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Direct Observation of New Antimony-containing Anions: SbH_2O^-, Sb_3^-, and Monomeric $Sb_3O_5^-$

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Abstract

The new anions SbH_2O^-, $Sb_3O_5^-$, and Sb_3^- were produced under negative chemical ionization conditions from $Sb(O{-}n\text{-}Bu)_3$ in the source of a mass spectrometer and their compositions confirmed by isotopic composition and high resolution tandem mass spectrometry. STO-3G-level calculations indicate that the isomer H_2SbO^- is more stable than $HSbOH^-$.

Of the analogs of hydroxylamine, H_2NOH, only hydroxylphosphine or phosphinous acid, H_2POH, has been reported; it is thought to exist in equilibrium with phosphine oxide, H_3PO, and decomposes even at −115 °C [1]. The antimony analog of hydroxylamine, H_2SbOH, hydroxystibine or stibinous acid, is unknown. Its conjugate base has now been observed by mass spectrometry.

Negative ions may be produced in a high-pressure (0.1 torr–2 torr) mass spectrometer by a chemical process (*e.g.*, a proton transfer) or by attachment or dissociative attachment of an electron; in both cases the process is commonly if not always correctly called negative chemical ionization (NCI) because the conditions are similar to those for chemical ionization [2] to form positive ions. Attachment processes occur because the gas molecules are abundant enough to decrease the energy of the electrons emitted from the filament to nearly thermal by numerous collisions, so that a significant fraction of electrons in the source have energies within the range for attachment and dissociative attachment. The ions formed by interaction with low-energy electrons under source pressure conditions capable of thermalizing ion energy have low internal energies. An ion with low internal energy tends to rearrange, rather than simply cleave bonds [3]. Recognition of this feature of the ionization method suggests that it can be used to produce spectra of inorganic esters containing simple anions formed by rearrangement of alkyl hydrogens to metal or oxygen. This new method of preparing new ions differs greatly from traditional synthetic methods and can be combined with direct mass spectrometric analysis of the ion 10–30 μs after its formation by the MS/MS technique [4] using collisionally activated decomposition (CAD). By using this approach, the new $H_2NO_2^-$ [5] and monomeric $HTiO_3^-$ [6] ions have been made and evidence for their structures obtained. The method has also been used to confirm the structure of monomeric HPO_3^-, first observed [7] in the spectra of organophosphorus pesticides.

Mass spectra were obtained with a ZAB-4F four-sector mass spectrometer (VG Instruments, Manchester, U.K.) when antimony tri-n-butoxide (Alfa Inorganics, Danvers, Mass.) was admitted through a capillary molecular leak to the source in NCI conditions (Ar buffer gas, 2×10^{-3} torr; 150 eV ionizing energy; 2.0 V repeller potential). Most ions observed were formed from halogenated intermediates in the preparation of $Sb(OBu)_3$ from $SbCl_3$, particularly $Cl_2Sb(OBu)_2^-$. We do not report complete spectra because most major peaks were due to minor (<5%) impurities in the sample. These impurities have much larger cross sections for electron capture and dissociative electron capture than the ester; such behavior is typical in our experience for NCI spectra of commercial samples synthesized from halides. Irrespective of origin, gas-phase ions with low internal energy, such as NCI species, are expected to rearrange [3], and formation of small closed-shell inorganic ions by loss of the organic portion of predecessor ions ban be anticipated with some confidence. The small (2%) peak at *m/z* 139 was a doublet, and collisionally activated decomposition tandem mass spectrometric (CAD MS/MS) analysis of the component of lower mass isolated by high resolution before the collision provided a two-peak negative ion spectrum with loss only of H and 2H; the presence of antimony was confirmed by an isotope peak of the correct height (75% of that of the lower-mass compo-

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nent of m/z 139) as the lower-mass component of a doublet at m/z 141 in the full-scan NCI spectrum. This information confirms the empirical formula as SbH_2O^-.

Hydroxystibine or stibinous acid has two proton environments. Although the CAD spectrum lacked useful information about the structure of SbH_2O^-, we were able to study the structure of the conjugate base computationally with an STO-3G basis set for fourth-period elements [8]. Using the energies thus obtained for H_2SbOH and H_2SbO^- and standard values [9] for other species, the isodesmic [10] process (1) was found to be exothermic by 54.0 kcal/mol.

$$H_2SbOH + OH^- \longrightarrow H_2SbO^- + H_2O \qquad (1)$$

The gaseous acidity of H_2O, or $-\Delta H_r^\circ$ for eqn. (2) in the gas phase, is 390.7 ± 1.6 kcal/mol [11], so that the O-acidity of hydroxystibine is 336.7 ± 1.6 kcal/mol (this error being only quoted experimental error).

$$H_2O \longrightarrow H^+ + OH^- \qquad (2)$$

By STO-3G energies for all species, isodesmic process (3) is exothermic by 4.8 kcal/mol.

$$H_2SbOH + SbH_2^- \longrightarrow HSbOH^- + SbH_3 \qquad (3)$$

The gaseous acidity of SbH_3 may be extrapolated from trends both across and down the periodic table [11, 12] to yield a value of 349 ± 4 kcal/mol. The Sb-acidity of hydroxystibine is then 343 ± 4 kcal/mol (this error being only quoted experimental error). If one assumes that the only error is quoted experimental error, calculation at this level suggests that the hydroxyl proton of hydroxystibine is the one that ionizes more readily.

The structures of H_2SbOH and associated species were optimized using GAUSSIAN 82 with the STO-3G fourth period basis set of Pietro *et al.* [8] and $\zeta_{5s} = \zeta_{5p} = 2.20$. The H_2SbO^- ion is pyramidal, with $R_{SbH} = 165.2$ pm, $R_{SbO} = 210.9$ pm, $\text{angle}_{HSbH} = 90.530°$, and the angular deviation of the SbO bond from the HSbH plane = 76.460°. For $HSbOH^-$, R_{SbH} (164.5 pm), R_{SbO} (200.1 pm), R_{OH} (99.4 pm) angle_{SbOH} (102.45°), and δ_{HSbOH} (90°) were optimized, with a separate optimization of angle_{HSbO} (90.61°). These bond lengths and angles can be compared with those of SbH_2^-: $R_{SbH} = 164.3$ pm, $\text{angle}_{HSbH} = 91.034°$. The geometry of SbH_3 found by Pietro *et al.* [8] has $R_{SbH} = 164.4$ pm, $\text{angle}_{HSbH} = 94.40°$, to which may be compared the optimized geometry of H_2SbOH (on the assumption that the HOSb plane bisects the HSbH plane): $R_{SbH} = 164.595$ pm, $R_{SbO} = 197.916$ pm, $R_{OH} = 98.819$ pm, $\text{angle}_{HSbH} = 93.66822°$, $\text{angle}_{SbOH} = 106.535°$, angular deviation of the SbO bond from the HSbH plane = 83.5727°.

Interesting comparisons may be made between the structures of H_2NOH, H_2POH (for which the structure has been calculated [13]), and H_2SbOH. On replacement of H by OH, the remaining HNH bond angle and HPH bond angle remain the same, while the HSbH bond angle increases by 2°. The angle_{HNO} is greater than angle_{HNH} by 12.4° in hydroxylamine [14], angle_{HPO} is greater than angle_{HPH} by 6.5° in phosphinous acid; and angle_{HSbO} is greater than angle_{HSbH} by only 0.83° in H_2SbOH. The Sb–O bond length is closely approximated from sums of ionic radii, or by simplistic extrapolation from H–P and O–P bond lengths in phosphinous acid and the H–Sb bond length found herein, but it is seriously overestimated (by 17 pm) from the extrapolation of H–N and O–N bond lengths in hydroxylamine and the H–Sb bond length; thus the N–O bond length in hydroxylamine is too short to model bonding of larger Group VA atoms to O successfully.

When antimony tri-n-butoxide is admitted to the source through the capillary neck of an ampoule located physically in the source housing, with instrument conditions otherwise remaining the same, ion-molecule reactions between Sb-containing species occur because there is a locally high partial pressure. The species $Sb_3O_5^-$ and Sb_3^- were observed under this alteration as relatively intense ions (5–15%) whose actual relative intensity was (as it should have been) dependent upon the local partial pressure of $Sb(OBu)_3$, which could be varied crudely but not measured accurately. Most other ions included Cl from minor impurities and are not presented here. Intensities of isotope peaks in $Sb_3O_5^-$ and Sb_3^- were consistent with the presence of three Sb atoms in each ion. The charge-reversal CAD [5, 15] spectrum of $^{121}Sb_3O_5^-$ (relative intensities in parentheses) includes $Sb_3O_4^+$ (86), $Sb_3O_3^+$ (13), $Sb_2O_3^+$ (19), $Sb_2O_2^+$ (72), Sb_2O^+ (7), SbO^+ (100), Sb^+ (11). In view of the unambiguous identification of all atoms in Sb_3^- by confirmation of the presence of three Sb atoms from isotope peaks, no further experiments were performed on it. We could not perform computational studies on species containing three Sb atoms because of the time requirements for the integrals that would be generated.

The $Sb_3O_5^-$ ion has been reported previously as a polymer [16], but the monomeric form is unknown. We are unaware of any reports of Sb_3^-, or of its conjugate acid. Neither are N, P, or As analogues reported for monomeric $Sb_3O_5^-$. For analogy to Sb_3^-, the azide ion is not necessarily appropriate; the P_3^- ion is known ($\Delta H_f^\circ = 38.2 \pm 4.5$ kcal/mol) from mass spectrometric studies [17] but its structure is not; semiempirical calculations on $HP_3^{+\bullet}$ indicate that its most stable form is isoelectronic with $NH_3^{+\bullet}$ [18], but this information is not necessarily relevant to the structure of P_3^-.

This report thus constitutes the first observation and identification of three new anions. The ease of access of these ions in the gas phase may encourage searches for ways to prepare them in solution.

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