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Unsupported monomeric stibine oxides (R₃SbO) remain undiscovered⁺

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Attempts to investigate the properties and reactivity of the stiboryl moiety ($R_3Sb^+-O^-$ or R_3Sb —O), as in monomeric stibine oxides free of interaction with Lewis acids/bases, led us to conclude that this functional group remains undiscovered. X-ray crystallographic, computational, and spectroscopic data indicate that previously proposed H-bonded stibine oxide adducts Mes₃SbO···HO₃SR are in fact hydroxystibonium salts [Mes₃SbOH][RSO₃].

Pentavalent pnictine oxides (oxo- λ^5 -pnictanes) of the general form $R_3 E = O \leftrightarrow R_3 E^+ - O^-$ (E = N, P, As, Sb, Bi) are of considerable interest to chemists because of the diverse roles that they play across a range of chemical fields. Trimethylamine N-oxide (Me_3NO) has long been used as an oxo transfer reagent in the decarbonylation of transition metal complexes through the loss of CO₂.¹ Triphenylphosphine oxide (Ph₃PO) and triphenylarsine oxide (Ph₃AsO) have been used as ligands for lanthanide ions with applications to catalysis and the reprocessing of nuclear fuels.²⁻⁴ Ph₃PO is perhaps best known as a stable end product of organic syntheses employing the Wittig, Staudinger, and Mitsunobu reactions. Part of the driving force of these successful and robust reactions is the stability of the phosphine oxide, which is intimately related to the nature of the pnictogenoxygen bond. The E-O bonding interaction of pentavalent pnictogen oxides has long been a substrate for interesting discussion, with much of the focus on phosphine oxides.⁵⁻⁸ Although pentavalent phosphine oxides are typically depicted with a phosphorusoxygen double bond (R₃P=O), this bonding is now accepted to be better described as a polar-covalent single bond $(R_3P^+-O^-)$ stabilized by π backdonation from the oxide lone pairs into the P–R σ^* orbitals.^{8,9} Descending the pnictogen family, this E⁺-O⁻ bonding interaction is expected to become less stable because of increased diffuseness of the pnictogen valence orbitals and a consequent reduction in overlap with oxygen-based orbitals. Another phenomenon that attends the increase in atom size as the family is descended is an increased propensity of the pnictogen to expand its coordination sphere. Moreover, the E^+-O^- bond becomes more polarized as E increases in atomic number and decreases in electronegativity, which increases the Lewis acidity of the E(V) center in a pnictine oxide. Alternatively put, the destabilization of the E-O σ bond lowers the energy of the corresponding E-O σ^* orbital that serves as the locus of Lewis acidity. This enhanced Lewis acidity coupled to a capacity for expanded coordination results in a fundamental change in the chemistry of the pnictine oxides down the group.^{6,10-12} For example, treatment of either Ph₃P or Ph₃As with oxidants such as H₂O₂ readily affords the oxides Ph₃PO and Ph₃AsO (Scheme 1a), but "triphenylstibine oxide" is not known to exist as the monomeric Ph₃SbO, despite the use of this structural formula for decades.

A series of experiments demonstrated that oxidation of Ph_3Sb yields five-coordinate dimers or oligomers (Scheme 1b).^{13,14} The increased bulk of the substituents in Mes₃Sb suppresses oligomerization upon oxidation with H_2O_2 , but not expansion of the coordination sphere; the product is the dihydroxystiborane *trans*-Sb(OH)₂Mes₃ (Scheme 1c).



Scheme 1 (a) Oxidation of Ph₃E with H₂O₂ give monomeric Ph₃EO when E = P or As. (b) Oxidation of Ph₃Sb with H₂O₂ affords dimers/polymers. (c) Oxidation of Mes₃Sb with H₂O₂ gives the monomeric stiborane *trans*-Sb(OH)₂Mes₃.

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We were interested in exploring the chemistry of the stiboryl functional group present in monomeric stibine oxides,¹⁵ but careful scrutiny of the literature revealed that these comprise a largely unexplored class of molecules. Lewis acids can disrupt stibine oxide dimers $(R_3SbO)_2$ and stabilize the Lewis-basic oxo unit (Scheme 2a).¹⁶ Alternatively, rigid scaffolds can poise a Lewis acid near a stibine to intercept a newly-formed stibine oxide before it can oligomerize (Scheme 2b).¹⁷ In both of these cases, an interaction of the stiboryl group with a Lewis acid appears to be essential to stabilize it.

To our knowledge, Huber and co-workers report the most, if not only, compelling case for an independently stable monomeric stibine oxide, trimesitylstibine oxide (Mes₃SbO). Treatment of trans-Sb(OH)₂Mes₃ with either benzenesulfonic acid or trifluoromethanesulfonic (triflic) acid was proposed to result in formation of Mes₃SbO (Scheme 2c).¹⁸ The strong acids were proposed to protonate an apical hydroxide ligand from the stiborane to effect the loss of a water molecule and the sulfonate anion generated was then believed to abstract a proton from the remaining Sb-OH moiety. The putative stibine oxide was ultimately isolated as a hydrogen-bonded adduct Mes₃SbO···HO₃SR. Elemental analysis, conductivity, and ¹H NMR and IR spectroscopic data were consistent with this proposed structure, but the strongest evidence offered in support of the identity of the Mes₃SbO···HO₃SR species was the X-ray crystal structure of the benzenesulfonate adduct, which features a hydrogen bond between the acid and the stibine oxide.

These substances appeared to offer the most direct route to an isolated stibine oxide *via* removal of the hydrogen-bonded acid. Intrigued by the possibility of studying the properties and reactivity of monomeric stibine oxides, we sought to gain



Scheme 2 (a) Product of Lewis acid-induced disaggregation of dimeric (Ph₃SbO)₂. (b) Product of the oxidation of triarylstibines held in proximity by a rigid scaffold. The chelating moiety represents $o-C_6Cl_4O_2$. (c) Treatment of *trans*-Sb(OH)₂Mes₃ with sulfonic acids to putatively afford monomeric stibine oxides hydrogen-bonded to Brønsted acids.



Fig. 1 Relaxed surface scan (BP86/def2-TZVP) of the hydroxytrimesitylstibonium benzenesulfonate SbO-H bond length.

preliminary insight into the structure of Mes₃SbO···HO₃SR by performing a geometry optimization at the PBE0/def2-TZVPP level of theory starting from the previously reported crystallographic coordinates. The optimization converged smoothly and bond lengths and angles agreed well between the computational and experimental data (see ESI⁺). Surprisingly, however, during the optimization, the hydrogen atom migrates from the sulfonic acid to the stibine oxide, forming the hydroxystibonium benzenesulfonate salt [Mes₃Sb(OH)][PhSO₃] with an O-H bond length of 1.035 Å. A relaxed surface scan (BP86/ def2-TZVP) in which the hydrogen atom is systematically moved from the Sb-bound O atom to the S-bound O atom revealed that there is only one minimum along this internal coordinate and that it corresponds to the hydroxytrimesitylstibonium benzenesulfonate (Fig. 1). One chemically intuitive means of interpreting these results is that PhSO₃H is a stronger Brønsted acid than Mes₃SbOH⁺. This interpretation is confirmed by the lower proton affinity computed for the conjugate base of the former (see ESI[†]). As discussed by Steiner,¹⁹ a hydrogen bond can be viewed as an incipient proton transfer. The discrepancy between the proton affinities of the donor and acceptor results in formal proton transfer and formation of a predominantly ionic interaction with a moderate hydrogen bond formed on top.¹⁹

Close analysis of the previously published crystallographic experiments uncovered no reported details regarding the placement or refinement of the PhSO₃*H* hydrogen atom in the Mes₃SbO···HO₃SPh model. Moreover, the previously reported elemental analysis and spectroscopic data (the *HO*₃SPh ¹H NMR resonance was not observed) do not speak directly to the location of the hydrogen atom in question. To further interrogate the differences that might be expected between Mes₃SbO and [Mes₃SbOH]⁺, the geometries of these isolated species were optimized computationally (PBE0/def2-TZVPP). As expected, the structure of Mes₃SbO exhibits an Sb–O bond length (1.827 Å) shorter than that calculated for [Mes₃SbOH]⁺ (1.932 Å), the latter of which agrees better with the previously reported experimental Sb–O bond length of 1.894(5) Å.

To resolve the apparent contradictions described above, we resynthesized the previously reported compounds by adding a



Scheme 3 Synthesis of hydroxystibonium salts 1, 2, and 3. BAr^F_4 is $[B(C_6H_3(3,5\text{-}CF_3)_2)_4]^-.$

DCM solution of the sulfonic acid to a DCM suspension of 1 equiv. of trans-Sb(OH)₂Mes₃. As the reaction proceeded, all solids were solubilized. Addition of hexanes to the reactions with PhSO₃H and CF₃SO₃H produced colorless crystals of 1 and 2, respectively, which feature analytical characteristics identical to those previously reported for the PhSO₃H and CF₃SO₃H adducts of Mes₃SbO. The ¹H and ¹³C NMR spectra of **1** feature a single set of mesityl resonances, consistent with maintenance of 3-fold rotational symmetry. In addition to the remaining phenyl signals of the acid, a broad signal at 9.10 ppm was observed, which we assign to the hydroxyl proton. The spectra of 2 can be interpreted similarly, but with the hydroxyl proton resonating at 7.51 ppm. The NMR spectroscopic data are consistent with the formulation of 1 and 2 as either Mes₃SbO···HO₃SR adducts or [Mes₃SbOH⁺][RSO₃⁻] salts (Scheme 3). We highlight that in contrast to the resonance structures shown in Scheme 2, the products depicted in equilibrium in Scheme 3 are chemically distinct.

Varying degrees of either ionic pairing (in the case of the hydroxystibonium salts) or hydrogen bonding (in the case of stibine oxide adducts) could readily account for the difference between the chemical shifts of the hydroxyl ¹H NMR resonances in 1 and 2. IR spectroscopy provides an opportunity to gain more direct insight into the bonding between the Sb and O atoms in these compounds. The IR spectra of 1 and 2 are broadly similar and feature strong signals at 612 cm⁻¹ and 637 cm⁻¹, respectively, which we assign as the $\nu_{\rm SbO}$ stretching frequency. These bands were previously interpreted as being indicative of an Sb=O double bond given that they are higher in energy than the $\nu_{\rm SbO}$ of species like trans-Sb(OH)₂Mes₃ $(\nu_{\rm SbO} = 520 \text{ cm}^{-1})$.^{18,20} The previous report of **1** and **2** provides the only compelling examples of well-characterized monomeric stibine oxides and so there are no literature comparators. Using the DFT-optimized structures of Mes₃SbO and [Mes₃SbOH]⁺, frequency calculations afforded $\nu_{\rm SbO}$ values of 817 cm⁻¹ for the stibine oxide and 647 cm⁻¹ for the hydroxystibonium. These values are consistent with the greater Sb-O bond strength/ stiffness expected for the stibine oxide. The significantly better agreement of the experimental $\nu_{\rm SbO}$ with that calculated for [Mes₃SbOH]⁺ provides a strong confirmation of proposal that 1 and 2 are in fact salts of hydroxystibonium cations that feature an Sb-O single bond.

The ionic nature of these species was further supported by the facile exchange of the triflate counterion in 2 for $[B(C_6H_3(3,5-CF_3)_2)_4]^-$, affording salt 3 (Scheme 3). Again, analytical and X-ray crystallographic data support the formulation of this species as a hydroxystibonium salt (see ESI†).

We grew diffraction-quality crystals of 1 and 2 to redetermine their structures. Solution and refinement of the structure of 1 proceeded smoothly and afforded a non-H atom model essentially identical to that reported previously. Inspection of the difference Fourier synthesis generated using a model in which all non-H atoms were refined anisotropically and all C-bound H atoms were included at geometrically calculated positions, clearly reveals a maximum electron density signal along the Sb-O···O-S vector at distance of 0.72 Å from the Sb-bound O atom (Fig. 2). This maximum indicates that, in contrast to the previous report, the H atom resides on the Sb-bound O atom.

Refinement of the crystal structure of 2 revealed that it also contains the $[Mes_3SbOH]^+$ cation. The quality of the collected data provides a high degree of confidence in the locations of these H atoms on the Sb-bound oxygen, despite the well-known difficulties associated with locating H atoms by X-ray crystal-lography. Moreover, the influence of the H atoms on the Sb–O bond lengths is unmistakable. The Sb–O bond lengths in 1 (1.9055(8) Å) and 2 (1.910(1) Å) are in good agreement with the computationally optimized Sb–O bond length of $[Mes_3SbOH]^+$ (1.932 Å) and are significantly longer than the Sb–O bond length calculated for Mes_3SbO (1.827 Å) (Fig. 3).

We were also successful in solving and refining the structure of $3 \cdot C_5 H_{12}$ (Fig. 3). The crystals were weakly diffracting, but the Sb–O bond length is 1.932(3) Å. Unlike the structures of 1 and 2, there are no strong H-bonds between the cation and anion, but a F atom of one CF₃ group is positioned 3.050(5) Å from the hydroxyl O atom and the O–H···F angle is 159(5)°. The weaker interaction allows a sharp ν_{OH} IR band to be observed at 3601 cm⁻¹;



Fig. 2 Thermal ellipsoid plot (50% probability, H atoms as spheres of arbitrary radius) of **1** less the protic hydrogen atom expanded about the residual electron density maximum (full plot in Fig. 3a). Overlaid in grey contours (0.075 e⁻ Å⁻³) is the F_o-F_c map plotted in the plane defined by Sb1, O1, and O2. Color Code: Sb teal, O red, S yellow, C black, H white.



Fig. 3 Thermal ellipsoid plots (50% probability) of (a) **1**, (b) **2**, and (c) **3**. H atoms and solvent omitted except Sb–OH, which is shown as a sphere of arbitrary radius. Ball-and-stick representations of the optimized (PBE0/ def2-TZVPP) structures of (d) [Mes₃SbOH]⁺ and (e) Mes₃Sb. Color Code: Sb teal, O red, S yellow, F green, C black, B pink, H white.

the moderate H-bonding in **1** and **2** produces a broad band in this region (Fig. S16, ESI[†]).

Our search of the literature uncovered only one other promising case of a monomeric stibine oxide, tris(2,6-dimethoxyphenyl)stibine oxide, (2,6-(OMe)₂C₆H₃)₃SbO.²¹ In contrast to the detailed spectroscopic data provided in the previous report of 1 and 2, the report of $(2,6-(OMe)_2C_6H_3)_3SbO$ includes only an IR-determined ν_{SbO} of 664 cm^{-1} . As noted above, this value already provides a strong indication that the species is not a stibine oxide. The reported assignment rested heavily on a single-crystal X-ray structural analysis. Although the refinement statistics for the reported structure are promising, inspection of the deposited data reveals that the structure contains voids that directly abut the Sb-bound O atoms of both non-crystallographically related molecules in the asymmetric unit; the SQUEEZE algorithm was employed to remove the contribution of the electron density within this region of space to the observed diffraction intensities.²¹ In addition to the presence of these voids, we note that the reported Sb-O bond length of 1.918(3) Å agrees with the Sb-O bond lengths that we obtained for the hydroxytrimesitylstibonium salts 1, 2, and 3. Following the strategy described above, we computationally optimized (PBE0/def2-TVZPP) the structures of both the stibine oxide (2,6-(OMe)₂C₆H₃)₃SbO and the hydroxystibonium cation $[(2,6-(OMe)_2C_6H_3)_3SbOH]^+$. The Sb-O bond length of the former was 1.818 Å and that of the latter was 1.920 Å. We suggest that the voids in the crystal structure contain either a neutral Lewis

acid or both a charged Lewis acid (such as a proton) and a chargebalancing counterion. The interaction of the acid with the Sb-bound O atom would afford a lengthened Sb–O bond, as observed previously and in this work.

In summary, our attempts to investigate the properties and reactivity of the Sb^+-O^- functional group in monomeric stibine oxides led to the discovery that the only previously reported examples are hydroxystibonium cations in which a Lewis acid interacts with the Sb-bound O atom. As such, this work demonstrates that monomeric stibine oxides unstabilized by interaction with a Lewis acid have still yet to be prepared. The lack of access to such molecules greatly hampers any effort to observe and understand the systematic variation in the nature and reactivity of pnictogen–oxygen bonds. Initial attempts to prepare stibine oxides *via* deprotonation of 1–3 have been unsuccessful, but the targeted synthesis of these molecules is underway.

Conflicts of interest

There are no conflicts to declare.

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