Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, ANTIMONY

Antimony forms both a trifluoride and a pentafluoride. It also forms the very stable hexafluoroantimonate ion [17111-95-4], $SbF^{-};_6$, present in solution and a number of salts.

1. Antimony Trifluoride

1.1. Properties

Antimony trifluoride [7783-56-4], SbF_3, is a very hygroscopic, white, crystalline solid, $mp = 292°C$. It can be sublimed under vacuum. It is very soluble in water, hydrofluoric acid, and polar organic solvents such as alcohols and ketones. Its solubility in water is 384.7 g/100 g at 0°C, 492.4 g/100 g at 25°C, and 563.6 g/100 g at 30°C (1). The solubility at 25°C is 154 g/100 mL CH_3OH, 33 g/100 mL C_3H_7OH, and 55.3 g/100 mL acetone. It is practically insoluble in benzene, chlorobenzene, and heptane. The density of SbF_3 at 25°C is 4.385 g/cm^3. It does hydrolyze in water, but the rate of hydrolysis is very slow, much slower than $SbCl_3$.

Antimony trifluoride is a mild fluorinating reagent. However, it is much more effective in the Swarts reactions where its effectiveness as a fluorinating reagent is dramatically increased by addition of Cl_2, Br_2, or $SbCl_5$ to the reaction mixture (2). Antimony trifluoride can be used for the replacement of chlorine or bromine in halocarbons, hydrohalocarbons, and nonmetal and metal halides. Typical reactions can be summarized as follows:

$$3\ RCCl_3 + 2\ SbF_3 \longrightarrow RCCl_2F + RCClF_2 + RCF_3 + 2\ SbCl_3$$

In aliphatic compounds, the ease of fluorination is of the order of $-CCl3 > -CCl_2F > -CClF_2$. Other groups, eg, $-C{=}CCl_2$ and $-CHCl_2$, react, but not readily. Antimony trifluoride is not a suitable reagent for the replacement of hydrogen in organic compounds.

Inorganic compounds also can be fluorinated using SbF_3, eg,

$$PCl_3 + SbF_3 \xrightarrow{SbCl_5} PF_3 + SbCl_3{\cdot}SbCl_5$$

$$SiHCl_3 + SbF_3 \xrightarrow{SbCl_5} SiHF_3 + SbCl_3{\cdot}SbCl_5$$

In aqueous solutions SbF_3 reacts with many metal fluorides to form compounds such as $MSbF_4$ where M = Li [72121-39-2], Na [34109-83-6], K [15273-81-1], Cs [36195-09-0], and Tl [54189-44-5], and M_2SbF_5 where M = K [20645-41-4], Cs [40902-54-3], and NH_4 [32516-50-0]. In addition, triantimonate [65176-04-7], Na_3SbF_6, and MSb_4F_{13} where M = Tl [60719-48-4], Na [56094-73-6], K [56094-72-5], Rb [12776-50-0], Cs [12775-92-7], and NH_4 [52015-24-4] have been reported (3).

1.2. Preparation

Antimony trifluoride can be readily prepared by dissolving Sb_2O_3 in an excess of anhydrous hydrogen fluoride or in aqueous acid of 40% or higher strength hydrofluoric acid, followed by evaporation of the solution to dryness (4). It can also be prepared by thermal decomposition of the graphite intercalation compound with SbF_3Cl_2 (5), by heating ammonium hexafluorantimonate (6), and by the reaction of metal with anhydrous hydrogen fluoride in the presence of nitrile (7).

1.3. Uses

Early manufacturing processes for fluorocarbons and chlorofluorocarbons used SbF_3 on a large scale, but development of alternative routes to the Swarts reactions have greatly reduced usage. Its main use is in the manufacture of antimony pentafluoride. The market for SbF_3 in the United States is less than 5 t/yr. More recent uses of SbF_3 have been in the manufacture of fluoride glass and fluoride glass optical fiber preform (8), and fluoride optical fiber (9) in the preparation of transparent conductive films (10) (see Fiber optics).

2. Antimony Pentafluoride

2.1. Properties

Antimony pentafluoride [7783-70-2], SbF_5, is a colorless, hygroscopic, very viscous liquid that fumes in air. Its viscosity at 20°C is 460 $\mathrm{mPa{\cdot}s}(=cP)$ which is very close to the value for glycerol. The polymerization of high purity SbF_5 at ambient temperature can be prevented by addition of 1% anhydrous hydrogen fluoride, which can be removed by distillation prior to the use of SbF_5. The pure product melts at 7°C (11), boils at 142.7°C, and has a specific gravity (12) of 3.145 g/cm^3 at 15.5°C. The viscous, pure liquid can be handled briefly in glass if moisture and air are carefully excluded. However, it must never be stored in glass because any HF or moisture present leads to a dangerous reaction. Any moisture reacts with SbF_5 to produce HF which reacts with glass to produce SiF_4 and water which, in turn, reacts with SbF_5 to again produce HF. The reaction continues until the SiF_4 pressure ruptures the container. Commercial antimony pentafluoride is shipped in steel cylinders or polytetrafluoroethylene bottles (generally 1-kg or less). Nickel is rapidly attacked by a mixture of SbF_5 and HF, although there is little effect on mild steel or aluminum.

2.2. Preparation

Antimony pentafluoride can be prepared by direct fluorination of SbF_3 or antimony or by reaction of $SbCl_5$ with HF (13). The reaction of $SbCl_5$ with anhydrous hydrogen fluoride proceeds with the formation of intermediate products. These chlorofluoroantimonates can be prepared separately (14). Reaction of $SbCl_5$ with anhydrous hydrogen fluoride at $-60°C$ produces $SbCl_4F$ [14913-58-7], mp = 83°C, which polymerizes on sublimation to $(SbCl_4F)_4$. $SbCl_4F$ can also be prepared by the reaction of $SbCl_5$ and anhydrous hydrogen fluoride in chlorofluorocarbons (15). Pure $SbCl_3F_2$ [24626-20-6], mp $\sim 55°C$, can be crystallized from a mixture of $SbCl_3F_2$ and $SbCl_2F_3$ [7791-16-4]. $SbCl_2F_3$, which is a thick liquid, can be prepared from the reaction of SbF_3 and Cl_2 at 135°C (16). $SbClF_4$ [15588-48-4] is obtained at 100°C by the reaction of $SbCl_5$ with a large excess of hydrogen fluoride. Other methods for preparation of antimony pentafluoride include reacting Sb with HF/F_2 (17) and fluorination of Sb using F_2 in a quartz tube (18).

2.3. Uses

Antimony pentafluoride is a moderate fluorinating reagent and a powerful oxidizer. It spontaneously inflames phosphorus and sodium but it is practically inert toward arsenic. Powdered antimony reduces SbF_5 to solid $SbF_5{\cdot}2SbF3$. SbF_5 reacts with water to form the solid antimony pentafluoride dihydrate [65277-49-8], $SbF_5{\cdot}2H_2O$, which reacts violently with an additional amount of water to form a clear solution. Antimony pentafluoride undergoes very slow hydrolysis in the presence of a dilute NaOH solution to form $Sb(OH)^-;_6$. Sulfur dioxide and nitrogen dioxide react with SbF_5 to form the adducts $SbF_5{\cdot}SO_2$ [19344-14-0] and $SbF_5{\cdot}NO_2$ [72121-47-2], respectively. These adducts decompose in water.

Antimony pentafluoride is used to saturate double bonds in straight-chain olefins, cycloolefins, aromatic rings (19–21), and in the fluorination of halocarbons and CrO_2Cl_2, $MoCl_5$, WCl_6, PCl_3, P_4O_{10}, $SiCl_4$, $TiCl_4$, and SiO_2.

Antimony pentafluoride forms intercalation compounds with graphite (22, 23) and fluorinated graphite (24), CF_x, where $x = 1.06$, which have much higher conductivity than graphite and fluorinated graphite, respectively (25). These nonstoichiometric substances may have potential use as superconducting materials. When a mixture of O_2, F_2, and SbF_5 or NF_3, F_2, and SbF_5 is subjected to elevated temperature and pressure, it gives the dioxygenyl salt O_2SbF_6 [51681-88-0] (26) and the perfluoroammonium salt NF_4SbF_6 [16871-76-4] (27), respectively. The dioxygenyl salt is a solid that can oxidize xenon (28) and has been used for removal of xenon, radon, and radon daughter elements from contaminated atmospheres. SbF_5 has also been used in the conversion of methane to gasoline range hydrocarbons (29), in the syntheses of fluorocarboranes (30), in superacids (31), and in the preparation of stable carbocations (32).

3. 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 (33) and in carbocation chemistry (34). Addition of SbF_5 drastically increases the acidities of HSO_3F and HF (35, 36).

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 (37) by the oxidation of Sb(III) with H_2O_2 or alkali metal peroxide in HF (38), by the action of HF on a mixture of $SbCl_5$ and MF where $M = NH_4$, Li, Na, K, Ru, Cs, Ag, and Tl (39). These compounds can be used as photoinitiatorsfor the production of polymers (40).

4. Environmental and Safety Aspects

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. 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.

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