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Methylated antimony(V) compounds: synthesis, hydride generation properties and implications for aquatic speciation

Matthew Dodd,* Stephen L Grundy,*† Kenneth J Reimer* and William R Cullen‡

*Department of Chemistry, Royal Roads Military College, FMO Victoria, British Columbia, Canada V0S 1B0 and ‡Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6

Reports in the literature that the compounds $MeSb(O)(OH)_2$ and $Me_2Sb(O)OH$ are present in marine and fresh-waters need to be re-examined. The results of several synthetic strategies suggest that these methylantimony(V) compounds are either environmentally inaccessible or polymeric in nature. Pure samples of various di- and trimethylated antimony(V) species were prepared and found to undergo molecular rearrangement reactions when subjected to hydride generation procedures typically used for aquatic speciation.

Keywords: Dimethylantimony, trimethylantimony, analysis, hydride generation, aquatic speciation, GCAA

INTRODUCTION

Antimony is present in the aquatic environment at the ng dm^{-3} (ng litre^{-1}) range as a result of authogenic input from weathering processes. However, levels can be substantially elevated (mg dm^{-3}) in the proximity of anthropogenic sources, e.g. mines and smelters. The US Environmental Protection Agency lists antimony and its compounds as priority pollutants. Studies on arsenic in the marine environment have highlighted the need for careful speciation before toxicity effects can be assessed;[1] it can be expected that antimony impact will also be species-dependent.

Standard methods for assaying biomethylated arsenic compounds in the ng dm^{-3} range have been developed,[2] and involve reaction of water-soluble arsenic(V) and arsenic (III) compounds with sodium borohydride ($NaBH_4$) to produce volatile arsenic(III) compounds (hydride generation, HG) which can be separated by gas chromatography (GC) and detected by atomic absorption spectroscopy (AA). This hydride generation technology (HG GC AA) relies on the availability of methylated arsenic(V) compounds, particularly trimethylarsine oxide (Me_3AsO), dimethylarsinic acid [$Me_2As(O)OH$] and methylarsonic acid [$MeAs(O)(OH)_2$] as standards. Preparative papers have been published for trimethylstibine oxide (Me_3SbO)[3] and dimethylstibinic acid ($Me_2Sb(O)(OH)$.[4] In addition, GC retention times have been quoted in hydride generation studies[5] using these compounds as precursors along with methylstibonic acid [$MeSb(O)(OH)_2$] and this information has been used in antimony speciation studies in the marine environment.[6, 7]

We, and others,[8] have had great difficulty accessing methylated antimony(V) compounds and it now appears that the original synthetic strategy did not produce pure materials (Meinema, H, personal communication). In this paper we present our results in the pursuit of methylated antimony(V) compounds and preliminary hydride generation studies of the compounds obtained. Implications for aquatic antimony cycling are discussed.

EXPERIMENTAL

General

All manipulations of air-sensitive materials were carried out using standard inert-atmosphere handling techniques and all solvents were dried and distilled under dry dinitrogen gas before use. ^1H NMR and IR spectra were recorded on a

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† Author to whom correspondence should be addressed.

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Bruker WM360 and Pye–Unicam SP3-200, respectively. Microanalyses were carried out by Canadian Microanalytical Services, Vancouver, BC, or the University of British Columbia Microanalytical Service. The syntheses of Me_3SbX_2 and Me_2SbX ($X = Cl$, Br) have been described elsewhere.[9]

Preparation of compounds

$Me_3Sb(OH)_2$ (1)

A suspension of Me_3SbCl_2 (1.00 g, 4.21 mmol) in water (20 mL) was treated dropwise with a solution of KBH_4 (0.50 g, 9.3 mmol) in water (10 cm^3). The gas evolved (Me_3Sb) was collected in a liquid nitrogen trap as the addition progressed. The trapped Me_3Sb was dissolved in acetone (30 cm^3) and treated with red HgO (1.0 g, 4.6 mmol). The mixture was stirred for 16 h and the resulting grey suspension filtered through Celite and the volume reduced to 10 cm^3. A white powder was obtained on evaporation of this solution and the product was isolated as small colourless needles (0.43 g, 51 %) by recrystallization from acetone.

IR (KBr), cm^{-1}: 3500 br, 1660 m, 1565 m. ^1H NMR ($(CD_3)_2CO$): δ 1.00 (s). Analysis: Calcd for $C_3H_{11}SbO_2$: C, 17.94: H, 5.52. Found: C, 18.21: H, 5.52 %.

$Me_3Sb(O_2CCF_3)_2$ (2)

A suspension of $Me_3Sb(OH)_2$ (100 mg, 0.498 mmol) in $CHCl_3$ (1 cm^3) was treated with CF_3CO_2H (0.1 cm^3). The resulting colourless solution was evaporated to dryness and the residue dissolved in diethyl ether. The product was obtained as colourless needles (150 mg, 76 %, m.p. 104 °C) by slow evaporation.

IR (KBr), cm^{-1}: 1720 s, 1404 m, 1190 br, 790 m, 729 m. ^1H NMR ($CDCl_3$): δ 1.23 (s). Analysis: Calcd for $C_7H_9SbO_4F_6$: C, 21.40; H, 2.31. Found: C, 21.33; H, 2.41 %.

Crystal structure of $Me_3Sb(O_2CCF_3)_2$

A suitable crystal was obtained by slow vacuum sublimation at 60 °C. The data were collected using a Picker four-circle diffractometer. The unit cell contained two distinct molecules differing in orientation of the two trifluoroacetate groups. The structure was solved by Patterson methods using SHELXS-86[10] and refined using SHELX-76[11] to $R = 0.08$. All atoms with the exception of fluorine were refined anisotropically.

$Me_3Sb(O_2H)_2$ (3)

A suspension of Me_3SbCl_2(1.00 g, 4.21 mmol) in water (20 cm^3) was treated dropwise with a solution of KBH_4 (0.50 g, 9.3 mmol) in water (10 cm^3). The gas evolved (Me_3Sb) was collected in a liquid nitrogen trap as the addition progressed. The trapped Me_3Sb was dissolved in diethyl ether (20 cm^3) and treated with hydrogen peroxide solution (10 cm^3, 30 %) in water accompanied by rapid stirring. The diethyl ether was separated and the aqueous solution washed with more diethyl ether (2 × 20 cm^3). The resulting solution was heated to 80 °C and the water removed under vacuum. The product was obtained as a white powder (0.55 g, 56 %) after drying under moderate vacuum (8 mm Hg) for 16 h. **Warning: This compound exploded spontaneously when heated with a heat-gun under vacuum to remove water; the explosion was severe and damaging. Under no circumstances should the suggested drying temperature of 80 °C be exceeded.**

IR (KBr), cm^{-1}; 3150 br, 2912 m, 2755 m, 1380 m, 829 s, 730 m. ^1H NMR (D_2O): δ 1.64 (s). Analysis: Calcd for $C_3H_{11}SbO_4$: C, 15.47; H, 4.76. Found: C, 15.39; H, 4.67 %.

$Me_2SbCl(O_2H)_2$ (4)

A solution of Me_2SbCl, prepared by thermolysis of Me_3SbCl_2 (1.00) g, 4.21 mmol) and trap-to-trap distillation,[10] in acetone (20 cm^3), was treated with a solution of hydrogen peroxide (2 cm^3, 30 %), water (5 cm^3) and acetone (20 cm^3) and refluxed for 16 h. The solution was evaporated to dryness and the residue washed with diethyl ether (2 × 20 cm^3), acetone (2 × 20 cm^3) and hot (80 °C) water. The product was obtained as a white microcrystalline solid (0.20 g, 19 %) after slow evaporation of the aqueous extract.

IR (KBr), cm^{-1}: 3400 br, 3025 m, 2925 m, 854 m, 839 s, 730 m, 630 m. ^1H NMR ($CDCl_3/CF_3CO_2H$): δ 2.60 (s). Analysis: Calcd for $C_2H_8SbO_4Cl$: C, 9.48: H, 3.18. Found: C, 9.48; H, 2.86 %.

$Me_2SbBr(O_2H)_2$ (5)

In a procedure similar to that outlined above, Me_3SbBr_2 was used instead of Me_3SbCl_2. The product was recovered as a white powder (0.20 g, 16 %).

IR (KBr), cm^{-1}: 3400 br, 3030 m, 2930 m, 850 m, 840 s, 718 m, 620 m. ^1H NMR

($CDCl_3/CF_3CO_2H$); δ 2.60 (s). Analysis: Calcd for $C_2H_8SbO_4Br$: C, 8.07; H, 2.71. Found: C, 8.24; H, 2.37 %.

($(Me_2Sb)_2O$ (6))

A solution of Me_2SbCl, made by thermolysis of Me_3SbCl_2 (1.00 g, 4.21 mmol) and trap-to-trap distillation, was treated with a solution of hydrogen peroxide (2 cm^3, 30 %) in acetone (20 cm^3), resulting in the formation of a white precipitate. The suspension was evaporated to dryness and the residue washed with ether (2 × 20 cm^3), acetone (2 × 20 cm^3) and hot methanol (2 × 20 cm^3). The methanolic solution was evaporated to dryness and the residue extracted with $CHCl_3$. The product was obtained as a white microcrystalline solid (0.25 g, 37 %) after slow evaporation of the $CHCl_3$.

IR (KBr), cm^{-1}: 3000 m, 2918 m, 820 m, 765 w, 655 s. ^1H NMR ($CDCl_3$): δ 1.32 (s). Analysis: Calcd for $C_4H_{12}Sb_2O$: C, 15.03; H, 3.78. Found C, 15.50; H, 3.80 %.

Hydride generation analysis

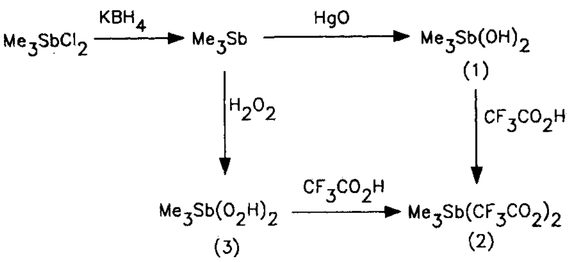
Antimony was detected by atomic absorption spectrometry after gas chromatographic separation of stibines and methylstibines produced by reaction with acidified potassium borohydride (HG GC AA). The apparatus was similar to that developed for arsenic.[12] Andreae and Froelich have suggested that the methylstibenes are produced at mildly acidic pH without addition of iodide, but the indicated reagent volumes were not consistent with the stated pH values. In order to explore the effect of reaction conditions on the observed results, experiments were conducted between pH 1.5 and 6, and in the presence and absence of KI. Briefly, an aliquot of the sample was introduced into a reaction vessel with deionized water (60 cm^3). Appropriate amounts of buffer [tris(hydroxymethyl)aminomethane; pH 6], hydrochloric acid and potassium iodide were then added to the reaction vessel. Slow addition of KBH_4 (6 cm^3, 4 % solution) released stibines from the solution. The stibines were sparged by a helium flow and passed through a lead acetate trap to remove hydrogen sulphide, then through a dry ice–isopropanol trap to remove water, and collected in a Teflon U-tube immersed in liquid nitrogen. The liquid nitrogen trap was removed and the U-tube immersed in a 50 °C water bath. The released stibines were separated on a silinized Porapak-PS (mesh 80–100) column using a Varian Model 3700 gas chromatograph (initial, 50 °C, 1 min; 25 °C min^{-1}; 150 °C, final). The separated stibines were carried into a hydrogen–air flame quartz cuvette held in the light path of an Instrumentation Laboratories 351 atomic absorption spectrometer. Antimony was detected at 217.6 nm and the signal processed by a Hewlett–Packard 3390A integrator. A standard curve was obtained with antimony(V) standard solutions prepared from a 1000 ppm standard stock solution (BDH Chemicals).

For HG GC AA analysis of the antimony compounds, 1 cm^3 of a 10 ppb solution was injected into the reaction vessel for hydride generation.

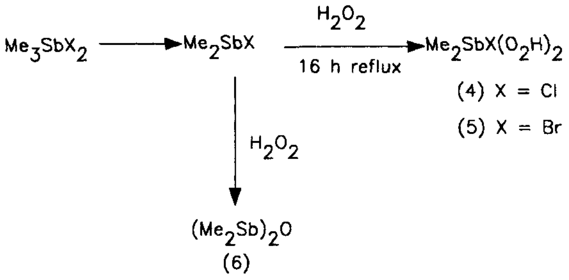
RESULTS AND DISCUSSION

Syntheses

Trimethylarsine oxide (Me_3AsO) can be prepared by the gentle oxidation of Me_3As using HgO or H_2O_2, whereas Me_3SbO has been prepared by the treatment of Me_3SbCl_2 with Ag_2O.[3] Hydrolysis of R_3Sb or R_3SbCl_2 is reported to give oxides, though the products are polymeric. In our study, treatment of Me_3Sb with HgO gave the dihydroxide $Me_3Sb(OH)_2$ (**1**), characterized by a singlet in the ^1H NMR spectrum at δ 1.00; IR and microanalytical data were also consistent with this formulation. However, treatment of Me_3Sb with H_2O_2 gave a new compound isolated as a white powder. This compound was insoluble in organic solvents and **exploded on heating**. A singlet was observed at δ 1.64 ppm in the ^1H NMR spectrum and the microanalytical results suggested a formulation of $Me_3Sb(O_2H)_2$ (**3**), i.e. a dihydroperoxide. The IR spectrum of compound **3** exhibits bands at 730 cm^{-1} and 2755 cm^{-1}, both of which disappear on heating at 80 °C for 18 h under vacuum. The absorption at 2755 cm^{-1} can be attributed to an intramolecular chelate hydrogen bond. The IR spectrum of the product obtained on heating compound **3** exhibits bands at 690 and 625 cm^{-1}; similar bands have been attributed to the Sb_2O_2 structural unit.[13] Indeed, it is known that treatment of triarylstibines with H_2O_2 results in compounds formulated as dimers, $(Ar_3SbO)_2$. In this case it appears that a dihydroperoxide (**3**) is isolated and heating this leads to the formation of $(Me_3SbO)_2$. Treatment of compounds **1** or **3** with trifluoroacetic acid led to the isolation of



Scheme 1



Scheme 2

small colourless needles of the very soluble ditrifluoroacetate, $Me_3Sb(CF_3CO_2)_2$ (**2**), characterized by IR, NMR and microanalytical data (Scheme 1). Crystals of compound **2** suitable for X-ray diffraction were obtained by vacuum sublimation and the molecular structure is presented in Fig. 1. Two distinct molecules were observed in the unit cell; both were trigonal-bipyramidal with the methyl groups occupying the equatorial positions. Molecule 1 is shown in Fig. 1; molecule 2 differed in the orientation of the trifluoroacetate groups. All bond lengths and angles were within normal ranges and will be reported in a subsequent paper.

Dimethylstibinic acid, $Me_2SbO(OH)$, has been reported to be formed by hydrolysis of $Me_2Sb(OMe)_3$[4] or the slow oxidation/hydrolysis of Me_2SbCl.[14] We have been unable to isolate pure compounds from either reaction and have only obtained what appear to be polymeric mixtures. Treatment of Me_2SbCl (purified by trap-to-trap distillation) with H_2O_2 and a 16 h reflux resulted in the isolation of a white powder (see Scheme 2). Analytical data are consistent with formulation as $Me_2SbCl(O_2H)_2$ (**4**), i.e. mirroring the reactivity of Me_3Sb to give compound **3**, the IR spectrum is similar to that of compound **3**, and the ^1H NMR spectrum consists of a singlet at δ 2.60. It should be noted that this compound is very insoluble and the ^1H NMR spectrum was obtained as a $CDCl_3/CF_3CO_2H$ solution, i.e. the singlet probably corresponds to the trifluoroacetate analogue of compound **2**, i.e. $Me_2Sb(CF_3CO_2)_3$. Comparable results were obtained using Me_2SbBr with $Me_2SbBr(O_2H)_2$, (**5**) as the isolated product. If the reflux step in the above procedure was omitted, then the colourless, highly soluble, microcrystalline $(Me_2Sb)_2O$ (**6**) was obtained. In this case, the peroxide is not acting as an oxidant but rather as a base. In an analogous reaction, alkaline hydrolysis of Ph_2SbCl has been reported to give $(Ph_2Sb)_2O$.[15]

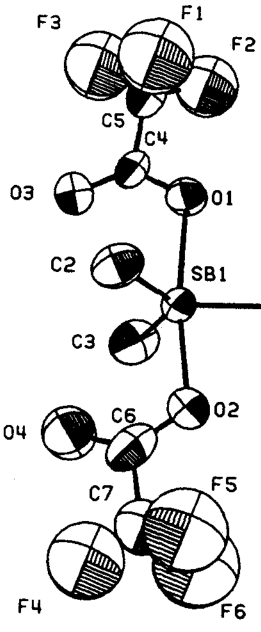


Figure 1 ORTEP diagram showing molecular structure of $Me_3Sb(CF_3CO_2)_2$ (**2**).

Attempts to make *mono*methylated Sb(V) compounds for use in hydride generation studies have been unsuccessful. The preparation of the highly unstable $MeSbH_2$ is possible[8] although this hydride spontaneously decomposes at low temperature under vacuum. Treatment of this hydride with a wide spectrum of oxidants (26 different reagents) has not resulted in the isolation of any pure compounds.[8] We have obtained similar results with attempted oxidation of $MeSbCl_2$. We have been informed (Meinema, H A, personal communication) that $MeSbO(OH)_2$ can be obtained by hydrolysis of $MeSb(OMe)_4$ [made by sequential treatment of $MeSb(NEt_2)_2$ with MeOH, SO_2Cl_2 and NaOMe] but have been unable to repeat this preparation and have only obtained insoluble polymeric products.

Hydride generation

Hydride generation studies were undertaken using very dilute solutions of Me_3SbCl_2, $Me_3Sb(OH)_3$ and $Me_2SbCl(O_2H)_2$. Both Me_3SbCl_2 and $Me_3Sb(OH)_2$ should react cleanly with $NaBH_4$ to give Me_3Sb and after passing the reaction products through a gas chromatograph fitted with an atomic absorption spectrometer detector a single peak should be detected. Similarly $Me_2SbCl(O_2H)_2$ should result in a single peak with somewhat shorter retention time corresponding to Me_2SbH. In fact, all three compounds gave chromatograms containing four peaks (presumably corresponding to SbH_3. $MeSbH_2$, Me_2SbH, and Me_3Sb) under all analytical conditions. The chromatogam for the hydride generation experiment using $Me_3Sb(OH)_2$ is given in Fig. 2. It is known that, on a synthetic scale, reaction of Me_3SbCl_2 with $NaBH_4$ gives Me_3Sb as the principal product.[16] However, under the conditions used here, i.e. those typical of HG GC AA, molecular rearrangement clearly occurs. these results cast some doubt on the ability of the hydride generation technique, in its currently configured form, to clearly distinguish different alkylated compounds of antimony. As a consequence, studies[6,7] that have suggested that antimony speciation in the aquatic environment is similar to that exhibited by arsenic, need to be reviewed in the light of the facts that:

(1) the compounds that are monomeric in arsenic chemistry are inaccessible or polymeric in antimony chemistry; and

(2) the behaviour of methylated antimony compounds to hydride generation is entirely different.

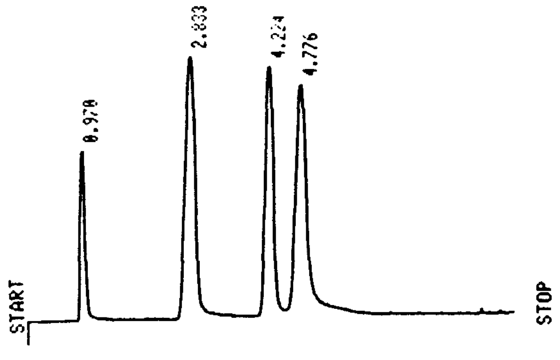


Figure 2 Chromatogram obtained from HG AA of $Me_3Sb(OH)_2$ (in minutes).

It is therefore unrealistic to assume that simple extrapolation from one element to another is possible; aquatic samples giving 'extra' peaks in the HG GC AA chromatogram are likely to be due to other, as yet undetermined, antimony precursors.

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REFERENCES

1. Cullen, W R and Reimer, K J *Chem. Rev.*, 1989, 89: 713
2. Andreae, M O In: *Trace Metals in Seawater*, Wong, C S, Boyle, E, Bruland, K W, Berton, J D and Goldberg, E D (eds), Plenum, New York, 1983, pp 1–19
3. Cremos, G and Zingaro, R A *J. Organomet. Chem.*, 1970, 22: 637
4. Meinema, H A and Noltes, J G *J. Organomet. Chem.*, 1972, 36: 313
5. Andreae, M O, Asmodé, J-F, Foster, P and Van'tdack, L *Anal. Chem.*, 1981, 53: 1766
6. Andreae, M O and Froelich, P N *Tellus*, 1984, 36B: 101
7. Bertine, K K and Lee, D S Antimony content and speciation in the water column and interstitial waters of Saanich Inlet. In: *Trace Metals in Seawater*, Wong, C S, Boyle, E, Bruland, K W, Berton, J D and Goldberg, E D (eds), Plenum, New York, 1983, pp 21–38
8. Rheingold, A L, Choudhury, P and El-Shazley M F *Synth. React. Inorg. Met. Org. Chem.*, 1978, 8: 453
9. Morgan, G T and Davies, G R *Proc. Royal Soc., Ser. A*, 1926, 523
10. Sheldrick, G M In: *Crystallographic Computing 3*, Sheldrick, G M, Kruger, C and Goddard R (eds), Oxford University Press, 1985, pp 175–189
11. Sheldrick, G M *SHELX-76 Program for Crystal Structure Determination*, 1976, Institut für Anorganische Chemie der Universitat Gottingen, Gottingen
12. Reimer, K J and Thompson, J A *J. Biogeochem.*, 1988, 6: 211
13. Westhoff, T, Huber, F, Ruther, R and Preut, H *J. Organomet. Chem.*, 1988, 352: 107
14. Wardell J L In: *Comprehensive Organometallic Chemistry*, Wilkinson, G, Stone, F G A and Abel E W (eds), Pergamon Press, 1982, vol 2, p 700
15. Cullen, W R and Trotter, J *Can J. Chem.*, 1963, 41: 2983
16. Kurosawa, S, Yasuda, K, Taguchi, M, Yamazaki, S, Toda, S, Uehiro, T and Fuiwa, K *Agric. Biol. Chem.*, 1980, 4: 1993