were determined previously.[22] However, being an integral part of the models proposed for the three systems investigated they are reported in Table 2.

SnMe$_2$–cit.—The protonation constants for citrate have been reported at $I = 0.1$ mol dm^{-3} and $T = 25$ °C (recommended values).[33] Protonation constants are also available from the literature at $I = 0.1$ mol dm^{-3} (KNO$_3$) and $T = 25$ °C,[34] *i.e.*, under the same experimental conditions used in the present study. However, since the values in ref. 34 are a bit low with respect to the 'recommended' values,[33] we verified them by alkalimetric titrations. The differences between the 'recommended' values and the values determined in the present investigation were found to be negligible; thus the latter values were used in the calculation of the stability constants of the SnMe$_2$–cit system. The values found are reported in Table 3.

For the SnMe$_2$–cit system the following species were considered: [SnMe$_2$(cit)H], [SnMe$_2$(cit)]$^-$, [SnMe$_2$(cit)H$_{-1}$]$^{2-}$, [(SnMe$_2$)$_2$(cit)$_2$H$_{-2}$]$^{4-}$, [(SnMe$_2$)$_2$(cit)H$_{-1}$], [(SnMe$_2$)$_2$(cit)H$_{-2}$]$^-$, [(SnMe$_2$)$_2$(cit)]$^+$, and [(SnMe$_2$)$_2$(cit)$_2$H$_{-1}$]$^{3-}$; the first three species were taken as the base model and the other species added in different combinations. The base model alone gave high statistical parameters (SUPERQUAD: $\sigma = 9$ and $\chi^2 = 43$), when refined without adding any other species. The species [(SnMe$_2$)$_2$(cit)$_2$H$_{-2}$]$^{4-}$, found for trivalent hard cations,[33] was always rejected as negative by both SUPERQUAD and MINIQUAD when added to the base model. A dramatic improvement in the statistical parameters (SUPERQUAD: $\sigma = 1.8$ and $\chi^2 = 6$), with respect to the base model, was obtained when processing the data by adding [(SnMe$_2$)$_2$(cit)H$_{-1}$] and [(SnMe$_2$)$_2$(cit)H$_{-2}$]$^-$ to the base model. Neither of these two species alone was able to cause such a significant improvement in the statistical parameters. The stability constant values for the proposed model are reported in Table 3.

Table 4. Stability constants of tripolyphosphate (tpp^{5-}) (L^{5-}) complexes together with protonation constants at 25 °C and $I = 0.1$ mol dm^{-3} (KNO$_3$)

Reaction	log β[a]
$L^{5-} + H^+ \rightleftharpoons HL^{4-}$	7.97(1)[b]
	8.00[c]
	8.06[d]
	8.10[e]
	7.9[f]
	8.73[g]
$L^{5-} + 2H^+ \rightleftharpoons H_2L^{3-}$	13.49(1)[b]
	13.50[c]
	13.49[d]
	13.65[e]
	13.50[f]
	14.73[g]
$L^{5-} + 3H^+ \rightleftharpoons H_3L^{2-}$	15.37(2)[b]
	16.10[f]
	16.88[g]
$[SnMe_2]^{2+} + L^{5-} + 2H^+ \rightleftharpoons [SnMe_2LH_2]^-$	17.67(3)[b]
$[SnMe_2]^{2+} + L^{5-} + H^+ \rightleftharpoons [SnMe_2LH]^{2-}$	15.02(3)[b]
$[SnMe_2]^{2+} + L^{5-} \rightleftharpoons [SnMe_2L]^{3-}$	9.88(1)[b]
$2[SnMe_2]^{2+} + L^{5-} \rightleftharpoons [(SnMe_2)_2L]^-$	16.07(6)[b]
$[SnMe_2]^{2+} + 2L^{5-} \rightleftharpoons [SnMe_2L_2]^{8-}$	12.11(3)[b]

[a] 3σ are given in parentheses. [b] This work. [c] Recommended values (ref. 33; $I = 0.1$ mol dm^{-3} and $T = 25$ °C). [d] Ref. 37; $I = 0.1$ mol dm^{-3} (KCl) and $T = 25$ °C. [e] M. M. Taqui Khan and P. Rabindra Reddy, *J. Inorg. Nucl. Chem.*, 1973, **35**, 179; $I = 0.1$ mol dm^{-3} (KNO$_3$) and $T = 25$ °C. [f] Ref. 35; $I = 0.1$ mol dm^{-3} (NaNO$_3$) and $T = 25$ °C. [g] Ref. 36; $I = 0.1$ mol dm^{-3} (NMe$_4$Cl)$^-$ and $T = 25$ °C.

SnMe$_2$–tpp.—The protonation constants (see Table 4) agree well with the 'recommended' values[33] obtained at $I = 0.1$ mol dm^{-3} and $T = 25$ °C, at least as far as the first and second steps are concerned. No comparison is possible for log K_3^H, since the value reported in ref. 33 was determined using NMe$_4^+$ as background electrolyte. The only value (2.6)[35] reported using a background [Na(NO$_3$)] other than an alkylammonium salt is surprisingly high and cannot be taken into consideration for comparison purposes. In fact this value is higher than (*i*) that determined in NMe$_4^+$ (2.15),[36] (*ii*) that 'recommended' in NMe$_4^+$,[33] and (*iii*) even that 'recommended' at zero ionic strength.[33] Indeed, log K^H values determined using alkylammonium salts as background electrolytes tend to be greater than those obtained using alkali-metal ion nitrates, owing to the weak complexing of alkali-metal ions (K$^+$ and Na$^+$ mainly) by tripolyphosphate.[37,38]

Various combinations of the following species were considered: [(SnMe$_2$)$_2$(tpp)H], [SnMe$_2$(tpp)H$_2$]$^-$, [SnMe$_2$(tpp)H]$^{2-}$, [SnMe$_2$(tpp)]$^{3-}$, [(SnMe$_2$)$_2$(tpp)]$^-$, [SnMe$_2$(tpp)$_2$]$^{8-}$, and [SnMe$_2$(tpp)H$_{-1}$]$^{4-}$. It was impossible to begin to reproduce the experimental data without simultaneously taking into account [SnMe$_2$(tpp)H]$^{2-}$, [SnMe$_2$(tpp)]$^{3-}$, and [(SnMe$_2$)$_2$(tpp)]$^-$ (which will be referred to as the base model). Neglecting one of these species gave, in some instances, $\sigma = 10$ and $\chi^2 = 120$ (when refining the data with SUPERQUAD), thus leaving no doubt as to their existence. In the low pH region, *i.e.*, pH < 4, however, the introduction of [SnMe$_2$(tpp)H$_2$]$^-$,

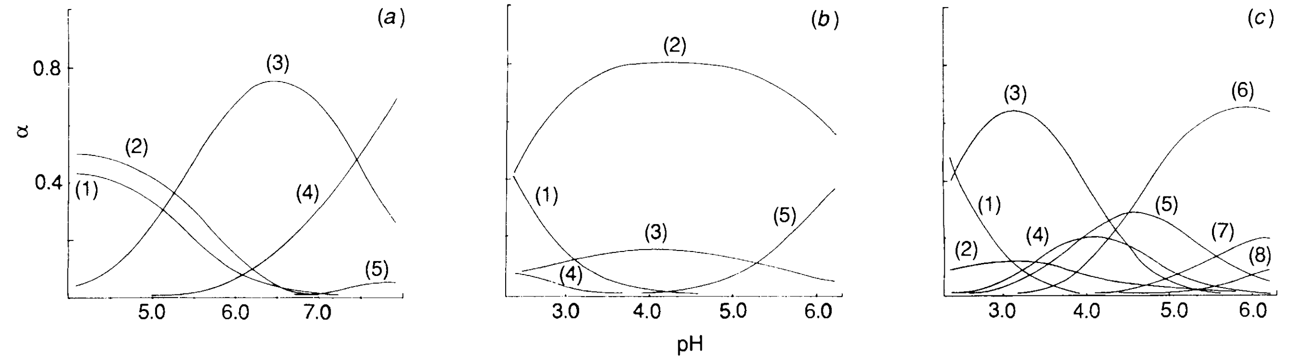

Figure. Species distribution diagrams for the $SnMe_2$–ttp, –nta, and –cit systems. (*a*) $[SnMe_2{}^{2+}] = [tpp^{5-}] = 4 \times 10^{-3}$ mol dm^{-3}; (1), $[SnMe_2(tpp)H]^{2-}$; (2), $[(SnMe_2)_2(tpp)]^-$; (3), $[SnMe_2(tpp)]^{3-}$; (4), $[SnMe_2(OH)_2]$; (5), $[SnMe_2(tpp)_2]^{8-}$. (*b*) $[SnMe_2{}^{2+}] = [nta^{3-}] = 4 \times 10^{-3}$ mol dm^{-3}; (1), free central ion; (2), $[SnMe_2(nta)]^-$; (3), $[SnMe_2(OH)]^+$; (4), $[SnMe_2(nta)H]$; (5), $[SnMe_2(OH)_2]$. (*c*) $[SnMe_2{}^{2+}] = [cit^{3-}] = 4 \times 10^{-3}$ mol dm^{-3}; (1), free central ion; (2), $[SnMe_2(OH)]^+$; (3), $[SnMe_2(cit)H]$; (4), $[(SnMe_2)_2(cit)H_{-1}]$; (5), $[SnMe_2(cit)]^-$; (6), $[(SnMe_2)_2(cit)H_{-2}]^-$; (7), $[SnMe_2(cit)H_{-1}]^{2-}$; (8), $[SnMe_2(OH)_2]$

Table 5. Stability constants of nitrilotriacetate (nta^{3-}) (L^{3-}) complexes together with protonation constants at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Reaction	log β[a]
$L^{3-} + H^+ \rightleftharpoons HL^{2-}$	9.66(2)[b] 9.71[c] 9.71[d] 9.73[e] 9.73[f] 9.65[g]
$L^{3-} + 2H^+ \rightleftharpoons H_2L^-$	12.12(1)[a] 12.20[c] 12.18[d] 12.22[e] 12.22[f] 12.13[g]
$L^{3-} + 3H^+ \rightleftharpoons H_3L$	13.86(2)[b] 14.06[c] 13.89[d] 14.11[e] 13.97[g]
$[SnMe_2]^{2+} + L^{3-} + H^+ \rightleftharpoons SnMe_2LH$	12.06(6)[b]
$[SnMe_2]^{2+} + L^{3-} \rightleftharpoons [SnMe_2L]^-$	10.38(3)[b]

[a] 3σ are given in parentheses. [b] This work. [c] Ref. 39; $I = 0.1$ mol dm^{-3} (KNO_3 or KCl) and $T = 20$ °C. [d] H. M. Irving, M. G. Miles, and L. D. Pettit, *Anal. Chim. Acta*, 1967, **38**, 475; $I = 0.1$ mol dm^{-3} (KCl) and $T = 20$ °C. [e] G. Schwarzenbach, H. Ackermann, and P. Ruckstuhl, *Helv. Chim. Acta*, 1949, **32**, 1175; $I = 0.1$ mol dm^{-3} (KCl) and $T = 20$ °C. [f] W. A. E. McBryde and J. L. McCourt, *J. Inorg. Nucl. Chem.*, 1973, **35**, 4193; $I = 0.1$ mol dm^{-3} (KNO_3) and $T = 25$ °C. [g] Ref. 40; $I = 0.1$ mol dm^{-3} (KNO_3) and $T = 25$ °C.

while leaving the values obtained for the base model above pH 4 virtually unaltered, improved the statistical parameters (both σ and χ^2 by a factor of *ca.* 8) quite significantly.

In neutral or alkaline regions (up to pH 8) a minor species, $[SnMe_2(tpp)_2]^{8-}$, was necessary to fit the experimental data and avoid 'systematic' differences between calculated and experimental values. Although this species never exceeds 15% of the total $[SnMe_2]^{2+}$, its introduction in the final model caused a greater than two-fold improvement of the statistical parameters. However, the 'best' model selected by using SUPERQUAD was also verified over the entire pH range by using MINIQUAD.

The 'best' model and the related stability constant values are listed in Table 4.

$SnMe_2$–nta.—Stability constants of nta complexes have been reviewed by Anderegg.[39] Unfortunately, Anderegg 'recommends' values for protonation constants at 20 °C only. The values 'recommended' by Martell and Smith[33] at 25 °C and $I = 0.1$ mol dm^{-3} virtually coincide with our values (see Table 5), as far as the first and second protonation steps are concerned. Our values of log K_1^H and log K_2^H also virtually coincide with those reported by Harris and Martell.[40] Our value for log K_3^H is lower than the 'recommended' value (1.9).[33] The reasons for this discrepancy are not understood. One reason may lie in the low percentage (20%) of species formed in the pH range investigated in the present study. We are inclined to believe that our value is the more reliable. In fact it would be rather surprising that a ligand, which has a tendency to form complexes with K^+ [38,39] would give the same log K_3^H value (1.9) in both KNO_3 and $NMe_4{}^+$ as reported in ref. 33.

For the $SnMe_2$–nta system the following species and combinations thereof were considered: $[SnMe_2(nta)H]$, $[SnMe_2(nta)_2H]^{3-}$, $[SnMe_2(nta)]^-$, $[SnMe_2(nta)_2]^{4-}$, and $[SnMe_2(nta)H_{-1}]^{2-}$. The experimental data points were ($\sigma = 0.9$ and $\chi^2 = 10$) fitted satisfactorily by the species $[SnMe_2(nta)H]$ and $[SnMe_2(nta)]^-$; the other species were either rejected $\{[SnMe_2(nta)_2H]^{3-}\}$ by the computer program or caused a marked worsening $\{[SnMe_2(nta)H_{-1}]^{2-}, [SnMe_2(nta)_2]^{4-}\}$ of the statistical parameters. However, even when not rejected, always less than 5% formed and therefore these species were not included in the final model reported in Table 5.

Given the discrepancy observed for log K_3^H, we also recalculated the stability constants for the species shown in Table 5 with the acidity constants recommended by Martell and Smith.[33] As predicted, whilst log β for the main species (1:1) remains virtually unaltered (10.40), the stability constant for the protonated species so obtained (11.98) changes by 0.08 log units, thus showing that the value used for log K_3^H has little influence.

Conclusion

There is good evidence to suggest that organotin compounds ultimately degrade in the environment to produce harmless inorganic forms of tin. However two major questions still remain unanswered: (*i*) how much organotin is mobilized from sediments, in biomethylation; (*ii*) how much and, more importantly, in which form, organotin is kept in solution as the result of interaction with sequestering agents.

The latter point and the lack of speciation of organotin compounds in aqueous solution, has been highlighted recently.[41] We stress that it is not the total amount so much as the species that are formed in solution that ultimately determine the fate and toxicity of organotin compounds.

Obviously, the species present depend upon the ligands that dimethyltin(IV) encounters as well as the pH. This concept is illustrated by the Figure. All three ligands are capable of complexing considerable amounts of organotin(IV) (for simplicity, species present at concentration levels lower than 5% are not reported). In doing so, they compete effectively with the hydrolytic forms of dimethyltin(IV) that would eventually transform into inorganic forms of tin. Tripolyphosphate [Figure (*a*)] exerts its maximum action, under the conditions investigated, up to pH 6.5, whereas nta [Figure (*b*)] competes most effectively up to pH 6. Citrate [Figure (*c*)] is able to sequester dimethyltin(IV) over a large range of pH, by forming various species; even in the proximity of the neutral region, the complexes with citrate still predominate over the hydrolytic forms of $[SnMe_2]^{2+}$. It is clear therefore that studies performed on a per-weight or on a total concentration of dimethyltin(IV) basis may be meaningless and are, however, misleading if the species that are formed with the sequestering agents present as buffers, as in the case of laboratory toxicity experiments, or as waste chemicals (in natural or waste waters), are not taken into account.

Acknowledgements

We thank the Consiglio Nazionale delle Ricerche (Rome) for partial support.

References

1 'Organometallic compounds in the environment,' ed. P. J. Craig, Longmans, London, 1986, ch. 4.
2 H. E. Guard, A. B. Cobet, and W. M. Coleman, *Science*, 1981, **213**, 770.
3 L. E. Hallas, J. C. Means, and J. J. Cooney, *Science*, 1982, **215**, 1505.
4 Y. K. Chau, P. T. S. Wong, O. Kramar, and G. E. Bengert, 'Proceedings of the International Conference on Heavy Metals in the Environment (Amsterdam),' ed. W. H. O. Ernst, CEP Consultants, Edinburgh, 1981.
5 J-A. Jackson, W. R. Blair, F. E. Brinkman, and W. P. Iverson, *Environ. Sci. Technol.*, 1982, **16**, 110.
6 W. P. Ridley, L. J. Dizikes, and J. M. Wood, *Science*, 1977, **197**, 329.
7 Y-T. Fanchiang, W. P. Ridley, and J. M. Wood, *ACS Symp. Ser.*, 1978, **82**, 59.
8 J. M. Wood, *Naturwissenschaften*, 1975, **62**, 357.
9 J. M. Wood and Y-T. Fanchiang, in 'Proceedings of the Third European Symposium on Vitamin B_{12} and Intrinsic Factors (Zurich),' ed. B. Zagalak, W. F. de Gruiter, Berlin and New York, 1979, ch. 3, p. 539.
10 P. J. Craig, in 'Handbook of Environmental Chemistry,' ed. O. Hutzinger, Springer, Berlin, Heidelberg, 1980, part A, vol. 1, p. 169.
11 P. J. Craig, in 'Comprehensive Organometallic Chemistry,' eds. E. W. Abel, F. G. A. Stone, and G. Wilkinson, Pergamon, Oxford, 1982, vol. 2, p. 979.
12 P. J. Craig, in 'Pollution: Causes, Effects and Control,' ed. R. M. Harrison, Royal Society of Chemistry, London, 1983, p. 277.
13 P. J. Craig, in 'Pollution: Causes, Effects and Control,' ed. R. M. Harrison, Royal Society of Chemistry, London, 1983, ch. 1.
14 A. J. Crowe, P. J. Smith, and G. Atassi, *Chem. Biol. Interact.*, 1980, **32**, 171.
15 F. Huber and R. Barbieri, in 'Tin as a vital nutrient,' ed. N. F. Cardarelli, CRC Press, Boca Raton, 1986, p. 175.
16 M. Gielen, in 'Tin as a vital nutrient,' ed. N. F. Cardarelli, CRC Press, Boca Raton, 1986, p. 169.
17 J. S. Thayer, 'Organometallic Compounds and Living Organisms,' Academic Press, Orlando, 1984.
18 M. Yamaguchi, K. Sugii, and S. Okada, *J. Toxicol. Sci. Jpn.*, 1981, **5**, 238.
19 V. L. Narayanan, in 'Structure-activity relationships of antitumor agents,' eds. D. N. Reinhoudt, T. A. Connors, H. M. Pinedo, and K. W. van de Poll, Martinus Nijhoff, The Hague, 1983, p. 5.
20 A. K. Saxena and F. Huber, *Coord. Chem. Rev.*, 1989, **95**, 109.
21 'The Importance of Chemical Speciation in Environmental Processes,' eds. M. Bernhard, F. E. Brinkman, and P. Sadler, Springer, Berlin, 1986.
22 G. Arena, A. Gianguzza, L. Pellerito, R. Purrello, and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1989, 773.
23 G. Arena, A. Gianguzza, S. Musumeci, L. Pellerito, R. Purrello, and E. Rizzarelli, *J. Chem. Soc., Dalton Trans.*, 1990, 2603.
24 A. E. Martell, *Pure Appl. Chem.*, 1975, **44**, 1.
25 O. Quimby, *J. Phys. Chem.*, 1954, **58**, 603.
26 G. Arena and V. Cucinotta, *Inorg. Chim. Acta*, 1981, **52**, 275.
27 G. Arena, C. Rigano, E. Rizzarelli, and S. Sammartano, *Talanta*, 1979, **26**, 1.
28 P. Gans, A. Vacca, and A. Sabatini, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
29 P. Gans, A. Vacca, and A. Sabatini, *Inorg. Chim. Acta*, 1978, **18**, 237.
30 A. Vacca, A. Sabatini, and M. A. Cristina, *Coord. Chem. Rev.*, 1972, **8**, 45.
31 R. Maggiore, S. Musumeci, and S. Sammartano, *Talanta*, 1976, **23**, 43.
32 S. Ahrland, *Struct. Bonding (Berlin)*, 1968, **5**, 118.
33 A. E. Martell and R. M. Smith, 'Critical Stability Constants,' First Supplement, Plenum Press, New York, 1982, vol. 5.
34 P. G. Daniele, G. Ostacoli, and A. Vanni, *Ann. Chim. (Rome)*, 1975, **65**, 465.
35 A. Johannson and E. Wamminen, *Talanta*, 1963, **10**, 769.
36 J. I. Watters, E. D. Loughran, and S. M. Lambert, *J. Am. Chem. Soc.*, 1956, **78**, 4855.
37 H. Ellison and A. E. Martell, *J. Inorg. Nucl. Chem.*, 1964, **26**, 1555.
38 P. G. Daniele, C. Rigano, and S. Sammartano, *Anal. Chem.*, 1985, **57**, 2956.
39 G. Anderegg, *Pure Appl. Chem.*, 1982, **54**, 2693.
40 W. R. Harris and A. E. Martell, *Inorg. Chem.*, 1976, **15**, 713 and refs. therein.
41 J. A. J. Thompson, M. G. Sheffer, R. C. Pierce, Y. K. Chau, J. J. Cooney, W. R. Cullen, and R. J. Maguire, 'Organotin Compounds in the Aquatic Environment,' National Research Council of Canada, Ottawa, 1985, no. 22494.

Received 27*th March* 1990; *Paper* 0/01322F