A Novel Synthesis of Methyltin Tri-iodide with Environmental Implications

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Methyltin tri-iodide and methylsulphur species are produced by an unusual heterogeneous reaction between MeI and SnS in water at room temperature which may bear on ubiquitous occurrence of methylstannanes in the environment.

We describe a convenient, one step synthesis of $MeSnI_3$ from the heterogeneous oxidative methylation of SnS by MeI in H_2O under mild anaerobic or aerobic conditions. The monomethyltin(IV) is the only organotin species obtained by this process, whereas both Me_4Sn[1] and Me_2SnI_2[2] have been reported as sole products of the reaction between tin metal and MeI. Previously reported syntheses of $MeSnI_3$ require high temperatures, catalysts, or multi-step procedures.[3]

The work leading to the novel synthesis described herein was prompted by our interest in environmental metal transformations and methylation in sediments by biogenic molecules. We have found that MeI reacts with bulk metals to form soluble metal species, and also with sulphide-containing sediments or authentic metal sulphides to produce methylated sulphur species.[4,5] SnS is likely to be a predominant tin mineral in anoxic, sulphidic sediments.[6] MeI is a ubiquitous biogenic molecule in seawater[7—9] and in the lower atmosphere,[7,9,10] and is found in highest concentrations near areas of marine biomass productivity. This communication shows that tin bound in a supposedly refractory, reduced mineral sulphide such as SnS (m.p. 882 °C) can be readily oxidized and methylated by a small biogenic molecule. Such processes, though expected to occur widely in nature only at very low concentrations, we find to be rapid, hence a substantial new extracellular pathway may exist to explain the global distribution of environmental methylstannanes.[11]

SnS was prepared by mixing 0.3 mol $SnCl_2$ in 50 ml H_2O with 0.5 mol $Na_2S{\cdot}9H_2O$ in 200 ml H_2O. The brown precipitate was washed several times with deionized water to remove soluble species and dried to give SnS as a fine black powder (yield 73%). A satisfactory elemental analysis was obtained.

For the bulk synthesis of $MeSnI_3$, 1.0 g SnS and 3.3 ml MeI were suspended in 100 ml H_2O. After shaking at 60 °C for 24 h in the dark all the SnS had reacted. Water was removed *in vacuo* at 60 °C and light yellow needles of pure $MeSnI_3$ (elemental analysis) were obtained by extracting the residue with cyclohexane and drying at 50 °C under a stream of nitrogen [yield, 33%; m.p. 86 °C (lit.[12] 85 °C)].

The 400 MHz ^1H n.m.r. spectrum of the heterogeneous

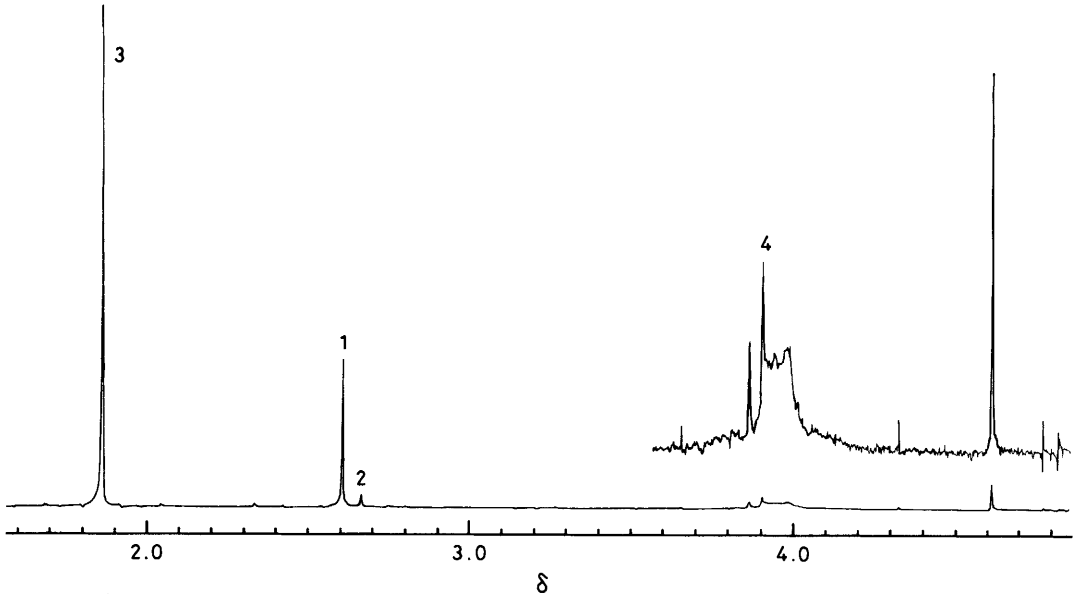

Figure 1. Typical 400 MHz ^1H n.m.r. spectrum of the heterogeneous reaction of a SnS suspension (3 mg) in 0.33 ml MeI and 0.5 ml D_2O at 27 °C after 9 days. Inset shows a 16× magnification of the upfield portion of the spectrum. Peaks for MeI (1), Me_2S (2), Me_3S^+ ion (3), and a methyltin species (4) are detected. Residual H_2O resonance is at 0.0 p.p.m.

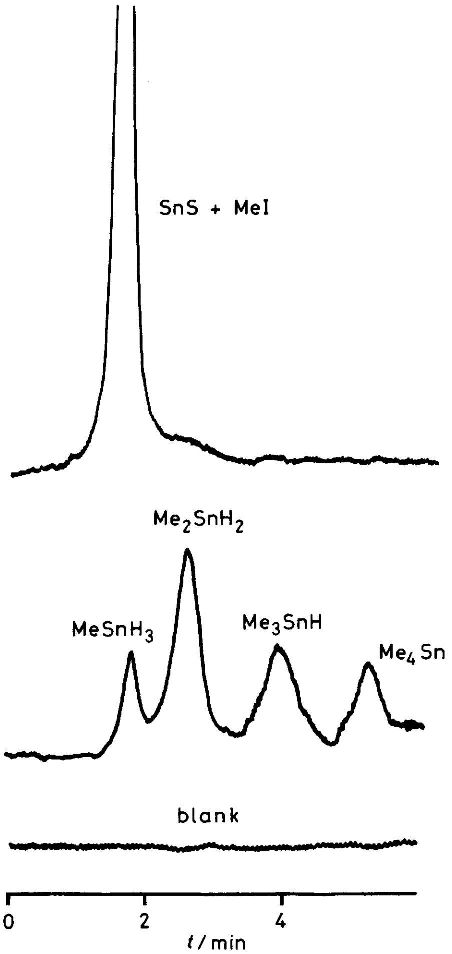

Figure 2. Tin-selective p.t.-g.c.-f.p.d. chromatograms compare (middle) authentic peaks for methylstannes (1 ng as tin) with (top) tin-containing products [following treatment with sodium borohydride (ref. 14)] in the aqueous reaction solution of SnS and MeI after 24 h at 60 °C with shaking. An analytical blank (bottom) is also shown.

reaction of particulate SnS and MeI in D_2O under N_2 is shown in Figure 1. The products trimethylsulphonium iodide and methyltin tri-iodide were identified by comparisons of ^1H n.m.r. chemical shifts of the commercially available materials as analogous chlorides in iodide solutions, and also from the literature,[13] with $MeSnI_3$. The reaction stoicheiometry which accounts for the products observed in the n.m.r. experiments is given in equation (1). After nine days, the reaction solution was further analysed for inorganic tin as well as mono-, di-, tri- and tetra-methyltins by tin-selective purge and trap flame photomeric gas chromatography (p.t.-g.c.-f.p.d.).[14] Monomethyltin was the only organotin species observed. The same results were obtained under an air atmosphere at room temperature or with the accelerated reaction of MeI with SnS at 60 °C after 24 h (Figure 2).

$$\mathrm{SnS} + 4\,\mathrm{MeI} \longrightarrow \mathrm{MeSnI_3} + \mathrm{Me_3SI} \qquad (1)$$

We examined several other inorganic tin compounds for reactions with methyl iodide under mild, aerobic conditions. In these experiments, 200 mg each of $SnCl_2$, SnS, or tin metal, or 500 mg SnI_2, were mixed separately with 0.05 ml MeI in 2 ml H_2O in gas-tight vials. After one week at room temperature in the dark, no Me_4Sn was observed (detection limit, 36 p.p.b. in gas phase) in the headspace above any of the reactions. Again, monomethyltin was the only organotin species detected in the solution following reaction of SnS. Smaller amounts of monomethyltin were detected in the homogeneous reaction with $SnCl_2$, and of mono- and di-methyltin in the heterogeneous reaction with SnI_2. Consequently, we believe that both of these reactions proceeded at a slower rate than that with SnS. Moreover, no methyltins were detected in the attempted heterogeneous reaction between SnS_2 or tin powder with aqueous MeI under these mild conditions.

Tin(II) sulphide is thus favourably activated toward oxidative methylation by MeI when compared to the halogenated or elemental forms of tin. A kinetic study of the homogeneous reaction between Na_2S and MeI was conducted in an attempt to isolate and discern the role of sulphur in the heterogeneous reaction with SnS. The reaction was followed by ^1H n.m.r. spectroscopy, and the reaction scheme [equations (2)—(4)] is

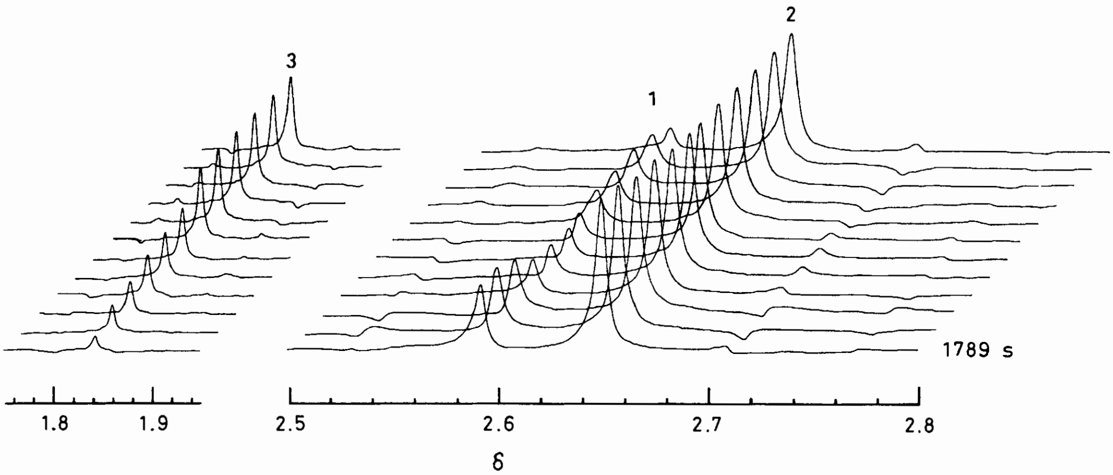

Figure 3. Successive 400 MHz ^{1}H n.m.r. spectra of the homogeneous reaction of 0.054 M MeI (1) with 0.020 M Na_2S to form Me_2S (2) and Me_3S^+ (3) in D_2O at 27 °C are shown at 1800 s intervals. Residual H_2O resonance is at 0.0 p.p.m.

consistent with the observed products. At concentrations of MeI less than or equal to twice the molar concentration of sulphide, Me_2S is the only product observed. With molar concentrations of MeI greater than twice that of sulphide, MeI reacts with Me_2S to produce $Me_3S^+{}_{aq}$ as shown in Figure 3.

$$S^{2-} + MeI \longrightarrow MeS^- + I^- \quad (2)$$

$$MeS^- + MeI \longrightarrow Me_2S + I^- \quad (3)$$

$$Me_2S + MeI \longrightarrow Me_3S^+ + I^- \quad (4)$$

The heterogeneous reaction between SnS and MeI is likely to proceed by initial methylation of sulphur in the (–Sn–S–Sn–S–) backbone slowly to release a tin-containing intermediate into solution.[4,5] In view of the rapid methylation of dissolved sulphide species to Me_2S by MeI [equations (2) and (3)], such an intermediate would be quickly methylated to produce Me_2S, which in turn can react with the excess of MeI present to form the observed product Me_3SI [equation (4)]. Further work is necessary to determine if the oxidative methylation of the remaining Sn^{II} moiety by MeI to form $MeSn^{3+}{}_{aq}$ precedes, coincides with, or follows Sn–S bond cleavage, though it is clear that this is a preferred pathway to Me–Sn bond formation. For example, reliance here on aquated tin(II) ion as the chief reactive intermediate is unreasonable since only low concentrations of the free ion are possible in the excess of iodide present [equation (1)]. Dissolved or heterogeneous $SnCl_2$ or SnI_2, respectively, are also not reasonable nucleophilic, reactive intermediates with MeI, in the absence of sulphide, in view of their slower production of mono- and di-methyltin species. However, with benzene rather than H_2O as the solvent, the rate of $MeSnI_3$ formation from SnS was only 10% of that in water, suggesting that oxidative methylation of tin(II) strongly depended on aquated intermediates. Ethyl iodide also reacted in water with SnS to form $EtSnI_3$ but at a much slower rate, consistent with S_N2 alkylation in protic solvents.[15]

The absence of H_2S and MeSH in the headspace gases (g.c.–f.p.d. analysis) suggests that little or no acidolysis occurs during the extended solubilization of SnS by MeI. We consequently see little prospect that H_2S-initiated Me–Sn bond redistributions subsequent to reaction (1) form volatile Me_4Sn *via* an intermediate like cyclic $(Me_2SnS)_3$, as has been proposed for the ubiquitous environmental trimethyltin moiety.[1] The absence of tetramethyltin in the gaseous products of any reaction reported here implies that any environmental abiotic pathways between mono- and per-methylated tin compounds remain to be discovered.

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References

1 P. J. Craig and S. Rapsomanikis, *J. Chem. Soc., Chem. Commun.*, 1982, 114.
2 T. Murphy and R. C. Poller, *J. Organomet. Chem. Library*, 1979, **9**, 189.
3 'Gmelin Handbuch der Anorganischen Chemie, Tin,' Part 10, Springer-Verlag, Berlin, 1981, pp. 135—138.
4 J. S. Thayer, G. J. Olson, and F. E. Brinckman, *Environ. Sci. Technol.*, in the press.
5 J. S. Thayer, T. W. Brueggemeyer, G. J. Olson, and F. E. Brinckman, *Am. Chem. Soc., Div. Environ. Chem., Prepr.*, 1983, **23**, 476.
6 P. Ramdohr, *Z. Kristallogr. Mineral.*, 1935, **92**, 186.
7 J. E. Lovelock, *Nature*, 1975, **256**, 193.
8 J. E. Lovelock, R. J. Maggs, and R. J. Wade, *Nature*, 1973, **241**, 194.
9 R. A. Rasmussen, M. A. K. Khalil, R. Gunawardena, and S. D. Hoyt, *J. Geophys. Res.*, 1982, **87**, 3086.
10 H. B. Singh, L. J. Salas, and R. E. Stiles, *Environ. Sci. Technol.*, 1982, **16**, 872.
11 J. T. Byrd and M. O. Andreae, *Science*, 1983, **218**, 565.
12 A. Tchakirian, M. Lesbre, and M. Lewinsohn, *C. R. Acad. Sci.*, 1936, **202**, 138.
13 S. J. Blunden, P. J. Smith, and D. G. Gillies, *Inorg. Chim. Acta*, 1982, **60**, 105.
14 J. A. Jackson, W. R. Blair, F. E. Brinckman, and W. P. Iverson, *Environ. Sci. Technol.*, 1982, **16**, 110.
15 J. Koivurinta, A. Kyllonen, L. Leinonen, K. Valaste, and J. Koskikallio, *Finn. Chem. Lett.*, 1974, 239.