Kirk-Othmer Encyclopedia of Chemical Technology.

FLUORINE COMPOUNDS, INORGANIC, SILVER

1. Silver Subfluoride

Pure silver subfluoride [1302-01-8], Ag_2F, is a greenish shiny crystalline material, or yellowish green solid if contaminated with AgF. It decomposes in water but is stable in alcohol and saturated solutions of AgF. Ag_2F disproportionate into Ag and AgF when heated above 100°C (1, 2).

Silver subfluoride is prepared by heating a concentrated solution of silver fluoride with metallic silver powder. It may also be obtained by electrolysis of a solution containing AgF, aqueous HF, and NH_4F at 50°C in a platinum dish using a silver electrode. Another process for the manufacture of Ag_2F involves heating a mixture of a saturated solution of AgF and fine Ag powder. This process yields a yellowish green solid mass. Silver subfluoride is a reagent of laboratory curiosity. No commercial applications are known.

2. Silver Fluoride

Anhydrous silver fluoride [7775-41-9], AgF, is a golden yellow solid in its pure form and is classified as a soft fluorinating agent (3). Several solid phases of the solvated species are reported for AgF in the system AgF–HF–H_2O (4), eg, $AgF{\cdot}2H_2O$ [72214-21-2], $AgF{\cdot}4H_2O$ [2242-42-6], $3AgF{\cdot}2HF$ [72318-57-1], $AgF{\cdot}2HF$ [12444-84-7], $AgF{\cdot}3HF$ [12444-85-8], $AgF{\cdot}5HF$ [12444-86-9], and $AgF{\cdot}7HF{\cdot}2H_2O$ [72318-56-0]. In addition, $AgF{\cdot}3HF$ is formed in the absence of water at 0°C. When this last is warmed to 25°C under an atmosphere of dry nitrogen it dissociates into $AgF{\cdot}HF$ or $AgHF_2$ [12249-52-4] and HF.

2.1. Preparation

Silver fluoride can be prepared by dissolving Ag_2O or Ag_2CO_3 in anhydrous hydrogen fluoride or aqueous hydrofluoric acid, evaporating to dryness, and then treating with methanol or ether.

2.2. Properties

Silver fluoride is light sensitive and has a specific gravity of 5.852. It melts at 435°C into a black liquid which boils at 1150°C. Unlike the other halides, it is extremely soluble (182 g/100 g) in water and in anhydrous hydrogen fluoride (83.2 g/100 g at 11.9°C). It is only slightly soluble in absolute methanol (1.5 g/100 mL). Its heat of formation, ΔH_f, is -204.6 kJ/mol (-48.9 kcal/mol); heat capacity, C_p, is 51.92 J/(mol·K) (12.4 cal/(mol·K)); and entropy, *S,* 83.7 J/(mol·K) (20.0 cal/(mol·K)).

Silver fluoride forms explosive adducts with ammonia (qv) (5, 6), and therefore all of the reactions involving liquid or gaseous ammonia should be carried out with extreme precautions.

2.3. Uses

Silver fluoride has found many laboratory and special industrial applications. It is used as a soft (mild) fluorinating agent for selective fluorination (7–17), as a cathode material in batteries (qv) (18), and as an antimicrobial agent (19). Silver fluoride is commercially available from Advance Research Chemicals, Inc., Aldrich Chemicals, Cerac Corp., Johnson/Matthey, PCR, Atochem, and other sources in the United States. The U.S. price of silver fluoride in 1993 was $1000–$1400/kg and the total U.S. consumption was less than 200 kg/yr.

3. Silver Difluoride

Silver difluoride [7783-95-1], AgF_2, is a black crystalline powder. It has been classified as a hard fluorinating agent (3) which liberates iodine from KI solutions and ozone from dilute aqueous acid solutions on heating. It spontaneously oxidizes xenon gas to Xe(II) in anhydrous hydrogen fluoride solutions (20).

AgF_2 is prepared by the action of elemental fluorine on AgF or AgCl at 200°C. Both processes result in quantitative yields. Silver difluoride should be stored in Teflon, passivated metal containers, or in sealed quartz tubes.

3.1. Properties

Silver difluoride melts at 690°C, boils at 700°C, and has a specific gravity of 4.57. It decomposes in contact with water. Silver difluoride may react violently with organic compounds, quite often after an initial induction period. Provisions must be made to dissipate the heat of the reaction. Small-scale experiments must be run prior to attempting large-scale reactions.

3.2. Uses

AgF_2 is a powerful fluorinating agent and is used for substitution of hydrogen by fluorine in hydrohalocarbons (21), preparation of perfluorocompounds (21–23), purification of perfluoromorpholines containing partially fluorinated hydrocarbons (24), fluorination of compounds containing triple bonds (25), addition of fluorine to unsaturated halocarbons (25), and conversion of carbon monoxide into carbonyl fluoride.

Silver difluoride, commercially available from the same sources as those of AgF, had a 1993 price between $1000–$1400/kg. In spite of the technical success in laboratory experiments, silver fluorides have found limited use on a large scale mainly because of the high cost of the reagents. Demand for silver difluoride is less than 100 kg/yr.

4. Silver Trifluoride

The existence of diamagnetic salts of $AgF^-{}_4$ was first reported in 1957 (26), but little was known about their properties. In 1988 (27) it was claimed that AgF_3 was prepared by a reaction of Ag metal and O_2F_2 in ClF_5. Silver trifluoride [91899-63-7], AgF_3, has since been prepared (28) from anhydrous HF solutions of $AgF^-{}_4$ salts by addition of BF_3, PF_5, or AsF_5.

If excess AsF_5 is added, silver(III) is reduced and the $AgFAsF_6$ salt is produced.

$$AgF_3 + AsF_5 \longrightarrow AgFAsF_6 + 1/2\ F_2$$

The red precipitates of AgF_3 are diamagnetic and isostructural with AuF_3. Silver trifluoride is a powerful oxidizing agent and thermodynamically unstable. Its powerful oxidizing properties result from the tight binding of its valence shell d-orbital electrons. No commercial source is available.

5. Silver Fluorocomplexes

The silver fluorocomplexes, ie, silver hexafluoroantimonate [26042-64-8], $AgSbF_6$; silver hexafluorophosphate [26042-63-7], $AgPF_6$; silver tetrafluoroborate [14104-20-2], $AgBF_4$; and other salts such as silver trifluoromethane sulfonate [2923-28-6], CF_3SO_3Ag, and silver trifluoroacetate [2966-50-9],CF_3COOAg, play an important role in the synthesis of organic compounds and have gained potential industrial importance.

These compounds perform a dual function in synthesis procedures. The introduction of a complex anion assists in the stabilization of the desired product and the generation of unique intermediates by chloride displacement, eg, silver hexafluorophosphate, $AgPF_6$, forms adducts with neutral diamagnetic organometallics which can act as controlled sources of highly reactive cations (29). Silver hexafluoroantimonate, $AgSbF_6$, is an electrophilic bromination catalyst (30) and is also used in promoting chlorination of reactive alkanes (31). Silver trifluoromethane sulfonate, CF_3SO_3Ag, is an excellent precursor to a number of derivatives useful as alkylating agents for aromatic compounds (32).

Silver fluorocomplexes are also used in the separation of olefin–paraffin mixtures (33), nitration (qv) of aromatic compounds (34), in the synthesis of *o*-bridged bicyclics (35), pyrroles (36), cyclo-addition of vinylbromides to olefins (37), and in the generation of thiobenzoyl cations (38).

These complex salts are very hygroscopic and light sensitive. They are slightly soluble in anhydrous hydrogen fluoride, very soluble in water, and soluble in organic solvents such as acetonitrile, benzene, toluene, and *m*-xylene. Except for the melting point of CF_3COOAg (257–260°C), not many other physical properties are known. Most of the salts decompose at higher temperatures.

These salts are corrosive and are to be considered toxic because of the presence of Ag^+ ions. The American Conference of Government Industrial Hygienists (ACGIH) (1992–1993) has adopted TWA values of 0.01 mg/m^3 for silver metal and 0.01 mg/m^3 for soluble silver salts. TWA for fluorides as F^- ions is 2.5 mg/m^3. The MSDS should be consulted prior to use. Skin contact and inhalation should be avoided.

These salts are commercially available. Worldwide consumption of fluorocomplex salts varies between 100 to 300 kg/yr. The most popular salt is $AgBF_4$. Prices vary between \$1000 and \$1400/kg.

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