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Dismutation of Trimethyltin Species Bound to Oxo-ligand Complexes

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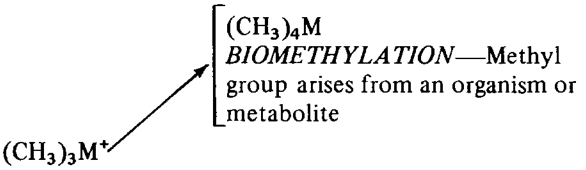
Introduction

In recent years there have been a number of reports of the methylation in the environment of group IV metals and their inorganic complexes to both partially and fully methylated species [1–4]. Interest in biomethylation derives from the increased toxicity of the methyl metal compounds, compared to the inorganic species from which they derive [5, 6]. For a multivalent metal such as tin, the process of biomethylation may be considered essentially as two stages, (i) the attachment of an initial methyl group to the inorganic metal substrate by biochemical or other mechanisms and (ii) the addition of subsequent methyl groups from the same or other sources to the monomethyl metal species. In the case of tin the monomethyl species are stable in water and methylation is not in principle an improbable process. Recently a number of methyl tin compounds have been detected in the natural aqueous environment and in quantities which suggest they derive from biomethylation of non methyl tin compounds used for example in agriculture, as plastics additives and in anti-fouling paints *etc.* [7, 8]. There is small scale use of methyl tin compounds as additives to PVC potable water pipes, particularly in North America [9], but the quantities seem insufficient and too localised to account for the widespread detection of methyl tins in the environment.

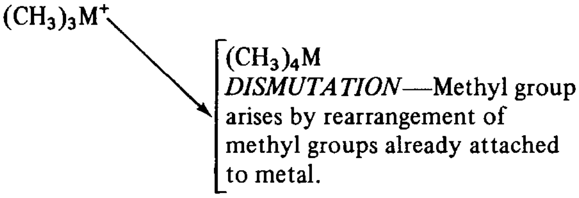
For both tin and lead there is uncertainty at present as to the mechanism of the final conversion of the trimethyl to the volatile tetramethyl species in the biomethylation process. This may arise through further methylation by microorganisms or perhaps by abiotic dismutation catalysed by the natural ligands to which the trimethyl species is bound, *viz.*



$(CH_3)_4M$

BIOMETHYLATION—Methyl group arises from an organism or metabolite

$(CH_3)_3M^+$



$(CH_3)_3M^+$

$(CH_3)_4M$

DISMUTATION—Methyl group arises by rearrangement of methyl groups already attached to metal.

There are reports in the literature which suggest variously that conversion from tri- to tetramethyl species is (i) a combination of the two processes above [10] or (ii) purely a dismutation process [11]. Recently, through the use of deuterium isotopes we have demonstrated for tin that the latter, abiotic, process is apparently the only one occurring in a natural sediment environment [12]. For some years we have been interested in the acceleration of abiotic dismutation by complexation with natural sulphide ligands, modelling the conditions to be found in the natural environment. For example $CH_3H_g^+$ and $(CH_3)_3Sn^+$ may be converted to the fully methylated products by the following reactions, *viz.* [13–16]:

$$2CH_3H_g^+ + S^{2-} \longrightarrow (CH_3H_g)_2S \longrightarrow (CH_3)_2H_g + H_gS$$

$$6(CH_3)_3Sn^+ + 3S^{2-} \longrightarrow 3[(CH_3)_3Sn]_2S \longrightarrow 3(CH_3)_4Sn + [(CH_3)_2SnS]_3$$

These reactions have been demonstrated under model environmental conditions and are of importance because the fully methylated species are volatile and allow transport of the metal over long distances in the biosphere. In the present work we present results from an investigation of the dismutation process for trimethyl tin species in the presence of the naturally occurring ligand tropolone [17] as a model system for oxo ligand complexation in the natural environment.

Experimental

It has been reported [18, 19] that tropolone, T, (2-hydroxycyclohepta-2,4,6-triene-1-one) forms complexes with tri- di- and monoorganotin compounds and it has been used in their extraction from aqueous solutions for analytical purposes. The present work is an investigation of a proposed dismutation for $(CH_3)_3SnT$ to $(CH_3)_4Sn$ and $(CH_3)_2SnT_2$ under mild conditions, *viz.*

$$2(CH_3)_3SnT \xrightarrow{h\nu,\ \Delta} (CH_3)_4Sn + (CH_3)_2SnT_2$$

thereby generating a volatile transportable tin species.

The starting material $(CH_3)_3SnT$ has been reported in a thesis [20] but was incompletely characterised.

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TABLE I. Methyltin Tropolone Compounds. Physical Data.

Mass Spectra[a]

$(CH_3)_3SnT$[b]		$(CH_3)_2SnT_2$[b]	
m/e	Assignment	m/e	Assignment
271[c]	$(CH_3)_2Sn^+T$	377[c]	$CH_3Sn^+T_2$
241	Sn^+T	362	Sn^+T_2
165	$(CH_3)_3Sn^+$	271	$(CH_3)_2Sn^+T$
150	$(CH_3)_2Sn^+$	241	Sn^+T
135	$(CH_3)Sn^+$	135	$(CH_3)Sn^+$
120	Sn^+	122	HT^+
		120	Sn^+

Nmr Spectra[d]

	δ(H–T)	δ(CH_3)	J($SnCH_3$) Hz[e]	Ratio of integrated peak areas H–T:CH_3
$(CH_3)_3SnT$	7.30m	0.42	66	0.55
$(CH_3)_2SnT_2$	7.36m	0.56	72	(I) 1.65; (II) 1.66
T	7.30m			

[a] VG micromass 16-F mass spectrometer. [b] m/e values quoted for the $_{50}Sn^{120}$ isotope but isotopic ratios for each cluster containing tin were correct. [c] No peaks higher than this were observed. [d] 60 MHz, Fourier Transform, $CDCl_3$ solvent and TMS reference. [e] $_{50}Sn^{117}$ and $_{50}Sn^{119}$ couplings with methyl protons not resolvable. m = multiplet.

In the present study it has been prepared from $(CH_3)_3SnOC_2H_5$, synthesised from the reaction (25 °C) of $(CH_3)_3SnCl$ (4.0 g, 0.02 mol) and $NaOC_2H_5$ (0.23 g Na, 0.02 mol in 20 cm^3 of C_2H_5OH). The NaCl was filtered off and the excess solvent removed by rotary evaporation at room temperature. To a solution of tropolone (1.83 g, 0.01 mol) in diethyl ether (50 cm^3) an equivalent amount of $(CH_3)_3SnOC_2H_5$ was added (3.15 g, 6.015 mol). The reactants were refluxed under nitrogen atmosphere at 34 °C. Following this most of the solvent was removed by rotary evaporation at room temperature leaving an oily residue consisting of $(CH_3)_3SnT$ and ethanol. Removal of ethanol by the same method at room temperature yielded a yellow solid $(CH_3)_3SnT$ (3.27 g, 76.2% yield, m.p. 52.5–54 °C, lit. 54.5–55.5 °C [20]). This product was not recrystallised because $(CH_3)_2SnT_2$ only would be produced but it was characterised for the first time by ir, nmr and ms (see Table I). The infrared spectrum showed that no free tropolone was present in the product. The nmr spectrum showed a chemical shift of 0.42 with a Sn–H coupling constant of 66 Hz for the methyl protons. The integral ratios of tropolone ring protons to methyl protons confirm the presence of $(CH_3)_3SnT$ rather than $(CH_3)_2SnT_2$. The mass spectrum also confirms that the product was $(CH_3)_3SnT$ (Table I).

For the investigation of the dismutation reaction, separate $(CH_3)_3SnT$ samples were placed in sealed vials (1.43 g, 0.005 mol) and exposed to: (I) daylight simulation radiation (>360 nm) for 24 h or (II) heating above the melting point (60 °C, 0.5 h). The head space gases were then analysed using gas chromatography with comparison with an authentic sample of $(CH_3)_4Sn$ (flame ionisation detector, all-glass column 1.8 m, 6 mm, packed with 3% SP-2100 on Supelcoport 80/100 mesh; N_2 flow 40 cm^3/min^{-1}, air flow 120 cm^3/min^{-1}, H_2 flow 20 cm^3 min^{-1}; injector temp. 100 °C, column temp. 50 °C, detector temp. 100 °C; retention time 4.95 min). $(CH_3)_4Sn$ was also identified using gc–ms.

Peaks clustered around m/e 120, 135, 150, 165 and 180 (corresponding to Sn^+, CH_3Sn^+, $(CH_3)_2Sn^+$, $(CH_3)_3Sn^+$ fragment ions) confirmed the generation of $(CH_3)_4Sn$. The isotopic ratios were as expected. The solid products from reactions I and II (*i.e.* $(CH_3)_2SnT_2$) were each separately recrystallised from hot diethyl ether and dried (m.p. 181 °C for (I), 181 °C for (II), lit. 184.5–186 °C [21], 180–181 °C [22]) and analysed by elemental analysis, ir, nmr and ms. Yields of $(CH_3)_2SnT_2$ were for (I) 70.5% and (II) 80.0%. Elemental analysis calculated for $(CH_3)_2SnT_2$; C, 48.98; H, 4.08. Found for (I) C, 49.10; H, 3.95 and for (II) C, 49.05; H, 4.05. The infrared spectra of (I) and (II) showed the absence of free tropolone. The nmr spectrum showed a chemical shift of 0.56 δ and Sn–H coupling constant of 72 Hz (lit. 0.56 δ, J = 72.4–75.8 Hz [21]; 0.97 δ, J = 67.9 Hz using C_6D_6 as solvent [22]). The integral ratios of tropolone ring protons to methyl protons confirm the presence of $(CH_3)_2SnT_2$. The mass spectra of (I) and (II) also confirm the production of $(CH_3)_2SnT_2$.

Results and Discussion

Benzene-tropolone solutions have been employed in extracting organotin species from dilute aqueous samples prior to analysis, and the complexes formed were considered to be stable. However this method was observed to extract poorly from known samples of $(CH_3)_3Sn^+$ species (0–30% extraction yield) [19, 23]. From the present work the known instability via dismutation of the $(CH_3)_3SnT$ complex appears to be responsible. We do not recommend tropolone extractions for this reason; in addition the production of di- from trimethyltin species in this extraction will exaggerate the amount of the former in environmental samples. Although $(CH_3)_3SnT$ was sufficiently stable for characterisation, dismutation does occur and the complex is not stable at room temperature for periods longer than a few hours. For this reason no elemental analysis was carried out on the $(CH_3)_3SnT$ complex.

The dismutation process may be encouraged by the fact that the hexacoordinated tin configuration in $(CH_3)_2SnT_2$ is more favourable than pentacoordinated configuration in $(CH_3)_3SnT$. It should also be noted that the ease of formation of $(CH_3)_3Sn\cdot$ radicals must be a driving force for the reaction [16].

In this work $(CH_3)_3SnT$ has been fully characterised for the first time and it has been demonstrated that $(CH_3)_3Sn^+$ species (present in the environment because of human activities or environmental methylation) in the proximity of oxygen containing ligands *e.g.* naturally occurring tropolone, will dismutate under mild conditions to give $(CH_3)_2SnT_2$ and $(CH_3)_4Sn$. The latter compound is hydrophobic and volatile, and although less toxic than the $(CH_3)_3Sn^+$ species [6] is subject to greater transport possibilities in the environment, and in addition decays by $(CH_3)_3Sn^+$ formation.

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