Interactions of the Trimethyltin(IV) Cation with Carboxylic Acids, Amino Acids, and Related Ligands

Michael J. Hynes* and Maire O'Dowd
Chemistry Department, University College, Galway, Ireland

The interactions of the trimethyltin(IV) cation, $[Sn(CH_3)_3(H_2O)_2]^+$, with water, acetic, oxalic, malonic, succinic, tartaric, and citric acids, 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione, pyridine, 2,2′-bipyridyl, pentane-2,4-dione, glycine, aspartic acid, histidine, 2-aminoethanethiol, cysteine, 2-mercaptoethanol, penicillamine, mercaptosuccinic acid, British Anti Lewisite (2,3-dimercaptopropan-1-ol), glutathione, orthophosphate, adenosine 5′-monophosphate, inosine 5′-monophosphate, and pyrophosphate were investigated at 25 °C and ionic strength 0.3 mol dm^{-3} ($NaClO_4$) using the potentiometric technique. The proton formation constants of the ligands have been determined and the compositions and log β values of the complexes formed with the trimethyltin(IV) cation are also reported.

Although the complexes of triorganotin(IV) species have been extensively investigated in the solid state[1,2] relatively little is known about their solution chemistry, in particular their aqueous chemistry. In general, the relatively weak acceptor strength of SnR_3X species (R = alkyl, X = halide or pseudohalide) favours an increase in co-ordination number to five to form a trigonal-bipyramidal complex in which the three organic groups are situated in the equatorial plane. With potentially bidentate ligands the triorganotin(IV) halides still form five-co-ordinate adducts by utilizing only one of the donor groups. The triorganotin(IV) thiocyanates are stronger Lewis acids than the halides and there is evidence that they form six-co-ordinate adducts with bidentate ligands.[3]

In aqueous solution $Sn(CH_3)_3Cl$ dissociates and aquates to form $[Sn(CH_3)_3(H_2O)_2]^+$. The structure of this ion is believed to be trigonal bipyramidal with the three CH_3 groups in equatorial positions and the two water molecules in axial positions.[4,5] Addition of sodium tetraphenylborate to aqueous solutions of trimethyltin chloride results in the precipitation of a species of composition $[Sn(CH_3)_3(H_2O)_2]BPh_4$.[6] The trimethyltin(IV) cation undergoes hydrolysis in aqueous solution according to equation (1) with log $\beta_{01-1} = -6.4$.[7]

$$[Sn(CH_3)_3(H_2O)_2]^+ + H_2O \longrightarrow Sn(CH_3)_3(H_2O)(OH) + H_3O^+ \ (\beta_{01-1}) \quad (1)$$

Although the degree of hydrolysis is considerably less than that of its dimethyltin counterpart (log $\beta_{01-1} = -3.2$)[8] it is considerably greater that for $[Ni(H_2O)_6]^{2+}$ (log β_{01-1} −9.86).[9] This suggests that the trimethyltin(IV) cation might have a relatively high affinity for ligands containing oxygen donor atoms.

The use of triorganotin(IV) compounds of the type SnR_3X as selective biocides and pesticides has risen rapidly in recent years. All trimethyl- and triethyl-tin(IV) derivatives have high mammalian toxicity.[10–12] Indeed the toxicity of tetraorganotin(IV) compounds, SnR_4, also appears to be due to trialkyltin(IV) species which are produced as a result of dealkylation *in vivo*.[10–14] The biological activity of toxic triorganotin(IV) compounds is believed to be due to their ability to bind to certain proteins,[13,15,16] and although the exact nature of the binding sites is unknown, it has been demonstrated that in cat haemoglobin, cysteine and histidine residues are associated with the trialkyltin moiety.[16,17]

We have recently begun a systematic investigation of the equilibria and kinetics of the reactions of trialkyltin(IV) and dialkyltin(IV) species with a variety of small ligands, particularly those of biological interest such as amino acids and nucleotides. The main objectives of the present researches were to establish the stoicheiometries and stability constants of the reactions of the trimethyltin(IV) cation with a range of ligands having a variety of donor atoms. The effect of varying the donor atom on the stability constants was also investigated.

The recent problems associated with the use of tributyltin(IV)-based 'antifouling' marine paints have given additional relevance to the present work.[18–21] Tributyltin(IV)-based antifouling paints were introduced in the late sixties and became widely used in the seventies by the end of which they dominated the market. Recent research has shown however that tributytin(IV)-based compounds are probably the most toxic pesticides deliberately introduced into the marine environment. A variety of organisms are harmed when exposed to concentrations of a fraction of one part per billion on a continual basis. Such concentrations have been shown to be present in U.K. coastal waters. The use of tributyltin(IV)-based antifoulings on pleasure craft has been banned in France and restrictions regarding their use have been introduced in the U.K.

Experimental

All ligands were reagent grade and most were used as purchased. Mercaptoacetic acid was purified by distillation under vacuum. Pentane-2,4-dione was purified by distillation. Solutions of the ligands were standardised by titration with sodium hydroxide. End-points were determined using an iterative computer program based on the method of Gran and Johansson.[22]

Trimethyltin chloride (Aldrich) was freshly prepared by subliming at low temperature. The chloride content of the sublimed product agreed with the calculated value.

Titration curves were recorded using a Radiometer TTT2 titrator equipped with an ABU13 autoburette and an SBR3 titrigraph. The titration data were subsequently digitized. Titrations were carried out in 100-cm^3 Radiometer titration vessels which had been sealed into purpose-built glass or brass jackets through which water could be circulated. The temperature was maintained at 25.0 (±0.1) °C by circulating water through the jacket of the titration vessel. All titrations were carried out under an atmosphere of nitrogen. This was particularly important in the case of the sulphur-containing ligands as they were air sensitive. Titrations were usually carried out over a period of *ca.* 1—2 h. Longer periods resulted in no change in the raw data.

The ionic strength was adjusted to 0.3 mol dm^{-3} using sodium perchlorate. The initial titrations were carried out at an ionic

strength of 0.1 mol dm^{-3}, but due to relatively weak complexing by the trimethyltin(IV) cation with many ligands and the resulting high concentrations of ligand and metal necessary, this proved unsatisfactory.

Sodium hydroxide solutions were freed from carbonate by passing them over a column of Zerolit FF in the hydroxide form.

The ligand and metal concentrations were in the range 0.005—0.050 mol dm^{-3}. The sodium hydroxide concentrations was adjusted to suit both the particular concentration of ligand and metal being used and the burette of the ABU13 autoburette. (Burettes of capacity 1.0 and 2.5 cm^3 were used.) Titrations were usually carried out up to a pH of not more than 6.5, above this pH appreciable hydrolysis of the trimethyltin(IV) cation takes place. Where necessary, acid was added to uncover the lower portion of the titration curves. A minimum of three titrations, each having a different ligand-to-metal ratio were carried out for each ligand system. In most cases the ligand-to-metal ratio was varied in the range 0.5:1—3:1. The hydrolysis constant of the trimethyltin(IV) cation was determined by titrating three solutions of the metal each containing a different total metal concentration with sodium hydroxide over the pH range 4.5—7.5.

The potassium chloride in the reference cell of the electrode system was replaced by 3 mol dm^{-3} sodium chloride solution. The linearity of the electrode system was established using pH 4, 7, and 9 buffers. The electrodes were calibrated to read hydrogen-ion concentration directly and not activity in the following manner. A series of solutions of acids, adjusted to the appropriate ionic strength with $NaClO_4$, were titrated with standard sodium hydroxide solution. The end-points of these titrations were determined using the method of Gran.[23] Thus the hydrogen-ion concentration at any point on the titration curve could be calculated and hence the pH meter reading could be directly related to the hydrogen-ion concentration.

Initially most of the stability constant refinement was carried out using MINIQUAD-75.[24,25] However, while the work was in progress, details of a new improved computer program for stability constant refinement were announced and all the titration data were subsequently reprocessed using SUPERQUAD.[26] Selection of the 'best' model is considerably simpler using SUPERQUAD as it has a certain amount of model selection and rejection criteria built in. In addition a number of titrations were evaluated using SCOGS.[27] The deviations quoted are those calculated by the computer programs. No refinement of either the reactant or burette concentrations was carried out, *i.e.* the SUPERQUAD facility for refining 'dangerous' parameters was not utilized.

Additionally, plots of the formation function Z[28] against pL, the negative logarithm of the free ligand concentration, were calculated for a number of systems. If solely mononuclear, non-protonated and non-hydroxo complex species were present, and if hydrolyzed forms of the free metal are absent, plots of Z against pL at different total concentrations of ligand and metal should be superimposable. In this event Z represents the average number of ligands bound per metal and is independent of the stoicheiometries of the complex species. In the present system however, due to the presence of the hydrolyzed form of $[Sn(CH_3)_3(H_2O)_2]^+$ at pH values above 5, these conditions were never realized. However comparison of the theoretical plots of Z against pL calculated from the theoretical titre values (as calculated using SCOGS) with the experimental data was very useful in determining which of a number of potential models was the best. This was particularly so in the earlier stages of the work when SUPERQUAD was not available. A computer program was written to carry out the necessary calculations and produce the resultant plots.

Nuclear magnetic resonance spectra were recorded on a JEOL JNM-GX 270 spectrometer.

Results and Discussion

The Table lists the stability constants determined in the present investigation together with their standard deviations as output by SUPERQUAD.

The hydrolysis constant of $[Sn(CH_3)_3(H_2O)_2]^+$ (M) was required as input for each of the ligand systems investigated. Consequently it was determined under the experimental conditions of this work (25 °C and 0.3 mol dm^{-3} $NaClO_4$). A value of -6.26 (± 0.01) was obtained for log β_{01-1}. This is in fair agreement with the value of -6.4 previously obtained in 2 mol dm^{-3} KCl.[7]

In the case of acetic acid, only one species having a ligand-to-metal ratio of 1:1 was found irrespective of the ligand-to-metal ratio at which the titration was carried out. There was no evidence for the formation of oxygen-bridged oligomers or other polymeric species. This is consistent with i.r. studies carried out in chloroform, where it was shown that polymerization of trimethyltin acetate did not occur at concentrations lower than 0.07 mol dm^{-3}.[29] Association would be expected to be less in the more polar aqueous medium.

In the case of the malonic acid (H_2L) system MINIQUAD refined two models. Model 1 contained the species [M(HL)] and $[ML]^-$ while model 2 contained $[M_2L]$. However from a consideration of the sums of the squares of the residuals and the standard deviations, it was apparent that model 2 was better and an examination of the Z against pL plots supported this assignment. Using SUPERQUAD, model 2 was clearly the best. The absence of an [M(HL)] species in any appreciable concentration is probably due to the presence of intramolecular hydrogen bonding in the monoanion as is reflected in the lower pK_1 of malonic acid compared to the pK of acetic acid. This is in contrast to succinic acid where a model containing both [M(HL)] and $[M_2L]$ refined. Although tartaric acid may be regarded as having four ionizable hydrogen atoms, it appears (see later) that the pK values of the OH groups are much too high to allow them to be displaced by the trimethyltin(IV) cation. Thus the ligand is regarded as having two ionizable protons (H_2L). The stability of the $[M_2L]$ complex is lower for tartaric acid than for either malonic or succinic acids. This is probably due to stabilization of the carboxylate groups *via* intramolecular hydrogen bonding to the adjacent hydroxyl group.

In the case of citric acid which has three carboxyl groups, a wide range of complexes is possible. Two models were refined using SUPERQUAD and the values obtained are reasonable when compared with the values obtained for other carboxylic acids.

No interactions could be discerned between the trimethyltin(IV) cation and either pentane-2,4-dione or glycine. In the case of the former ligand it would appear that the oxygen is too basic towards hydrogen to be replaced by the trimethyltin(IV) cation. Additionally, the fact that only one co-ordination site on the tin species is utilized would reduce the tendency towards complexing with β-diketones. A similar situation exists for glycine and the proton on the $-NH_3^+$ group is not replaced on co-ordination to the tin species. The absence of a carboxylate bonded complex is probably due to the extensive intramolecular hydrogen bonding in the zwitterion. In fact it would appear that α-amino acids having only $-NH_2$ and carbonyl donor groups do not form complexes to any appreciable extent with the trimethyltin(IV) cation in aqueous solution. Formation of the $[M(HL)]^+$ species when histidine is the ligand (HL) obviously displaces the proton from the secondary amino nitrogen in the imidazole ring and the $-NH_2$ group remains protonated. Under the experimental conditions, the [ML] species is present in only relatively small concentrations.

In the case of ligands having a sulphur donor atom co-ordination appears to take place almost exclusively *via* this

Table. Log β values for species $L_pM_qH_r$ at 25 °C and ionic strength 0.3 mol dm^{-3} ($NaClO_4$). L = Ligand (number of ionizable protons varies), M = $[Sn(CH_3)_3(H_2O)_2]^+$; K_{MHL} = [M(HL)]/[M][HL] = β_{111}/β_{101}

Ligand	p	q	r	log β [a]	log K_{MHL}
H_2O	0	1	−1	6.26 (±0.01)	
Acetic acid	1	0	1	4.59 (±0.01)	
	1	1	0	1.25 (±0.01)	
Oxalic acid	1	0	1	3.74 (±0.01)	
	1	1	0	1.49 (±0.03)	
Malonic acid	1	0	1	5.19 (±0.01)	
	1	0	2	7.79 (±0.01)	
	1	2	0	3.37 (±0.01)	
Succinic acid	1	0	1	5.25 (±0.01)	
	1	0	2	9.27 (±0.01)	
	1	1	1	6.69 (±0.03)	1.44
	1	2	0	3.93 (±0.04)	
Tartaric acid	1	0	1	3.86 (±0.01)	
	1	0	2	6.59 (±0.01)	
	1	2	0	3.07 (±0.04)	
Citric acid	1	0	1	5.66 (±0.01)	
	1	0	2	9.94 (±0.01)	
	1	0	3	12.74 (±0.01)	
Model 1	1	1	1	7.09 (±0.05)	1.43
	1	1	0	1.79 (±0.04)	
Model 2	1	1	1	6.93 (±0.04)	1.27
	1	2	0	3.86 (±0.03)	
Htftbd [b]	1	0	1	6.26 (±0.01)	
	1	1	0	2.05 (±0.03)	
Pyridine	1	0	1	5.41 (±0.01)	
	1	1	0	1.13 (±0.06)	
2,2′-Bipyridyl	1	0	1	4.51 (±0.01)	
	Little or no interaction with metal species				
Pentane-2,4-dione	1	0	1	8.75 (±0.01)	
	Little or no interaction with metal species				
Glycine	1	0	1	9.78 (±0.01)	
	1	0	2	11.92 (±0.01)	
	Little or no interaction with metal species				
Aspartic acid	1	0	1	10.03 (±0.01)	
	1	0	2	13.93 (±0.02)	
	1	1	1	11.58 (±0.02)	1.55
Histidine [c]	1	0	1	9.34	
	1	0	2	15.65	
	1	1	1	11.10 (±0.01)	1.76
	1	1	0	4.87 (±0.02)	
2-Aminoethanethiol	1	0	1	10.92 (±0.02)	
	1	0	2	19.32 (±0.02)	
	1	1	1	15.52 (±0.01)	4.60
Cysteine [c]	1	0	1	10.54 (±0.01)	
	1	0	2	18.97 (±0.01)	
	1	1	1	15.21 (±0.01)	4.67
Mercaptoacetic acid	1	0	1	10.08 (±0.01)	
	1	0	2	13.44 (±0.02)	
	1	1	0	6.35 (±0.01)	
2-Mercaptoethanol	1	0	1	9.64 (±0.01)	
	1	1	0	5.94 (±0.01)	
Penicillamine	1	0	1	10.86 (±0.02)	
	1	0	2	18.94 (±0.02)	
	1	1	1	14.50 (±0.01)	3.64
Mercaptosuccinic acid	1	0	1	10.27 (±0.01)	
	1	0	2	14.76 (±0.01)	
	1	0	3	17.79 (±0.01)	
	1	1	0	5.98 (±0.03)	
	1	2	0	8.48 (±0.08)	
British Anti Lewisite [d]	1	0	1	10.62 (±0.02)	
	1	0	2	19.37 (±0.03)	
	1	1	1	16.22 (±0.01)	5.60
	1	1	0	8.50 (±0.04)	
Glutathione	1	0	1	9.78 (±0.03)	
	1	0	2	18.60 (±0.03)	
	1	0	3	22.18 (±0.03)	
	1	1	1	14.17 (±0.05)	4.39
$Na[H_2PO_4]$	1	0	1	6.92 (±0.01)	
	1	1	1	8.20 (±0.05)	1.35
	1	1	0	3.53 (±0.02)	
	1	2	0	5.32 (±0.03)	
Adenosine 5′-monophosphate	1	0	1	6.33 (±0.02)	
	1	0	2	10.23 (±0.03)	
	1	1	1	7.92 (±0.03)	1.59
	1	1	0	3.31 (±0.02)	
	1	2	0	4.73 (±0.09)	
Inosine 5′-monophosphate	1	0	1	8.89 (±0.02)	
	1	0	2	14.80 (±0.02)	
	1	1	1	11.41 (±0.06)	2.52
	1	2	1	14.26 (±0.05)	
$P_2O_7^{4-}$	1	0	1	8.09 (±0.03)	
	1	0	2	13.91 (±0.04)	
	1	1	1	10.80 (±0.02)	2.71

[a] A. E. Martell and L. G. Sillen, 'Stability Constants of Metal-ion Complexes,' Special Publication, No. 17, The Chemical Society, London, 1964. [b] 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione. [c] M. J. Hynes and M. O'Dowd, *Biochem. Soc. Trans.*, 1985, **13**, 490. [d] 2,3-Dimercaptopropan-1-ol.

atom. This is clearly illustrated by the fact that K_{MHL} for both 2-aminoethanethiol and cysteine are very similar in magnitude, the $-NH_2$ group remains protonated in both instances.

The interactions of the trimethyltin(IV) cation with phosphate ligands are also rather weak. In the case of adenosine 5′-diphosphate (ADP) and adenosine 5′-triphosphate (ATP) the titration data refine rather poorly and have not been included. Models containing a large number of species refine. The reasons for this are two-fold. First, only one co-ordination site on the trimethyltin(IV) cation is normally utilized and secondly these ligands have a very large number of co-ordination sites. Thus there are potentially a large number of complex species and if a number of these are in equilibrium, it is unlikely that they would be adequately refined. The fact that the interactions are rather weak makes the situation even more difficult. From a consideration of the formation constants obtained using orthophosphate ($H_2PO_4^-$) and adenosine 5′-monophosphate (AMP), it would appear that in the case of the latter only the phosphate moiety is involved in co-ordination. This was confirmed by n.m.r. It has been demonstrated[30] that n.m.r. can be used to determine the binding positions in AMP and related ligands. If the metal species is paramagnetic, the H^2 and H^8 peaks of the purine base broaden if the metal is interacting with the base moiety. This was observed to occur on the addition of copper(II). If the metal species is diamagnetic these peaks are observed to shift. In the present investigation, no shift of either the H^2or H^8 hydrogens was observed, confirming that the interactions were limited to the phosphate portion of the ligand. Interestingly, the stability of the [M(HL)] complex with inosine 5′-monophosphate (H_2L) is higher than that of the complex with adenosine 5′-monophosphate. A similar order has been observed for the interaction of nickel(II) with the protonated forms of the ligands.[31]

Of the ligands studied, the most stable complexes are formed with those having sulphur donor atoms. For these ligands the stability order is: British Anti Lewisite > mercaptoacetic acid > 2-mercaptoethanol > cysteine ≃ 2-aminoethanethiol > penicillamine. This order cannot be directly compared to that obtained for other metal ions due to the fact that in the case of most other metal ions two or more donor atoms are involved

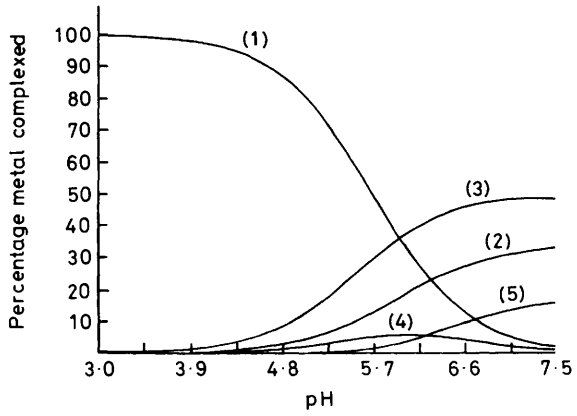

Figure. COMICS[32] computer distribution of free metal, hydrolyzed metal, and complex species with pH for a mixture of trimethyltin(IV), cysteine (H_2cys) and histidine (Hhis). The total concentration of each component is 0.01 mol dm^{-3}; (1) free metal, (2) [M(OH)], (3) [M(Hcys)], (4) $[M(Hhis)]^+$, (5) [M(his)]; M = $[Sn(CH_3)_3(H_2O)_2]^+$

in complex formation. The low stability of the penicillamine complex is rather surprising and may be due to steric factors. At physiological pH (7.4) it is apparent that 2-mercaptoethanol and mercaptoacetic acid are considerably more efficient at binding the trimethyltin(IV) cation than penicillamine. Indeed it is only in the case of the former two ligands that complex formation predominates over the formation of the hydrolysis products at pH values greater than 7.

Previous studies have suggested that in cat haemoglobin, triethyltin is bound at both cysteine and histidine residues.[16,17] The present work clearly supports the plausability of this suggestion and in view of the results obtained with glycine, it is highly unlikely that the tin moiety would be bound at any other location. It is possible however that the bonding order would be different in the hydrophobic cavity in the protein and that competition from the hydrolysis products would be greatly reduced. The Figure shows a species distribution curve for the trimethyltin complexes of both cysteine and histidine. These were calculated using the COMICS program.[32] Most of the unhydrolyzed tin is present as the cysteine complex.

In general it appears that in aqueous solutions only one of the two co-ordinated water molecules on the trimethyltin(IV) cation is replaced by other ligands, irrespective of the donor atom involved. Under the experimental conditions used, there is no evidence for oligomerization. This is in marked contrast to the situation in the solid state where extensive bridging frequently occurs.[1,2] However, a recent crystallographic investigation reports an example of a unidentate carboxylate group (3-indolyl acetate) bonded to a triorganotin(IV) moiety.[33]

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