ANTIMONY COMPOUNDS

1. Introduction

Antimony [7440-36-0] is the fourth member of the nitrogen family and has a valence shell configuration of $5s^25p^3$. The utilization of these orbitals and, in some cases, of one or two $5d$ orbitals permits the existence of compounds in which the antimony atom forms three, four, five, or six covalent bonds.

The valence bond theory in its most elementary form predicts that trivalent compounds of antimony should have pyramidal structures derived from the $5p$ orbitals and that the $5s$ electrons should act as an inert pair. Many trivalent derivatives of antimony, however, have intervalency angles significantly larger than the 90° angle predicted by this model. The size of these angles as well as the general chemical behavior of the trivalent compounds suggest that sp^3 hybridized antimony orbitals are being employed and that the lone pair occupies one of the tetrahedral positions. The fact that the bond angles are often considerably less than the regular tetrahedral value of 109.5° may be ascribed to repulsion by the lone pair.

Pentacoordinate compounds of antimony usually exhibit trigonal bipyramidal geometry corresponding to the sp^3d hybridized antimony orbitals of valence bond theory. The antimony atom in the octahedral sp^3d^2 valence state is present in numerous complex anions of the SbX_6^- type and in neutral complexes of pentavalent halides with electron-donating molecules such as alcohols, ethers, and nitriles. Ions of the type SbX_5^{2-} are also known and possess a square pyramidal configuration in which the antimony atom is located slightly below the basal plane of the pyramid. A lone pair of electrons presumably occupies one of the octahedral positions and repels the Sb–X bonding pairs.

2. Inorganic Compounds of Antimony

2.1. Stibine.

Stibine [7803-52-3], SbH_3; mp, −88°C; bp, −18°C; density of the liquid at its bp, 2.204 g/mL; sp gr at 18°C with respect to air as 1.000, 4.344, is a colorless, poisonous gas having a disagreeable odor (1). It is the only well-characterized binary compound of antimony and hydrogen, although distibine [14939-42-5], Sb_2H_4, has been reported. The vapor pressure, heat of vaporization, heat capacity, density, viscosity, heat of formation, free energy of formation, surface tension, and thermal conductivity of stibine as a function of temperature have been reported (2). The formation is endothermic, 145.1 kJ/mol (34.7 kcal/mol); the compound decomposes slowly at room temperature and readily at 200°C, to give metallic antimony and hydrogen. The decomposition is autocatalytic and under certain conditions can be explosive. The molecule is trigonal pyramidal (3). Stibine is readily soluble in organic solvents such as carbon disulfide or ethanol, and is slightly soluble in water. In aqueous solution there is no measurable tendency to form a stibonium ion analogous to $NH^+{}_4$ and $PH^+{}_4$.

Stibine may be prepared by the treatment of metal antimonides with acid, chemical reduction of antimony compounds, and the electrolysis of acid or alkaline solutions using a metallic antimony cathode:

$$Zn_3Sb_2 + 6\ H_3O^+ \longrightarrow 3\ Zn^{2+} + 2\ SbH_3 + 6\ H_2O$$

$$SbO_3^{3-} + 9\ H_3O^+ + 3\ Zn \longrightarrow SbH_3 + 3\ Zn^{2+} + 12\ H_2O$$

The classical synthesis involves the dissolution of a 33% Sb–67% Zn alloy by hydrochloric acid; the evolved gases contain up to 14% stibine. A detailed procedure using a Sb–Mg alloy has also been described (4). Aluminum hydride or alkali metal borohydrides have been used to reduce antimony(III) in acidic aqueous solution to produce stibine. A 23.6% yield of stibine, based on the borohydride used, has been reported (5). A 78% yield based on Sb has been obtained by gradually adding a solution that is 0.4 *M* in $SbCl_3$ and saturated in NaCl, to aqueous $NaBH_4$ at mol ratios of $NaBH_4{:}SbCl_3 > 10$ (6).

Stibine is readily oxidized and may be ignited in the presence of air or oxygen to form water and antimony trioxide; at lower temperatures metallic antimony and water are slowly formed. Sulfur and selenium react with stibine at 100°C in the presence of light to form antimony trisulfide [1345-04-6], Sb_2S_3, and antimony selenide [1315-05-5], Sb_2Se_3, respectively. At elevated temperatures stibine reacts with most metals to give antimonides. Heavy metal salts react with stibine to produce dark, metallic-appearing precipitates. In the case of silver nitrate, silver antimonide is first formed, and this reacts in turn with additional silver nitrate to produce metallic silver and antimony trioxide:

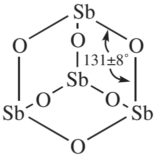
$$2\ SbH_3 + 12\ Ag^+ + 15\ H_2O \longrightarrow 12\ Ag + Sb_2O_3 + 12\ H_3O^+$$

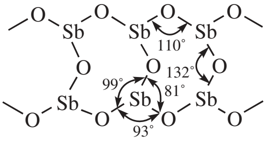
High purity stibine is used as an n-type, gas-phase dopant for Si in semiconductors (2). Low temperature distillation of stibine at <53.3 kPa (400 torr) yields a product that on decomposition gives metallic antimony having less than $8 \times 10^{-4}\%$ impurity (6). A method for determining quantities of stibine in the neighborhood of 0.1 mg/m^3 in air has been reported (7).

Stibine may be inadvertently formed by acidified reducing agents reacting with antimony-containing materials. It is an extremely poisonous gas which causes blood destruction and damage to the liver and kidneys (8).

2.2. Metallic Antimonides. Numerous binary compounds of antimony with metallic elements are known. The most important of these are indium antimonide [1312-41-0], InSb, gallium antimonide [12064-03-8], GaSb, and aluminum antimonide [25152-52-7], AlSb, which find extensive use as semiconductors. The alkali metal antimonides, such as lithium antimonide [12057-30-6] and sodium antimonide [12058-86-5], do not consist of simple ions. Rather, there is appreciable covalent bonding between the alkali metal and the Sb as well as between pairs of Na atoms. These compounds are useful for the preparation of organoantimony compounds, such as trimethylstibine [594-10-5], $(CH_3)_3Sb$, by reaction with an organohalogen compound.

2.3. Antimony Trioxide. Antimony(III) oxide (antimony sesquioxide) [1309-64-4], Sb_2O_3, is dimorphic, existing in an orthorhombic modification; valentinite [1317-98-2] is colorless (sp gr 5.67) and exists in a cubic form; and senarmontite [12412-52-1], Sb_4O_6, is also colorless (sp gr 5.2). The cubic modification is stable at temperatures below 570°C and consists of discrete Sb_4O_6 molecules. The molecule is similar to that of P_4O_6 and As_4O_6 and consists of a bowed tetrahedron having antimony atoms at each corner united by oxygen atoms lying in front of the edges. This solid crystallizes in a diamond lattice with an Sb_4O_6 molecule at each carbon position.





At higher temperatures the stable form is valentinite, which consists of infinite double chains. The orthorhombic modification is metastable below 570°C; however, it is sufficiently stable to exist as a mineral. Antimony trioxide melts in the absence of oxygen at 656°C and partially sublimes before reaching the boiling temperature, 1425°C. The vapor at 1500°C consists largely of Sb_4O_6 molecules, but these dissociate at higher temperatures to form Sb_2O_3 molecules.

Common methods of preparation include direct combination of metallic antimony with air or oxygen, roasting of antimony trisulfide, and alkaline hydrolysis of an antimony trihalide and subsequent dehydration of the resulting hydrous oxide; when heated too vigorously in air, some of the Sb(III) is converted to Sb(V).

Antimony trioxide is insoluble in organic solvents and only very slightly soluble in water. The compound does form a number of hydrates of indefinite composition which are related to the hypothetical antimonic(III) acid (antimonous acid). In acidic solution antimony trioxide dissolves to form a complex series of polyantimonic(III) acids; freshly precipitated antimony trioxide dissolves in strongly basic solutions with the formation of the antimonate ion [29872-00-2], $Sb(OH)^{3-}{}_6$, as well as more complex species. Addition of suitable metal ions to these solutions permits formation of salts. Other derivatives are made by heating antimony trioxide with appropriate metal oxides or carbonates.

Antimony trioxide has numerous practical applications (9). Its principal use is as a flame retardant in textiles and plastics (see FLAME RETARDANTS; FLAME RETARDANTS IN TEXTILES). It is also used as a stabilizer for plastics, as a catalyst, and as an opacifier in glass (qv), ceramics (qv), and vitreous enamels (qv).

2.4. Antimony Tetroxide. Antimony(III,V) oxide, antimony dioxide [1332-81-6], SbO_2 and Sb_2O_4, occurs in two modifications. Orthorhombic antimony tetroxide has long been known as the mineral cervantite [1332-81-6], α-Sb_2O_4, (colorless, sp gr 4.07). More recently a monoclinic modification, β-Sb_2O_4, has been recognized. In both dimorphs half of the antimony is in the +3 oxidation state, half in the +5 state (10,11). The antimony environments are quite similar in both modifications. The Sb(V) atoms are surrounded by a slightly distorted octahedron of oxygens, and the Sb(III) atoms are coordinated to four oxygens, all on the same side of the Sb(III). The α-modification may be formed by heating Sb_2O_3, valentinite, in air between 460 and 540°C; β-Sb_2O_4 is obtained either by heating α-Sb_2O_4 at 1130°C in dry air or in oxygen (12) or by heating antimonic(V) acid above 900°C (11). At higher temperatures the solid vaporizes without first undergoing any transformation; the recondensed vapors consist of a mixture of β-Sb_2O_4 and antimony trioxide (11).

Antimony tetroxide finds use as an oxidation catalyst, particularly for the dehydrogenation of olefins.

2.5. Antimony Pentoxide Hydrates. Antimonic acid (antimony(V) acid) [12712-36-6], and antimony(V) oxide [1314-60-9], $Sb_2O_5{\cdot}nH_2O$, are both hydrates of Sb_2O_5. Commercial antimony pentoxide is either hydrated Sb_2O_5 or at times β-Sb_2O_4. Material having the approximate composition $Sb_2O_5{\cdot}3.5H_2O$ may be prepared by hydrolysis of antimony pentachloride or by acidification of potassium hexahydroxoantimonate(V) [12208-13-8], $KSb(OH)_6$, followed by filtration and drying to constant weight in air at room temperature. This substance is a white solid which loses water upon heating and becomes yellow in color. This loss of water fails to correspond to definitive ratios of $H_2O{:}Sb_2O_5$, nor is the composition Sb_2O_5 attained. At about 700°C the material is anhydrous and white in color; this is an antimony oxide [12165-47-8], Sb_6O_{13}, containing both Sb(III) and Sb(V) and having a cubic pyrochlore-type structure.

Hydrated antimony pentoxide (antimonic acid) is essentially insoluble in nitric acid solutions, only very slightly soluble in water, but dissolves in aqueous KOH. Numerous hydrated antimonate(V) salts have been reported in which the Sb(V) atom is octahedrally surrounded by six OH groups. Among these are derivatives of magnesium, cobalt, and nickel that have formulas $M(SbO_3)_2 \cdot 12H_2O$, and a compound referred to as sodium pyroantimonate [10049-22-6], $Na_2H_2\ Sb_2O_7 \cdot 5H_2O$. X-ray studies show that these are actually $M(H_2O)_6[Sb(OH)_6]_2$ and sodium hexahydroxantimonate(V) [12339-41-2], $Na[Sb(OH)_6]$, respectively. The latter compound is one of the least soluble sodium salts known and is useful in sodium analysis. Numerous polyantimonate(V) derivatives are prepared by heat treatment of mixtures of antimony trioxide and other metal oxides or carbonates. Of these, $K_3Sb_5O_{11}$ [12056-59-6] and $K_2Sb_4O_{11}$ [52015-49-3] have been characterized by x-ray. These consist of three-dimensional networks of SbO_6 in which corners and edges are shared with K^+ ions located in tunnels through the network (13). Simple species such as $SbO_4{}^{3-}$ and $Sb_2O_7{}^{2-}$, analogous to orthophosphate and pyrophosphate, apparently do not exist.

Antimonic acid has been used as an ion-exchange material for a number of cations in acidic solution. Most interesting is the selective retention of Na^+ in 12 *M* HCl, the retention being 99.9% (14). At lower acidities other cations are retained, even K^+. Many oxidation and polymerization catalysts are listed as containing Sb_2O_5.

2.6. Antimony Trifluoride.

Antimony(III) fluoride [7783-56-4], SbF_3, is a white, crystalline, orthorhombic solid; vapor pressure at the mp, 26.34 kPa (0.26 atm); Sb−F bond energy, 437.4 kJ (104.5 kcal) (15). The molecule shows a very distorted octahedral arrangement. Antimony trifluoride is extremely soluble in water, the solubility being increased by the presence of hydrofluoric acid. It is also very soluble in polar solvents such as methanol, 154 g/100 mL, and acetone. Table 1 lists physical constants for the antimony halides.

Antimony(III) fluoride may be prepared by treating antimony trioxide or trichloride with hydrofluoric acid. Pure SbF_3 is then obtained by carefully evaporating all of the water from the crude product, which is subsequently sublimed. SbF_3 does not hydrolyze as readily as do the other antimony trihalides. When heated in open air at 100°C, a crystalline solid quickly forms of composition $Sb_3O_2(OH)_2F_3$, which, upon further heating, is transformed into antimony oxide fluoride [11083-22-0], SbOF. This compound may also be prepared by heating 1:1 mixtures of Sb_2O_3 and SbF_3. There are three known crystalline modifications.

In the presence of excess fluoride, antimony trifluoride forms numerous types of complex ions, eg, $SbF_4{}^-$, $SbF_5{}^{2-}$, $Sb_4F_{13}{}^-$, and $Sb_2F_7{}^-$; but $SbF_6{}^{3-}$ is unknown (16).

Antimony trifluoride is used as a fluorinating agent to replace nonmetal chloride with fluorine. Tri- and difluoromethyl groups are readily formed from the corresponding chlorine groups, but CH_2Cl and CHCl groups are usually unaffected. Antimony trifluoride can also be used to effect the replacement of chlorine bonded to other elements; thus trichloromethylphosphonous dichloride [3582-11-4], CCl_3PCl_2, can be converted to trichloromethylphosphonous difluoride [1112-03-4], CCl_3PF_2.

Uses of SbF_3 have been reported in the manufacture of fluoride glass and fluoride glass optical fiber preform (17) and fluoride optical fiber (18) in the preparation of transparent conductive films (19) (see FIBER OPTICS).

2.7. Antimony Trichloride.

Antimony(III) chloride [10025-91-9], $SbCl_3$, is a colorless, crystalline solid, readily soluble in hydrochloric acid; water, ca 9%

Table 1. **Physical Constants of the Antimony Halides**

Parameter	Antimony trifluoride	Antimony trichloride	Antimony tribromide	Antimony triiodide[a]	Antimony pentafluoride	Antimony pentachloride
formula	SbF_3	$SbCl_3$	$SbBr_3$	SbI_3	SbF_5	$SbCl_5$
CAS Registry Number	[7783-56-4]	[10025-91-9]	[7789-61-9]	[7790-44-5]	[7783-70-2]	[7647-18-9]
mp, °C	291 ± 1	73.2	96.0 ± 0.5	170.5	6	3.2 ± 0.1
bp, °C	346 ± 10	222.6	287	401	150	68^b, 140^c
Δ_f° at 298°C, kJ/mol[d]	−915.5	−382.2	−259.4	−100.4		-450.8 ± 6.2
S° at 298°C, J/(mol·K)[d]	127	184	207	216 ± 1		263 ± 12
ΔH_{fusion}, kJ/mol[d,e]	21.4			$22.7_{444} \pm 0.2$		
ΔS_{fusion}, J/(mol·K)[d,e]	38.2			$51.5_{444} \pm 0.4$		
ΔH_{vap}, kJ/mol[d,e]	$102.8_{298} \pm 1.3$	46.72_{496}	53.2_{560}			43.45_{449}
ΔS_{vap}, J/(mol·K)[d,e]	$175.8_{298} \pm 2.5$	93.3_{496}	94.9_{560}			95.44_{449}
C_p, J/mol·K[d]		108^f		96^f, 144^g		

[a] The ΔH_{subl} at 298°C is 101.6 ± 0.4 kJ/mol (24.3 ± 0.1 kcal/mol).

[b] At a pressure of 1.82 kPa.

[c] Decomposes at atmospheric pressure, 101.3 kPa.

[d] To convert from J to cal, divide by 4.184.

[e] At the temperature in °C indicated by the subscript.

[f] Value given is for solid.

[g] Value given is for liquid.

at 25°C, increasing with temperature; $CHCl_3$, 22%; CCl_4, 13%; benzene; CS_2; and dioxane.

Antimony trichloride may be prepared by chlorination of antimony metal, Sb_2O_3, or Sb_2S_3, or by reaction of Sb_2O_3 with concentrated HCl. $SbCl_3$ hydrolyzes readily, giving hydrous Sb_2O_3 with excess water, but when limited quantities of water are used, a large number of partially hydrolyzed products has been claimed, eg, SbOCl, Sb_2OCl_4, $Sb_4O_5Cl_2$, $Sb_4O_3(OH)_3Cl_2$, $Sb_8O_{11}Cl_2$, and Sb_8OCl_{22}, some of which are listed in Table 2. The hydrolysis product most frequently obtained and best characterized is tetraantimony dichloride pentoxide [12182-69-3], $Sb_4O_5Cl_2$, which is initially precipitated as a thick white solid, changing to well-defined colorless crystals. By carefully controlled hydrolysis SbOCl is obtained, which, upon further dilution with water, changes to $Sb_4O_5Cl_2$.

In many situations $SbCl_3$ behaves as a Lewis acid. In the presence of excess Cl^-; and suitable cations, numerous chloroantimonate(III) ions are formed, eg, $SbCl_6{}^{3-}$, $SbCl_5{}^{2-}$, $SbCl_4{}^-$, $Sb_2Cl_7{}^{2-}$, $Sb_2Cl_7{}^{3-}$, $Sb_2Cl_9{}^{3-}$, and $Sb_2Cl_{11}{}^{5-}$. The first two of these are simple discrete ions. A large number of adducts have been formed by reaction of $SbCl_3$ with organic bases, eg, $SbCl_3{\cdot}(C_2H_5)_2O$, $SbCl_3{\cdot}H_2NC_6H_4NO_2$, $SbCl_3{\cdot}(CH_3)_3N$, $2SbCl_3{\cdot}(CH_3)_3N$, and $SbCl_3{\cdot}2CH_3COCH_3$. Isolable adducts are also formed with aromatic hydrocarbons, eg, $2SbCl_3{\cdot}C_6H_6$ and $SbCl_3{\cdot}C_6H_6$. In a few situations $SbCl_3$ apparently acts as an electron donor; thus the carbonyl complexes $Ni(CO)_3SbCl_3$ and $Fe(CO)_3(SbCl_3)_2$ have been isolated (20). Adducts and compounds are listed in Table 2.

Antimony trichloride is used as a catalyst or as a component of catalysts to effect polymerization of hydrocarbons and to chlorinate olefins. It is also used in hydrocracking of coal (qv) and heavy hydrocarbons (qv), as an analytic reagent for chloral, aromatic hydrocarbons, and vitamin A, and in the microscopic identification of drugs. Liquid $SbCl_3$ is used as a nonaqueous solvent.

Table 2. **Inorganic Antimony Compounds and Adducts**

Compound	CAS Registry Number	Formula
trifluorotetraoxotriantimonic(III) acid	[65229-25-6]	$Sb_3O_2(OH)_2F_3$
antimony chloride oxide	[7791-08-4]	SbOCl
diantimony tetrachloride oxide	[65229-26-7]	Sb_2OCl_4
tetraantimony dichloride pentoxide	[12182-69-3]	$Sb_4O_5Cl_2$
tetraantimony trihydroxydichlorotrioxide		$Sb_4O_3(OH)_3Cl_2$
antimony trichloride diethyl ether	[10025-91-9]	$SbCl_3\ (C_2H_5)_2O$
antimony trichloride aniline	[21645-17-0]	$SbCl_3\ H_2NC_6H_5$
antimony trichloride trimethylamine	[65186-11-0]	$SbCl_3\ (CH_3)_3N$
bis(antimony trichloride) trimethylamine	[65186-12-1]	$2SbCl_3\ (CH_3)_3N$
antimony trichloride bisacetone	[65186-13-2]	$SbCl_3\ 2CH_3COCH_3$
bis(antimony trichloride) benzene	[1123-15-5]	$2SbCl_3\ C_6H_6$
(antimony trichloride)tricarbonylnickel	[65208-44-8]	$Ni(CO)_3SbCl_3$
bis(antimony trichloride)tricarbonyliron	[65208-43-7]	$Fe(CO)_3(SbCl_3)_2$
antimony pentachloride bis(iodine chloride)	[65186-14-3]	$SbCl_5\ 2ICl$
antimony pentachloride tris(iodine chloride)	[65186-15-4]	$SbCl_5\ 3ICl$
antimony pentachloride sulfur tetrachloride	[15597-82-7]	$SbCl_5\ SCl_4$
bis(hexachloroantimonic(III) acid) nonahydrate	[65208-45-9]	$HSbCl_6\ 4.5H_2O$
antimony pentabromide diethyl ether	[29702-86-1]	$SbBr_5\ O(C_2H_5)_2$

2.8. Antimony Tribromide and Triiodide. Antimony(III) bromide [7789-61-9], $SbBr_3$, is a colorless, crystalline solid having a pyramidal dimorphic molecular structure and an acicular (α-$SbBr_3$) and a bipyramidal (β-$SbBr_3$) habit.

Antimony(III) iodide [7790-44-5], SbI_3, forms red rhombohedral crystals, intermediate in structure between a molecular and an ionic crystal. In SbI_3 vapor there is no indication of association.

Both antimony tribromide and antimony triiodide are prepared by reaction of the elements. Their chemistry is similar to that of $SbCl_3$ in that they readily hydrolyze, form complex halide ions, and form a wide variety of adducts with ethers, aldehydes, mercaptans, etc. They are soluble in carbon disulfide, acetone, and chloroform. There has been considerable interest in the compounds antimony bromide sulfide [14794-85-5], antimony iodide sulfide [13868-38-1], ISSb, and antimony iodide selenide [15513-79-8] with respect to their solid-state properties, ferroelectricity, pyroelectricity, photoconduction, and dielectric polarization.

2.9. Antimony Pentafluoride. Antimony(V) fluoride [7783-70-2], SbF_5, is a colorless, hygroscopic, viscous liquid that has SbF_6 units with *cis*-fluorines bridging to form polymeric units. ^{19}F nmr shows that at low temperatures there are three different types of F atoms (21). Contamination with a small amount of HF markedly decreases the extent of polymerization. The vapor density at 150°C corresponds to the trimer. The solid is a *cis*-fluorine-bridged tetramer (22).

Antimony pentafluoride may be prepared by fluorination of SbF_3 or by treatment of $SbCl_5$ with HF. In the latter method the fifth chlorine is removed with difficulty; failure to remove the chlorine completely results in contamination of the distilled SbF_5 with Sb(III) (20).

Antimony pentafluoride is a strong Lewis acid and a good oxidizing and fluorinating agent. Its behavior as a Lewis acid leads to the formation of numerous simple and complex adducts. It reacts vigorously with water to form a clear solution from which antimony pentafluoride dihydrate [65277-49-8], $SbF_5 \cdot 2H_2O$, may be isolated. This is probably not a true hydrate, but may well be better formulated as $[H_3O][SbF_5OH]$.

Antimony pentafluoride reacts with iodine to form bis(antimony pentafluoride) iodide [12324-61-7], $Sb_2F_{10}I$, and antimony pentafluoride iodide [12324-57-1], SbF_5I; with nitrosyl fluoride to give a very stable compound nitrosyl hexafluoroantimonate(V) [16941-06-3], $NOSbF_6$; with sulfur to give a dark blue solution from which antimony pentafluoride sulfur can be isolated; and with NO_2 to form nitrosyl pentafluoronitratoantimonate(V) [26117-73-7], $NO[SbF_5(NO_3)]$. Combinations of Sb(V) and Sb(III) fluorides give fluorides of the general formula $SbF_5(SbF_3)_n$ where n may be 2, 3, 4, or 5. In combination with hydrofluoric acid or other fluorides the hexafluoroantimonate(V) ion [17111-95-4], SbF_6^-, is formed. This is frequently used as a negative counterion for compounds containing rather unstable, highly oxidizing, or highly fluorinated cations. The $SbF_6{}^-$ anion has been shown to have an octahedral structure and may be hydrolyzed to $Sb(OH)_6{}^-$. Combinations of SbF_5, with either HSO_3F alone or with HSO_3F and SO_3, have extremely high acidities (23,24). A 1:1 mixture of HSO_3F and SbF_5 is frequently used for stabilization of carbocations and has been referred to as magic acid.

Treatment of graphite with SbF_5 liquid or vapor results in intercalation of SbF_5 between the graphite layers, and at 70°C a blue-black solid, antimony graphite fluoride [56126-99-9], $C_{13}Sb_2F_{10}$, is formed (25). This modifies the fluorinating properties of SbF_5, and such materials are used as specific fluorinating agents. Several mixed pentahalides are known. Thus fluorination of $SbCl_3$ yields antimony trichloride difluoride [31244-70-9], $SbCl_3F_2$, and chlorination of SbF_3 gives antimony dichloride trifluoride [7791-16-4], $SbCl_2F_3$. The latter compound has been shown to consist of $SbCl_4{}^+$ and $Sb_2Cl_2F_9{}^-$ (26).

Antimony pentafluoride is used as a catalyst in conjunction with IF_5 for the production of telomers, used in stain resistant products. Antimony pentafluoride is a powerful oxidizer and also a moderate fluorinating reagent, capable of fluorinating PCl_3, $SiCl_4$ and WCl_6 to PF_3, SiF_4, and WF_6. It has been used extensively in conjunction with HSO_3F or solutions of SO_3 in HSO_3F to produce "super acid" systems. Alkenes react to form stable carbocations by SbF_5, either neat or in Freon 113. Neat SbF_5 is capable of converting aldehydes to oxocarbonium ions, RCO^+. Antimony pentafluoride yields intercalation compounds when combined with graphite. The resulting material is a black powder that is relatively stable to moisture. It is useful for the exchange of fluorine with organic chloride (27).

2.10. Antimony Pentachloride. Antimony(V) chloride [7647-18-9], $SbCl_5$, is a colorless, hygroscopic, oily liquid that is frequently yellow because of the presence of dissolved chlorine; it cannot be distilled at atmospheric pressure without decomposition, but the extrapolated normal boiling point is 176°C. In the solid, liquid, and gaseous states it consists of trigonal bipyramidal molecules with the apical chlorines being somewhat further away than the equatorial chlorines (20).

Antimony pentachloride is usually prepared by chlorination of molten $SbCl_3$. It undergoes partial dissociation to Cl_2 and $SbCl_3$; ΔH_{496} for this equilibrium is -76.69 kJ/mol (-18.33 kcal/mol) and ΔS_{496} is -145 J/mol (-34.7 cal/mol) (28).

Antimony pentachloride is a strong Lewis acid and a useful chlorine carrier. Chlorine is lost in a number of chemical reactions resulting in the formation of adducts. Thus iodine is chlorinated to form ICl, which in turn combines with additional $SbCl_5$ to give $SbCl_5{\cdot}2ICl$ and $SbCl_5{\cdot}3ICl$. A similar reaction occurs with sulfur, giving $SbCl_5{\cdot}SCl_4$. These adducts are listed in Table 2. In the presence of excess hydrochloric acid or metal chlorides the hexachloroantimonate(V) ion [17949-89-2], $SbCl_6{}^-$, is formed. The strong acid, $HSbCl_6{\cdot}4.5H_2O$, as well as many hexachloroantimonate salts can be isolated. With a 1:1 mol ratio of water to $SbCl_5$, antimony pentachloride monohydrate [14215-03-3], $SbCl_5{\cdot}H_2O$, which is insoluble in $CHCl_3$, is formed; with a 4:1 mol ratio, chloroform soluble antimony pentachloride tetrahydrate [52940-44-0], $SbCl_5{\cdot}4H_2O$, can be isolated. Numerous examples can be cited where the Lewis acid $SbCl_5$ forms 1:1 adducts with oxygen- and nitrogen-containing bases, eg, sulfur nitride, ethers, nitriles, alcohols, or esters. Some of these are given in Table 2.

2.11. Antimony Trisulfide. Antimony(III) sulfide (antimony sesquisulfide) [1345-04-6], SbS_3, exists as a black crystalline solid, stibnite [1317-86-8], and as an amorphous red to yellow-orange powder. Stibnite melts at 550°C and has $\Delta H^\circ_{f,298}$, -175 kJ/mol (-41.8 kcal/mol)); S°_{298}, 182 J/(182 mol·K) [43.5 cal/(43.5 mol·K)]; for the amorphous solid $\Delta H^\circ_{f,298}$ is -147 kJ/mol (-35.1 kcal/mol) (29). The crystal structure of stibnite contains two distinctly different antimony sites and consists of two parallel Sb_4S_6 chains that are linked together to form crumpled sheets (two per unit cell).

Amorphous Sb_2S_3 can be prepared by treating an $SbCl_3$ solution with H_2S or with sodium thiosulfate, or by heating metallic antimony or antimony trioxide with sulfur. Antimony trisulfide is almost insoluble in water but dissolves in concentrated hydrochloric acid or in excess caustic. In the absence of air, Sb_2S_3 dissolves in alkaline sulfide solutions to form the thioantimonate(III) ion [43049-98-5]; SbS_2^-, in the presence of air the tetrathioantimonate(V) ion [17638-29-8], SbS_4^{3-}, is formed. The lemon-yellow crystalline salt, $Na_3SbS_4{\cdot}9H_2O$, known as Schlippe's salt [1317-86-8], contains the tetrahedral tetrathioantimonate(V) ion.

Antimony trisulfide is used in fireworks, in certain types of matches, as a pigment, and in the manufacture of ruby glass.

2.12. Antimony Pentasulfide. Antimony pentasulfide [1315-04-4], Sb_2S_5, is a yellow to orange to red amorphous solid of indefinite composition. It is frequently given the formula Sb_2S_5, but actually consists of Sb(III) with a variable quantity of sulfur (30). The product is prepared commercially by the conversion of Sb_2S_3 to tetrathioantimonate(V) by boiling with sulfur in alkaline solution. The antimony pentasulfide is liberated as a yellowish orange precipitate when the resulting mixture is acidified with hydrochloric acid.

The product is commercially known as golden sulfide of antimony, and is used in vulcanization to produce a red variety of rubber. The material is also used as a pigment and in fireworks.

2.13. Antimony(III) Salts. Concentrated acids dissolve trivalent antimony compounds. From the resulting solutions it is possible to crystallize normal and basic salts, eg, antimony(III) sulfate [7446-32-4], $Sb_2(SO_4)_3$; antimonyl sulfate [14459-74-6], $(SbO)_2SO_4$; antimony(III) phosphate [12036-46-3], $SbPO_4$; antimony(III) acetate [6923-52-0], $Sb(C_2H_3O_2)_3$; antimony(III) nitrate [20328-96-5], $Sb(NO_3)_3$; and antimony(III) perchlorate trihydrate [65277-48-7], $Sb(ClO_4){\cdot}3H_2O$. The normal salts all hydrolyze readily.

2.14. Hexafluoroantimonates. Hexafluoroantimonic acid [72121-43-8], $HSbF_6 \cdot 6H_2O$, is prepared by dissolving freshly prepared hydrous antimony pentoxide in hydrofluoric acid or adding the stoichiometric amount of 70% HF to SbF_5. Both of these reactions are exothermic and must be carried out carefully.

The superacid systems $HSO_3F \cdot SbF_5$ [33843-68-4] and $HF \cdot SbF_5$ [16950-06-4] (fluoroantimonic acid) are used in radical polymerization (31) and in carbocation chemistry (32). Addition of SbF_5 drastically increases the acidities of HSO_3F and HF (33,34).

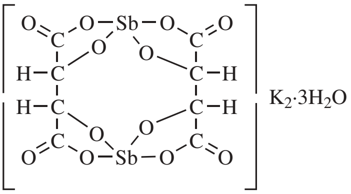
Anhydrous salts, $MSbF_6$, where $M = H$, NH_4, and alkali metal, and $M(SbF_6)_2$, where M is an alkaline-earth metal, can be prepared by the action of F_2 on MF or MF_2 and SbF_3 (35) by the oxidation of Sb(III) with H_2O_2 or alkali metal peroxide in HF (36), by the action of HF on a miture of $SbCl_5$ and MF where $M = NH_4$, Li, Na, K, Ru, Cs, Ag, and T1 (37). These compounds can be used as photoinitiators for the production of polymers (38).

2.15. Compounds Containing Sb–O–C or Sb–S–C Linkages. A large number of compounds have been prepared in which the antimony atom is linked to carbon through an oxygen or sulfur atom. The simplest of these compounds are esters of the hypothetical antimonic acid [13453-11-7], H_3SbO_3, or thioantimonic acid [65277-44-3], H_3SbS_3. The esters of H_3SbO_3 can be prepared by refluxing antimony trioxide with the appropriate alcohol and removing the water formed by means of anhydrous copper sulfate. They may also be obtained by ester exchange. For example, tributyl antimonate [2155-74-0], $C_{12}H_{27}O_3Sb$, is formed by the interaction of the triethyl ester, triethyl antimonate [10433-06-4], $C_6H_{15}O_3Sb$, and butyl alcohol. Esters of thioantimonic(III) acid are easily synthesized by the reaction of antimony trichloride and a mercaptan. A series of these thioantimonic esters have been prepared in the search for compounds of medicinal value (39).

By far the largest group of compounds containing the Sb−O−C linkage are those obtained by reaction of an antimony oxide with an α-hydroxy acid, *o*-dihydric phenol, sugar alcohol, or some other polyhydroxy compound containing at least two adjacent hydroxyl groups. The best known compound of this type is antimony potassium tartrate (tartar emetic) [28300-74-5] prepared by refluxing potassium hydrogen tartrate with freshly precipitated antimony trioxide.

Tartar emetic has been used as an antiparasitic agent in medicine, as an insecticide, and as a mordant in the textile and leather industries.

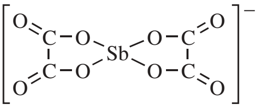
Tartar emetic was the subject of controversy for many years, and a variety of incorrect structures were proposed. In 1966, x-ray crystallography showed that tartar emetic contains two antimony(III) atoms bridged by two tetranegative D-tartrate residues acting as double bidentate ligands to form dipotassium bis[D-μ-(2,3-dihydroxybutanedioato)]diantimonate [28300-74-5] (40).

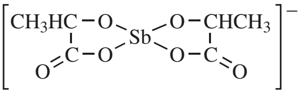


The four 5-membered chelate rings are nearly planar, and the oxygen atoms about the antimony atoms occupy four corners of a distorted square pyramid, the apex of which is presumably occupied by an unshared electron pair. Later work (41) has also shown that the three water molecules in the structure are hydrogen bonded to each other and to the carboxyl oxygen atoms and they connect the anions in infinite sheets. Essentially the same tartrato-bridged binuclear anion has been found in the racemic salts $(NH_4)_2Sb_2(\text{D,L-}C_4H_2O_6)_2 \cdot 4H_2O$ (42) and $K_2Sb_2(\text{D,L-}C_4H_2O^6)_2 \cdot 3H_2O$ (43), and in the ammonium (44) and the tris(*o*-phenanthroline)iron(II) (45) analogues of tartar emetic. It has been suggested that the formation of a bridged *meso*-tartrato dimer of antimony(III) requires an unfavorable eclipsed conformation for the bridging ligands (46), as*meso*-tartrate complexes similar to tartar emetic have never been prepared.

Two five-membered chelate rings per antimony atom are present in antimony hydrogen bis(thioglycolate) [65277-45-4], $C_4H_7O_4S_2Sb$, a compound prepared by the interaction of antimony trioxide and thioglycolic acid in aqueous solution (47). The coordination around the antimony has been described as a distorted trigonal bipyramid in which the two axial apices are occupied by oxygen atoms, and two of the equatorial apices are occupied by sulfur atoms. The third equatorial position is presumably occupied by an unshared electron pair which is responsible for the deformation of the bipyramid. Each unit of antimony hydrogen bis(thioglycolate) is joined to two other units by hydrogen bonds, forming endless zig-zag chains.

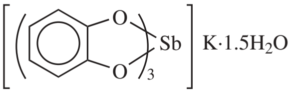
Lactic, malic, mandelic, and oxalic acids also give antimony(III) derivatives in which two molecules of acid are associated with one atom of antimony. Studies of the reaction between antimony trioxide and lactic or oxalic acid as a function of pH have suggested the following structures for the oxalate and lactate complexes (48,49).





The reaction of toluene-3,4-dithiol(3,4-dimercaptotoluene) and antimony trichloride in acetone yields a yellow solid $Sb_2(tdt)_3$, where tdt is the toluene-3,4-dithiolate anionic ligand (50). With the disodium salt of maleonitriledithiol ((*Z*)-dimercapto-2-butenedinitrile), antimony trichloride gives the complex ion $[Sb(mnt)_2]^-$, where mnt is the maleonitriledithiolate anionic ligand. This complex has been isolated as a yellow, crystalline, tetraethylammonium salt. The structures of these antimony dithiolate complexes have apparently not been unambiguously determined.

Antimony pentoxide also reacts with a variety of dihydroxy compounds. Thus pyrocatechol yields a crystalline substance in which three molecules of the diol are associated with one atom of antimony (51). The configuration of this substance has not been established, but the following structure seems reasonable:



A number of complex derivatives of antimony pentoxide with polyhydroxy compounds have been investigated as drugs. The most important of these substances is known as antimony sodium gluconate [16037-91-5], $C_{12}H_{20}O_{17}Sb_2 \cdot 9H_2O \cdot 3Na$, which is prepared by the reaction of antimony pentoxide, gluconic acid, and sodium hydroxide (52).

3. Organoantimony Compounds

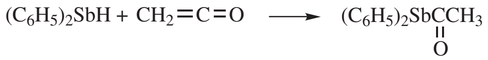
A wide variety of compounds containing the Sb–C bond is known. Organoantimony compounds can be broadly divided into Sb(III) and Sb(V) compounds. The former may contain from one to four organic groups, and the Sb(V) compounds from one to six organic groups. With a few exceptions, the nomenclature used here is that proposed by the International Union of Pure and Applied Chemistry (53). There are a number of heterocyclic compounds in which one or more antimony atoms are members of the heterocycle. Such compounds have been thoroughly discussed (54). A more recent but less comprehensive report on heterocyclic antimony compounds has also been published (55). The synthesis of organoantimony compounds has been described (56). Organoantimony(III) compounds (57) and organoantimony(V) compounds containing four, five, or six C−Sb bonds (57) and three C−Sb bonds (57), respectively, have been summarized, and a summary of organoantimony(V) compounds containing one, two, or three C−Sb bonds has also been published (58). Two lists of all organoantimony compounds prepared or studied between 1937 and 1968 have been published (59). Another monograph, published in 1970, critically discusses organoarsenic, -antimony, and -bismuth chemistry (60). Work on organoantimony compounds is reviewed annually, and the use of organoantimony and organobismuth compounds in organic synthesis has been reviewed (61).

3.1. Primary and Secondary Stibines. Relatively few primary ($RSbH_2$) and secondary (R_2SbH) stibines are known. Methylstibine [23362-09-6], CH_5Sb, ethylstibine [68781-03-3], C_2H_7Sb, isopropylstibine, C_3H_9Sb, and butylstibine [68781-04-4], $C_4H_{11}Sb$, have been prepared by the reduction of the corresponding alkyldichlorostibines using lithium aluminum hydride or sodium borohydride (62). All of the alkylstibines are thermally unstable, easily oxidizable, colorless liquids with strong alliaceous odors. Decomposition products include hydrogen and nonvolatile black solids analyzing for $(RSb)_x$. Reaction of the alkylstibines with hydrogen chloride produces lustrous, pale green polymeric solids also analyzing for $(RSb)_x$ (63). Diethylstibine, $C_4H_{11}Sb$, (64), di-*tert*-butylstibine, $C_8H_{19}Sb$, (65), and dicyclohexylstibine [1011-94-5], $C_{12}H_{23}Sb$, (66) have been obtained by reduction of the corresponding dialkylhalostibines with lithium aluminum hydride. Dimethylstibine [23362-10-9], C_2H_7Sb, was first prepared by the interaction of dimethylbromostibine [53234-94-9], C_2H_6BrSb, and $LiHB(OCH_3)_2$ at temperatures below −40°C (67). Treatment of dimethylstibine with hydrogen chloride yields hydrogen:

$$(CH_3)_2SbH + HCl \longrightarrow H_2 + (CH_3)_2SbCl$$

Phenylstibine [58266-50-5], C_6H_7Sb, has been obtained by the reduction of phenyldiiodostibine [68972-61-2], $C_6H_5I_2Sb$, (68) or phenyldichlorostibine [5035-52-9], $C_6H_5Cl_2Sb$, (69) with lithium borohydride. It has also been prepared by the hydrolysis or methanolysis of phenylbis(trimethylsilyl)stibine [82363-95-9], $C_{12}H_{23}Si_2Sb$ (70). Diphenylstibine [5865-81-6], $C_{12}H_{11}Sb$, can be prepared by the interaction of diphenylchlorostibine [2629-47-2], $C_{12}H_{10}ClSb$, with either lithium borohydride (71) or lithium aluminum hydride (72). It is also formed by hydrolysis or methanolysis of diphenyl(trimethylsilyl) stibine [69561-88-2], $C_{15}H_{19}SbSi$ (70). Dimesitylstibine [121810-02-4] has been obtained by the protonation of lithium dimesitylstibide with trimethylammonium chloride (73). The x-ray crystal structure of this secondary stibine has also been reported.

The aromatic primary and secondary stibines are readily oxidized by air, but they are considerably more stable than their aliphatic counterparts. Diphenylstibine is a powerful reducing agent, reacting with many acids to liberate hydrogen (74). It has also been used for the selective reduction of aldehydes and ketones to the corresponding alcohols (75). At low temperatures, diphenylstibine undergoes an addition reaction with ketene (76):



$$(C_6H_5)_2SbH + CH_2{=}C{=}O \longrightarrow (C_6H_5)_2Sb\underset{\underset{O}{\|}}{C}CH_3$$

3.2. Tertiary Stibines.

A large number of trialkyl- and triarylstibines are known (57). They are usually prepared by the interaction of a reactive organometallic compound and an antimony trihalide, a halostibine, or a dihalostibine. The type of organometallic compound most widely employed in these syntheses is the Grignard reagent (77,78). Organolithium (79,80), organocadmium (81,82), organoaluminum (83), and organomercury (84) compounds have also been used. Triarylstibines can be readily prepared from an aryl halide, an antimony trihalide, and sodium (85).

Another excellent method for preparing tertiary stibines involves the interaction of an organostibide and an alkyl or aryl halide (86,87). This method is of particular value in preparing unsymmetrical tertiary stibines. For example, an interesting hybrid ligand has been obtained by the following reaction carried out in liquid ammonia (88):

$$CH_3SeC_6H_4Br + NaSb(CH_3)_2 \longrightarrow CH_3SeC_6H_4Sb(CH_3)_2 + NaBr$$

Trialkylstibines are sensitive to oxygen, and in some cases they ignite spontaneously in air. Trimethylstibine [594-10-5], C_3H_9Sb, may explode on contact with atmospheric oxygen (89). Triarylstibines usually do not react with air, and they are quite stable thermally (90). Trialkylstibines are powerful reducing agents and can convert halides of phosphorus or antimony to the corresponding elements (91). Triarylstibines are much less reactive as reducing agents, but they are readily oxidized by halogens, interhalogens, pseudohalogens, sulfur, and fuming nitric acid (92,93).

Tertiary stibines have been widely employed as ligands in a variety of transition metal complexes (94), and they appear to have numerous uses in synthetic organic chemistry (61), eg, for the olefination of carbonyl compounds (95). They have also been used for the formation of semiconductors by the metal–organic chemical vapor deposition process (96), as catalysts or cocatalysts for a number of polymerization reactions (97), as ingredients of light-sensitive substances (98), and for many other industrial purposes.

3.3. Halostibines, Dihalostibines, and Related Compounds.

Alkyldichloro- and alkyldibromostibines are readily prepared by the alkylation of the corresponding antimony trihalide with an organolead reagent (62,99):

$$R_4Pb + 3\ SbX_3 \longrightarrow 3\ RSbX_2 + PbX_2 + RX$$

The alkylation can also be accomplished using tetraalkyltin compounds. Alkyldiiodostibines are formed in about 20% yield via the interaction of alkylmagnesium iodides and antimony trichloride (62). Dialkylchlorostibines are obtained in good yields by the cleavage of tetraalkyldistibines using sulfuryl chloride (86):

$$R_2SbSbR_2 + SO_2Cl_2 \longrightarrow 2\ R_2SbCl + SO_2$$

Dialkylbromo- and dialkyliodostibines can similarly be prepared by the cleavage of tetraalkyldistibines using equimolar amounts of bromine or iodine (X_2) (100):

$$R_2SbSbR_2 + X_2 \longrightarrow 2\ R_2SbX$$

The thermal decomposition of trialkylantimony dihalides has been used for the preparation of chloro-, bromo-, and iodostibines (101):

$$R_3SbX_2 \xrightarrow{\Delta} R_2SbX + RX$$

The interaction of triarylstibines and antimony trichloride or tribromide is a convenient and efficient method for preparing aryldihalo- and diarylhalostibines (99,102,103):

$$Ar_3Sb + 2\ SbX_3 \longrightarrow 3\ ArSbX_2$$

$$2\ Ar_3Sb + SbX_3 \longrightarrow 3\ Ar_2SbX$$

Compounds $ArSbX_2$ and Ar_2SbX, in which X is Cl or Br and Ar is an aryl group, have also been obtained by the reduction of the corresponding stibonic or stibinic acids in hydrochloric or hydrobromic acid. The usual reducing agent is sulfur dioxide catalyzed by iodide ion, although stannous chloride has also been employed (104). The reduction of unsymmetrical diarylantimony trihalides is probably the best method for the synthesis of unsymmetrical chloro- and bromostibines (105). Aryldiiodostibines can be prepared by the reaction of the corresponding oxides with hydriodic acid (106):

$$\frac{1}{x}\,(ArSbO)_x + 2\ HI \longrightarrow ArSbI_2 + H_2O$$

Diaryliodostibines are usually obtained by the metathetical reaction of the chlorostibines with sodium iodide (106,107). Diphenylfluorostibine [6651-55-4], $C_{12}H_{10}FSb$, can be prepared from an organosilicon species (108):

$$2\ (NH_4)_2(C_6H_5SiF_5) + SbF_3 \longrightarrow (C_6H_5)_2SbF + 2\ (NH_4)_2SiF_6$$

Alkyldihalo- and dialkylhalostibines are highly reactive substances which are rapidly oxidized in air. Some are spontaneously inflammable (109). The aromatic counterparts are less susceptible to air oxidation but are readily oxidized by halogens. Alkaline hydrolysis (104,110,111) of the dihalo- and halostibines yields compounds of the types $(RSbO)_x$ and $R_2SbOSbR_2$, respectively, whereas reaction of the stibine with sodium sulfide (110) gives the analogous sulfur compounds. An interesting method for obtaining the bis(diarylantimony) oxides is by thermal disproportionation of the corresponding polymeric oxides (104,112):

$$\frac{4}{x}\,(\mathrm{ArSbO})_x \longrightarrow (\mathrm{Ar_2Sb})_2\mathrm{O} + \mathrm{Sb_2O_3}$$

A number of compounds of the types $RSbY_2$ and R_2SbY, where Y is an anionic group other than halogen, have been prepared by the reaction of dihalo- or halostibines with lithium, sodium, or ammonium alkoxides (113,114), amides (115), azides (116), carboxylates (117), dithiocarbamates (118), mercaptides (119,120), or phenoxides (113). Dihalo- and halostibines can also be converted to compounds in which an antimony is linked to a main group (121) or transition metal (122).

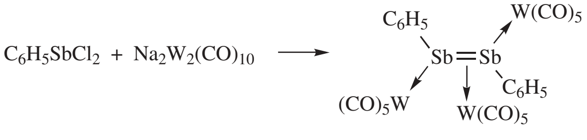
3.4. Distibines and Distibenes.

A considerable number of tetraalkyl- and tetraaryldistibines have been investigated. These are usually obtained by the reduction of a dialkyl- or diarylhalostibine with sodium hypophosphite (106,107) or magnesium (103,111). Distibines can also be prepared by the treatment of a metal dialkyl- or diarylstibide with a 1,2-dihaloethane (65,66,72,86, 123)

$$2\,\mathrm{R_2SbM} + \mathrm{XCH_2CH_2X} \longrightarrow \mathrm{R_2SbSbR_2} + \mathrm{CH_2{=}CH_2} + 2\,\mathrm{MX}$$

whereM = Li, Na, or K and X = Cl or Br. Distibines undergo a variety of interesting reactions (64–67,80,100,103,106) and have also attracted attention because a number of these substances are thermochromic (80,123,124).

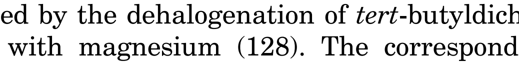
Although distibenes, the antimony analogues of azo compounds, have never been isolated as free, monomeric molecules (125), a tungsten complex, tritungsten pentadecacarbonyl[μ_3-η^2-diphenyldistibene] [82579-41-7], $C_{27}H_{10}O_{15}Sb_2W_3$, has been prepared by the reductive dehalogenation of phenyldichlorostibine (126):



As expected, the Sb–Sb bond distance in this complex is significantly shorter than the Sb–Sb single bond distance. Chromium and tungsten complexes of dialkyldistibines have also been isolated (127).

3.5. Cyclic and Polymeric Substances Containing Antimony–Antimony Bonds.

A number of organoantimony compounds containing rings of four, five, or six antimony atoms have been prepared. The first such compound to be adequately characterized, tetrakis-1,2,3,4-*tert*-butyltetrastibetane [47191-73-5], $C_{16}H_{36}Sb_4$, was obtained by the interaction of a dialkylstibide and iodine (65):

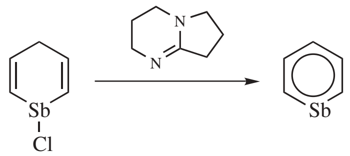


It has been prepared by the dehalogenation of *tert*-butyldichlorostibine [67877-43-4], $C_4H_9Cl_2Sb$, with magnesium (128). The corresponding five-membered ring compound, (*tert*-$C_4H_9Sb)_5$, is also formed in this reaction, but it has not yet been isolated in pure form (129). A tristibirane can also be formed by the dehalogenation of a dichlorostibine, but this substance has likewise been obtained only in admixture with a tetrastibetane (130). Compounds containing rings of six antimony atoms have been prepared by the slow air oxidation of bis(trimethylsilyl)phenylstibine [82363-95-9], $C_{12}H_{23}SbSi_2$, dissolved in 1,4-dioxane, benzene, or toluene (131):

$$6\ C_6H_5Sb\left[Si(CH_3)_3\right]_2 + 3\ O_2 + \text{solvent} \longrightarrow (C_6H_5Sb)_6\cdot\text{solvent} + 6\ \left[(CH_3)_3Si\right]_2O$$

Polymeric substances, $(RSb)_x$ or $(ArSb)_x$, have been obtained by the decomposition of primary stibines (62,69), the reaction of primary stibines with hydrogen chloride (63), the treatment of primary stibines with dibenzylmercury (132), or the reduction of dihalostibines (133–135). Most of these polymers have not been well characterized.

3.6. Antimonin and its Derivatives. Antimonin(stibabenzene) [289-75-8], C_5H_5Sb, the antimony analogue of pyridine, can be prepared by the dehydrohalogenation of a cyclic chlorostibine using 1,5-diazabicyclo[4.3.0]non-5-ene (136):



A number of derivatives of antimonin are also known (136,137). The potential aromaticity of this ring system has aroused considerable interest and has been investigated with the aid of spectroscopy as well as *ab initio* molecular orbital calculations (138). There seems to be no doubt that antimonin does possess considerable aromatic character.

3.7. Stibonic and Stibinic Acids. The stibonic acids, $RSbO(OH)_2$, and stibinic acids, $R_2SbO(OH)$, are quite different in structure from their phosphorus and arsenic analogues. The stibonic and stibinic acids are polymeric compounds of unknown structure and are very weak acids. IUPAC classifies them as oxide hydroxides rather than as acids. Thus $C_6H_5SbO(OH)_2$ is named phenylantimony dihydroxide oxide [535-46-6]; the *Chemical Abstracts* name is dihydroxyphenylstibine oxide [535-46-6], $C_6H_7O_3Sb$.

Methylstibonic acid, the only alkylstibonic acid known with certainty, was not reported until 1990 (139). Previous attempts to obtain alkylstibonic acids were unsuccessful (139). The methyl compound was prepared by two methods, the hydrolysis of a tetraalkoxymethylantimony compound or the oxidation of dimethoxymethylstibine [54553-25-2], $C_3H_9O_2Sb$, with hydrogen peroxide:

$$CH_3Sb(OR)_4 + 3\ H_2O \xrightarrow[0^\circ C]{CH_2Cl_2} CH_3SbO_3H_2 + 4\ ROH$$

$$CH_3Sb(OCH_3)_2 + H_2O_2 + H_2O \longrightarrow CH_3SbO_3H_2 + 2\ CH_3OH$$

Dialkylstibinic acids can be readily prepared. The preferred method is the aqueous hydrolysis of trialkoxydialkylantimony compounds (140):

$$R_2Sb(OR')_3 + 2\ H_2O \longrightarrow R_2SbO(OH) + 3\ R'OH$$

Dimethylstibinic acid [35952-95-5], $C_2H_7O_2Sb$, diethylstibinic acid [35952-96-6], $C_4H_{11}O_2Sb$, dipropylstibinic acid [35952-97-7], $C_6H_{15}O_2Sb$, and dibutylstibinic acid [35952-98-8], $C_8H_{19}O_2Sb$, have been prepared in this manner. Except for the dimethyl compound, they can be readily recrystallized from organic solvents.

Aromatic stibonic acids are readily prepared by the diazo reaction:

$$ArN_2Cl + SbCl_3 \longrightarrow ArSbCl_4 + N_2$$

$$ArSbCl_4 + 3\ H_2O \longrightarrow ArSbO(OH)_2 + 4\ HCl$$

where Ar represents aryl. The arylstibonic acids prepared by this procedure are invariably contaminated with inorganic antimony compounds. Purification is usually effected by dissolving the crude product in hydrochloric acid and adding ammonium chloride or an amine hydrochloride, whereupon crystalline salts of the type $[R_4N][ArSbCl_5]$ separate from solution. These may be recrystallized and then hydrolyzed to the pure stibonic acids. The diarylstibinic acids are also usually prepared by the diazo reaction by substituting an aryldihalostibine for antimony trichloride:

$$ArN_2Cl + Ar'SbCl_2 \longrightarrow ArAr'SbCl_3 + N_2$$

$$ArAr'SbCl_3 + 2\ H_2O \longrightarrow ArAr'SbO(OH) + 3\ HCl$$

Diphenylstibinic acid [22811-63-8], $C_{12}H_{11}O_2Sb$, can be readily prepared in good yield from triphenylstibine by an oxidative cleavage reaction in which the stibine is heated with alkali and hydrogen peroxide (141). Stibonic and stibinic acids have had few industrial uses. A patent covering the use of stibonic or stibinic acids as catalysts for the condensation-polymerization of ethylene glycol and terephthalic acid has been issued (142). Another patent describes the use of diphenylstibinic acid as a cocatalyst with triisobutylaluminum for the polymerization of epichlorohydrin (143). The use of stibonic acids as catalysts for the epoxidation of alkenes by hydrogen peroxide is the subject of another patent (144). Anhydrides of arylstibonic acids, $(ArSbO_2)_n$, obtained by heating stibonic acids *in vacuo* at 100°C, have proved to be effective catalysts for the polymerization of oxiranes (145).

3.8. Stibine Oxides and Related Compounds. Both aliphatic and aromatic stibine oxides, R_3SbO, or their hydrates, $R_3Sb(OH)_2$, are known. Thus both dihydroxotrimethylantimony [19727-41-4], $C_3H_{11}O_2Sb$, and trimethylstibine oxide [19727-40-3], C_3H_9OSb, have been prepared. The former may be readily obtained by passing an aqueous solution of dichlorotrimethylantimony [13059-67-1], $C_3H_9Cl_2Sb$, through an anionic-exchange resin (146). When heated to 110°C, the dihydroxy compound loses one mole of water to form the oxide. Aliphatic stibine oxides containing larger alkyl groups have been obtained by oxidation of tri-alkylstibines using mercury(II) oxide (147). The trialkylstibine oxides are hygroscopic crystalline solids. Molecular weights in solution are usually two to three times the values calculated for monomeric structures. The Mössbauer spectrum of trimethylstibine oxide was consistent with a trigonal-bipyramidal structure having three methyl groups in equatorial positions (148). The use of dihydroxotrimethylantimony as a catalyst for the epoxidation of alkenes by aqueous hydrogen peroxide has been the subject of a patent (149).

The structure of triphenylstibine oxide [4756-75-6], $C_{18}H_{15}OSb$, has been the subject of considerable controversy. Apparently it can exist in two different forms; as prismatic crystals, mp 221–222°C, and as an amorphous powder. The structure of the crystalline form was shown by x-ray diffraction to be a dimer containing a planar four-membered ring with Sb–O–Sb bonds (150,151). It can be prepared by a number of synthetic methods including the thermal decomposition of hydroxotetraphenylantimony [19638-16-5], $C_{24}H_{21}OSb$, (152) or methoxotetraphenylantimony [14090-94-9], $C_{25}H_{23}OSb$ (153). The amorphous form of triphenylstibine oxide, termed poly(triphenylstibine oxide) [36562-85-3], $(C_{18}H_{15}OSb)_x$, is insoluble in water and in organic solvents; its structure is unknown. A number of papers have been published on the use of triphenylstibine oxide as a catalyst for various reactions which may be of considerable commercial value. It has been used as a catalyst for the condensation of diamines and carbon dioxide to form cyclic urea compounds (153), for the ring-opening polymerization of ethylene oxide or propylene oxide (154), and for the formation of 2-oxazolidinones from carbon dioxide and 2-aminoalcohols (155). It has been claimed that triphenylstibine oxide and triphenylstibine sulfide are of value as catalyst modifiers in the polymerization of propene by Ziegler catalysts (156,157), and a number of patents have been issued on the use of the oxide as a catalyst in various industrial processes. In addition to triphenylstibine oxide, other triarylstibine oxides have been synthesized by the oxidation of the corresponding triarylstibines with hydrogen peroxide (158). Dihydroxotriphenylantimony [896-29-7], $C_{18}H_{17}O_2Sb$, has been reported a number of times in the chemical literature. There has been, however, no investigation utilizing analytical instrumental techniques on this compound. Dihydroxotris(2,4,6-trimethylphenyl)antinomy [113002-54-3], $C_{27}H_{35}O_2Sb$, is the only compound of this class, the structure of which has been confirmed by x-ray diffraction (158).

Both trialkyl- and triarylstibine sulfides and selenides are known. Trimethylstibine sulfide [15082-93-6], C_3H_9SSb, has been prepared from trimethylstibine oxide and hydrogen sulfide (159). It is monomeric in benzene and chloroform. Trialkylstibine sulfides and selenides have been prepared from trialkylstibines and sulfur or selenium, respectively (160). Unlike triphenylstibine oxide, the structure of triphenylstibine sulfide is tetrahedral, as shown by both Mössbauer and x-ray diffraction studies (148). A patent covering the synergistic use of triphenylstibine sulfide with aromatic amines as antioxidants in lubricating oils has been issued (161).

3.9. Pentacovalent Antimony Halides and Related Compounds. Antimony halides of the types $RSbX_4$, R_2SbX_3, R_3SbX_2, and R_4SbX, where X is a halogen, are known, but compounds of the first type have only been isolated and characterized where R is aryl. Tetrachloromethylantimony has been prepared at

$-70°C$, but not isolated (162):

$$CH_3SbCl_2 + SO_2Cl_2 \xrightarrow{-70°C} CH_3SbCl_4 + SO_2$$

$$CH_3SbCl_4 + (CH_3)_4NN_3 \xrightarrow{-70°C} [CH_3SbCl_4N_3]\,[(CH_3)_4N]$$

The aryl compounds are unstable substances which decompose on standing and are hydrolyzed in moist air. The chlorides are readily prepared by the action of hydrochloric acid on the corresponding arylstibonic acids. Tetraacetatophenylantimony [116122-86-27], $C_{14}H_{17}O_8Sb$, has been prepared:

$$C_6H_5SbCl_2 + SO_2Cl_2 + 4\,Ag(O_2CCH_3) \xrightarrow{CH_2Cl_2} C_6H_5Sb(O_2CCH_3)_4 + 4\,AgCl + SO_2$$

The Sb atom in this tetraacetato compound is hexacoordinate with three monodentate acetate groups and one symmetrically bonded bidentate acetate group.

Both dialkyl- and diaryltrihaloantimony compounds are known, although only a few dialkyl compounds have been described. The trichlorides have been obtained by the chlorination of either dialkylchlorostibines (163) or tetraalkyldistibines (164) with sulfuryl chloride. Dimethyltrichloroantimony [7289-79-4], $C_2H_6Cl_3Sb$, is dimeric in the solid state but is monomeric in solution (165). The dimer exists in two different forms, covalent and ionic (166). The covalent form contains bridging chlorine atoms; the ionic form possesses the structure $[(CH_3)_4Sb]\,[SbCl_6]$. The diaryl compounds, both symmetrical and unsymmetrical, are best prepared from a diazonium halide and an aryldihalostibine:

$$ArN_2Cl + Ar'SbCl_2 \longrightarrow ArAr'SbCl_3 + N_2$$

When a diazonium salt is allowed to react with antimony pentachloride or an aryltetrachloroantimony compound, the onium salts $[ArN_2][SbCl_6]$ or $[ArN_2]\,[Ar'SbCl_5]$, respectively, are formed. These can be decomposed in an organic solvent by the addition of a powdered metal such as iron or zinc, with the formation of a diaryltrichloroantimony compound:

$$2\,[ArN_2]\,[SbCl_6] + 3\,Fe \longrightarrow Ar_2SbCl_3 + 2\,N_2 + SbCl_3 + 3\,FeCl_2$$

This is known as the Nesmeyanov reaction. The trichloro compounds are somewhat more stable than the tetrachloro compounds and can usually be readily recrystallized. These are also formed from diarylstibinic acids and hydrochloric acid, and, because they usually possess sharp melting points, they can be used for the characterization of the corresponding stibinic acids. Trichlorodiphenylantimony [21907-22-2], $C_{12}H_{10}Cl_3Sb$, crystallizes from hydrochloric acid as trichlorophenylantimony monohydrate [18762-79-9], $(C_6H_5)_2SbCl_3{\cdot}H_2O$, but this readily loses water on heating to form the anhydrous trichloro compound which exists in the solid state as a dimer (167). The hydrate can also be prepared from $SbCl_5$ and $(C_6H_5)_4Sn$ (168). In addition to the trichlorides and tribromides, the mixed compounds, for example, dibromochlorodiphenylantimony [71191-19-0], $(C_6H_5)_2SbBr_2Cl$, and bromodichlorodiphenylantimony [71191-18-9],

$(C_6H_5)_2$-$SbBrCl_2$, have been prepared (169):

$$(C_6H_5)_2SbCl + Br_2 \xrightarrow[CH_2Cl_2]{-196^\circ C} (C_6H_5)_2SbBr_2Cl$$

$$(C_6H_5)_2SbBr + Cl_2 \xrightarrow[CH_2Cl_2]{-90^\circ C} (C_6H_5)_2SbBrCl_2$$

In contrast to the trichloro compound, these mixed halo compounds, as well as tribromodiphenylantimony [62170-61-0], $(C_6H_5)_2SbBr_3$, are monomeric in the solid state.

In addition to the trihalo compounds, triacetatodiphenylantimony [93833-20-6], $C_{18}H_{19}O_2Sb$, has been prepared (170):

$$(C_6H_5)_2SbCl_3 + 3\ Ag(O_2CCH_3) \longrightarrow (C_6H_5)_2Sb(O_2CCH_3)_3 + 3\ AgCl$$

The best known of the halides are the trialkyldihalo- and triaryldihaloantimony compounds. The dichloro, dibromo, and diiodo compounds are generally prepared by direct halogenation of the corresponding tertiary stibines. The difluoro compounds are obtained by metathasis from the dichloro or dibromo compounds and silver fluoride. The diiodo compounds are the least stable and are difficult to obtain in a pure state. The trialkyl- and triaryldichloro- and dibromoantimony compounds are all crystalline solids which are stable at room temperature that but decompose on heating:

$$R_3SbX_2 \xrightarrow{\Delta} R_2SbX + RX$$

The difluoro compounds, however, do not undergo this thermal decomposition.

Dichlorotriphenylantimony has been suggested as a flame retardant (171,172) and as a catalyst for the polymerization of ethylene carbonate (173). Dibromotriphenylantimony has been used as a catalyst for the reaction between carbon dioxide and epoxides to form cyclic carbonates (174) and for the oxidation of α-keto alcohols to diketones (175).

In addition to the trialkyldihalo- and triaryldihaloantimony compounds, mixed dihalo compounds such as chloroiodotriphenylantimony [7289-82-9], $(C_6H_5)_3SbClI$, have been reported (176). It has been shown, however, that such compounds disproportionate in solution to give a mixture of starting material plus products (177):

$$2\ R_3SbXY \leftrightarrows R_3SbX_2 + R_3SbY_2$$

Other trialkyl and triaryl compounds of the type R_3SbY_2, where Y is a pseudohalide or a group such as NO_3, ClO_4, or $\frac{1}{2}\,SO_4$, have been prepared. They are usually obtained from the dihalides by metathesis with a silver salt, eg:

$$R_3SbCl_2 + 2\ AgNO_3 \longrightarrow R_3Sb(NO_3)_2 + 2\ AgCl$$

Compounds of the type $R_3Sb(OSO_2R')_2$, and $R_3Sb(O_2CR')_2$, where R is an alkyl or an aryl group, have been prepared from a dihydroxide or oxide and the appropriate acid:

$$R_3Sb(OH)_2 + 2\ R'SO_3H \longrightarrow R_3Sb(OSO_2R')_2 + 2\ H_2O$$

$$(Ar_3SbO)_2 + 4\ R'CO_2H \longrightarrow 2\ Ar_3Sb(O_2CR')_2 + 2\ H_2O$$

Hydrolysis of trialkyl- and triaryldihaloantimony compounds generally leads to the isolation of compounds of the type $(R_3SbX)_2O$ rather than compounds of the type $R_3Sb(OH)X$. However, hydroxoiodobis(2,6-dimethylphenyl)antimony [112515-20-5], $(2,6(CH_3)_2C_6H_3)_2Sb(OH)I$, (178) and four cyclohexyl compounds have been prepared (179): chlorohydroxotricyclohexylantimony [85362-32-9], $C_{18}H_{34}ClOSb$, bromohydroxotricyclohexylantimony [85362-33-0], $C_{18}H_{34}BrOSb$, acetatohydroxotricyclohexylantimony [85362-34-1], $C_{20}H_{37}O_3Sb$, and hydroxonitratotricyclohexylantimony [85362-35-2], $C_{18}H_{34}NO_4Sb$.

Tetraalkyl and tetraaryl compounds, R_4SbX, are well-known and are often referred to as stibonium salts. There is evidence, however, that most of the tetraaryl compounds contain pentacovalent antimony. The perchlorate $[(C_6H_5)_4Sb](ClO_4)$, however, is ionic (180). The tetraalkyl halides are readily prepared by quaternization of the corresponding tertiary stibines:

$$R_3Sb + RI \longrightarrow R_4SbI$$

The tetraaryl compounds can be prepared by employing anhydrous aluminum chloride (181):

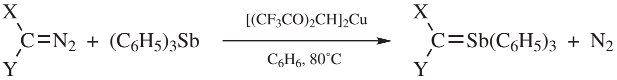
$$(C_6H_5)_3Sb + C_6H_5Cl \xrightarrow[230^\circ C]{AlCl_3} (C_6H_5)_4SbCl$$

Both the tetraalkyl and tetraaryl compounds can be prepared by cleavage of the corresponding pentaalkyl- or pentaarylantimony by a halogen or a hydrogen halide:

$$R_5Sb + HX \longrightarrow R_4SbX + RH$$

The cleavage of pentamethylantimony [15120-50-0], $C_5H_{15}Sb$, with HN_3, HCN, or HSCN gives the corresponding tetramethylantimony azides, cyanides, or thiocyanates (182); cleavage with one molecular equivalent of a carboxylic acid gives compounds of the type $(CH_3)_4SbO_2CR$ (183). Tetraphenylantimony iodide [13903-91-8], $C_{24}H_{20}ISb$, has been found to catalyze the condensation of oxetanes with carbon dioxide to give dioxanones (184) and the cycloaddition of oxiranes or oxetanes with diphenylketene to give γ- or δ-lactones (185).

3.10. Stibonium Ylids and Related Compounds. In contrast to phosphorus and arsenic, only a few antimony ylids have been prepared. Until quite recently triphenylstibonium tetraphenylcyclopentadienylide [15081-36-4], $C_{47}H_{35}Sb$, was the only antimony ylid that had been isolated and adequately characterized (186). A new method, utilizing an organic copper compound as a catalyst, has resulted in the synthesis of a number of new antimony ylids (187):



$$\overset{X}{\underset{Y}{C}}{=}N_2 + (C_6H_5)_3Sb \xrightarrow[C_6H_6,\ 80^\circ C]{[(CF_3CO)_2CH]_2Cu} \overset{X}{\underset{Y}{C}}{=}Sb(C_6H_5)_3 + N_2$$

Among the ylids prepared by this method are those in which X and Y are $C_6H_5SO_2$, $4{-}CH_3C_6H_4SO_2$, or CH_3CO or where X is CH_3CO and Y is C_6H_5CO. These ylids are solids, stable in a dry atmosphere, but readily hydrolyzed in protic solids by traces of moisture. Attempts to carry out the Wittig reaction with the stibonium ylids containing sulfonyl or carbonyl substituents, using highly reactive 2,4-dinitrobenzaldehyde as the substrate, were unsuccessful (188). Closely related to the ylids are imines of the type $R_3Sb{=}NR'$, where R is either an alkyl or an aryl group. The alkyl compounds, where R is ethyl or propyl and Ar is phenyl or 4-tolyl, have been prepared from trialkylstibines and arenesulfonyl azides (189):

$$R_3Sb + ArSO_2N_3 \longrightarrow R_3Sb{=}NSO_2Ar + N_2$$

The reaction of triphenylstibine with chloramine-T leads to the formation of a tosylimine (190):

$$(C_6H_5)_3Sb + CH_3C_6H_4SO_2N(Na)Cl \longrightarrow (C_6H_5)_3Sb{=}NSO_2C_6H_4CH_3 + NaCl$$

3.11. Organoantimony Compounds with Five Sb–C Bonds. A number of pentaalkyl- and pentaalkenylantimony compounds have been prepared from tetraalkyl- or tetraalkenylstibonium halides and alkyl or alkenyllithium or Grignard reagents, for example:

$$(CH_3)_4SbBr + CH_3Li \longrightarrow (CH_3)_5Sb + LiBr$$

Rather than using the stibonium halide, a trialkyl- or trialkenyldihaloantimony compound can be used, as in the preparation of pentavinylantimony [65277-46-5], $C_{10}H_{15}Sb$:

$$(CH{=}CH)_3SbBr_2 + 2\ CH_2{=}CHMgBr \longrightarrow (CH_2{=}CH)_5Sb + 2\ MgBr_2$$

Pentaarylantimony compounds can be readily prepared in a similar fashion:

$$(C_6H_5)_3SbF_2 + 2\ C_6H_5MgBr \longrightarrow (C_6H_5)_5Sb + MgBr_2 + MgF_2$$

Pentaphenylantimony [2170-05-0], $C_{30}H_{25}Sb$, has attracted considerable attention because it possesses square-pyramidal rather than the expected trigonal-bipyramidal geometry, both in the solid state and in solution. The cyclohexane solvate $(C_6H^5)^5Sb\cdot 1/2\,C_6H_{12}$ and penta-4-tolylantimony [51017-91-5], $C_{35}H_{35}Sb$, however, both possess trigonal-bipyramidal geometry. In addition to compounds of the type R_5Sb, mixed compounds of the type $R_4R'Sb$ or $R_3R'_2Sb$, where R and R′ may be alkyl, alkenyl, alkynyl, or aryl groups, are known. Thus triethyldimethylantimony [67576-92-5], $C_8H_{21}Sb$, has been prepared (191):

$$(C_2H_5)_3SbCl_2 + 2\ CH_3Li \xrightarrow[-10^\circ C]{(C_2H_5)_2O} (C_2H_5)_3Sb(CH_3)_2 + 2\ LiCl$$

Methyltetraphenylantimony [33756-93-3], $C_{25}H_{23}Sb$, is readily prepared (192):

$$(C_6H_5)_4SbF + CH_3MgBr \longrightarrow (C_6H_5)_4SbCH_3 + MgBrF$$

Compounds containing aryl and alkynyl groups have also been prepared (193):

$$Ar_3SbBr_2 + 2\ C_6H_5C{\equiv}CLi \longrightarrow Ar_3Sb(C{\equiv}CC_6H_5)_2 + 2\ LiBr$$

Antimony trioxide is the most important of the antimony compounds. It is used primarily in flame retardant formulations. These formulations uses include as retardants, in children's clothing, toys, aircraft, and automobile seat covers.

In 1999, production of antimony trioxide was 30.8×10^6 kg (68×10^6 lb). In 2003, production of flame retardants from antimony trioxide is expected to reach 34×10^6 kg (75×10^6 lb) (194).

Table 3 and 4 give United States import and export information on antimony oxide by country (29).

Table 3. **U.S. Exports of Antimony Oxide, by Country**[a]

	2000			2001		
Country	Gross weight, t	Antimony content, t[b]	Value × 10^3\$	Gross weight, t	Antimony content, t	Value, × 10^3\$
Argentina	115	95	302	83	69	272
Australia	128	106	254	72	60	145
Belgium	13	11	40	19	16	26
Brazil	98	81	386	277	230	727
Canada	1,730	1,440	3,930	1,380	1,140	3,240
China	134	111	264	11	9	112
Colombia	118	98	214	67	56	133
France	50	42	130	28	23	76
Germany	102	85	438	68	56	178
Indonesia	0	0	0	6	5	13
Italy	0	0	0	5	4	20
Japan	130	108	509	41	34	214
Korea, Republic of Mexico	55	46	135	15	12	38
	3,820	3,170	5,680	4,360	3,620	6,930
Singapore	77	64	158	74	61	225
Spain	48	40	181	56	46	237
Taiwan	29	24	78	20	17	53
Turkey	62	51	189	83	69	239
United Kingdom	402	334	834	194	161	700
other	157[c]	130[c]	479[c]	242	199	715
Total	*7,280*	*6,040*	*14,200*	*7,090*	*5,880*	*14,300*

[a] Ref. 8, and the U.S. Census Bureau, data are rounded to no more than three significant digits; may not add to totals shown.

[b] Antimony content is calculated by the U.S. Geological Survey.

[c] Revised

Table 4. **U.S. Imports for Consumption of Antimony Oxide, by Class and Country**[a]

	2000			2001		
Country	Gross weight, t	Antimony content, t[b]	Value × 10^3\$	Gross weight, t	Antimony content, t[b]	Value, × 10^3\$
Belgium	3,690	3,070	6,560	3,770	3,130	6,450
Bolivia[c]	1,150	957	1,220	40	33	49
China	13,100	10,900	17,300	11,000	9,150	14,600
France	66	54	230	14	11	61
Germany	47	39	802	24	20	362
Guatemala	77	64	132	0	0	0
Hong Kong	453	376	622	790	656	966
Japan	33	27	274	69	57	429
Kyrgyzstan	224	186	247	0	0	0
Mexico	5,530	4,590	7,660	8,080	6,710	15,600
South Africa	3,830	3,180	999	3,750	3,110	900
Taiwan	29	24	53	41	34	63
Thailand	60	50	11	0	0	0
United Kingdom	176	146	298	60	50	65
Total	*28,500*	*23,700*	*36,500*	*27,700*	*23,000*	*39,500*

[a] Ref. 8 and U.S. Census Bureau, data are rounded to no more than three significant digits; may not add to totals shown.

[b] Antimony ore and concentrate content reported by the U.S. Census Bureau. Antimony oxide content is calculated by the U.S. Geological Survey.

[c] Antimony oxide from this country believed to be "crude" and would probably be shipped to refineries for upgrading.

4. Analytical Methods

A wide variety of titrimetric methods for the determination of antimony in the macro and semimicro range are available. Potassium bromate in strongly acid solution is probably the most widely used oxidimetric titrant. The end point can be determined either potentiometrically or by the use of an indicator. Organic dyes such as methyl red are used as indicators, but amaranth [915-67-3], $C_{20}H_{11}N_2Na_3O_{10}S_3$, has been reported as the indicator of choice (195). Potassium dichromate in hydrochloric acid–acetic acid solution with ferroin as the indicator has also been used (196). Other oxidimetric reagents used for the titration of antimony(III) include potassium iodate in acid solution, iodine in the presence of sodium tartrate and bicarbonate, and potassium permanganate in acid or alkaline solution. A number of organic compounds have been recommended as oxidimetric titrants. Such compounds are usually *N*-haloimides, and *N*-chlorophthalimide (197) and *N*-bromosuccinimide [128-08-5], $C_4H_4BrNO_2$, (198) have been used for this purpose. Sodium diethyldithiocarbamate has also been used for titrating antimony(III); the end point is determined potentiometrically (199). Because arsenic interferes with most methods used for determining antimony, the separation of the two elements is of great importance. It is possible to remove the arsenic as the trichloride by boiling a hydrochloric acid solution containing arsenic and antimony in the trivalent state. However, a method for determining both arsenic and antimony employs cerium(IV) sulfate as the titrant and ferroin as the indicator (200). A spectrofluorimetric method for determining antimony, based on the reduction of cerium(IV) to fluorescent cerium(III), has also been described (201). This method can also be used for determining antimony(III) in the presence of antimony(V).

A widely used colorimetric method for the estimation of microgram quantities of antimony is based on the reaction of antimony(V) with rhodamine B [81-88-9], $C_{28}H_{31}ClN_2O_3$, in hydrochloric acid solution to form a colored complex that is extracted with organic solvents and measured spectrophotometrically (202). For the determination of antimony in trace amounts, methods employing neutron activation or atomic absorption have been widely used. A comparison of the two methods has been reported (203). Both methods gave satisfactory results when used to determine specified values of antimony in several different biological materials. An excellent description of the determination of antimony involving the generation of stibine by sodium borohydride, followed by atomic absorption analysis, has also been reported (204).

5. Health and Safety Factors

OSHA has a TWA standard on a weight of Sb basis of 0.5 mg/m^3 for antimony in addition to a standard TWA of 2.5 mg/m^3 for fluoride. Most antimony compounds are poisonous by ingestion, inhalation, and intraperitoneal routes locally antimony compounds irritate the skin and mucous membranes (205). NIOSH has issued a criteria document on occupational exposure to inorganic fluorides. Antimony pentafluoride is considered by the EPA to be an extremely hazardous substance and releases of 0.45 kg or more reportable quantity (RQ) must be reported. Antimony trifluoride is on the CERCLA list and releasing of 450 kg or more RQ must be reported.

6. Environmental Impact

Antimony is a common air pollutant that occurs at an average concentration of 0.001 μg/m^3. Antimony is released into the environment from burning fossil fuels and from industry. In the air, antimony is rapidly attached to suspended particles and thought to stay in the air for 30 to 40 days. Antimony is found at low levels in some lakes, rivers, and streams, and may accumulate in sediments. Although antimony concentrations have been found in some freshwater and marine invertebrates, it does not biomagnify in the environment. The impact of antimony and antimony compounds on the environment has not been extensively studied to date (206).

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LEON D. FREEDMAN
G. O. DOAK
G. GILBERT LONG
North Carolina State University
TARIQ MAHMOOD
CHARLES B. LINDHAL
Elf Atochem North America, Inc.