Laboratory Preparation of the Fluorinating Agents SbF_3 and AgF

F. ALLAN ANDERSEN, BØRGE BAK, and ANNY HILLEBERT

Chemical Laboratory of the University of Copenhagen, Copenhagen, Denmark

I. ANTIMONY TRIFLUORIDE
(B. B. and A. H.)

Although SbF_3 is a compound which is necessary in carrying through the Swarts reaction in which chlorine may be replaced by fluorine, detailed instructions for its preparation on a laboratory scale is missing in the literature. Usually it is briefly reported that the substance has been prepared by the action of HF on Sb_2O_3, evaporation of excess HF and sublimation of the crude product. None of these operations can take place in glass vessels.

$$Sb_2O_3 + 6HF \rightarrow 2SbF_3 + 3H_2O$$

In the procedure given here it is described how great quantities of highly purified SbF_3 may be rapidly prepared in a platinum dish (or other dish resistent to HF and SbF_3) and purified in glass equipment without using the difficult and time-consuming sublimation.

Procedure. 100 g commercial Sb_2O_3 (0.34 mole) is gradually added to 200 g (4 mole) of freshly destilled hydrofluoric acid (37—40 %), placed in a platinum dish of known weight. The addition requires about 10 minutes. The dish is then placed on a sand-bath in a good hood and excess HF is evaporated. The heating is interrupted when the contents of the dish weigh 120 g (theoretical yield of SbF_3). After cooling to room temperature in a desiccator the crude SbF_3 is stirred with 120 ml methanol in the platinum dish for ten minutes. By rapid suction through filter-paper on a Büchner-funnel the methanolic solution of SbF_3 is freed from insoluble material and again placed in the platinum dish as fast as possible. The methanol is evaporated on a steambath, the process of evaporation being accelerated by the use of an upside-down funnel through which air is rapidly sucked. In twenty minutes the methanol is removed. The separated white crystals are crushed to a powder in the dish and treated with 100 ml anhydrous ethyl ether which dissolves the remaining traces of methanol. The SbF_3 crystals are separated by suction through filter-paper on a Büchner-funnel, washed twice with 50 ml anhydrous ethyl ether, dried for five minutes in the air and finally stored in a paraffined vessel *in vacuo* over concentrated sulfuric acid. Yield: 100 g (78 %).

Properties. SbF_3 is a white, crystalline compound. It attacks glass slowly and hydrolyzes in the air. 500 mg, placed on platinum in the atmosphere, gains 3 mg in 30 minutes at 22° C (relative humidity 60 %). If placed on glass 500 mg gains 6 mg in the same period. Thus, rapid operations in the air, involving the use of glass apparatus, are possible.

The purity of the preparation was controlled by determining the antimony and the fluorine equivalent weights. The former, found by titration with $KBrO_3$, was found to be 90.2 (theory 89.4), the latter, found by titration with $Th(NO_3)_4$ after precipitation of Sb^{3+} as Sb_2S_3 by H_2S, was 60.2 (theory 59.6). SbF_3 melts at 292° and boils at 319° C but these physical data are difficult to apply as criteria of purity in the ordinarily equipped laboratory.

SbF_3 is soluble in methanol (1 ml methanol dissolves 1.54 g of SbF_3 at 20° C) without chemical change as found and utilized by the present authors.

II. SILVER FLUORIDE.
(F.A.A. and B.B.)

AgF is of equal importance for fluorinating processes on a laboratory scale as SbF_3, but instructions for the preparation of this highly hygroscopic substance are not available in the literature.

$$Ag_2CO_3 + 2\ HF \rightarrow 2\ AgF + CO_2 + H_2O$$

Procedure. A solution of 38 g NaOH (0.95 mole) in 1 200 ml water is saturated with CO_2. The resulting solution of $NaHCO_3$ is slowly added to a solution of 136 g (0.80 mole) $AgNO_3$ in 400 ml water under vigorous shaking. This operation and the following must take place under exclusion of day-light (red light is permissable). The Ag_2CO_3 precipitate is separated from the $NaNO_3$-solution by decantation and afterwards washed four times with 500 ml water which is also removed by decantation. The remaining, moist Ag_2CO_3 is transferred to a platinum dish where 47 g 40 % HF (0.94 mole) is added in small portions under good stirring. When the initial, rapid evolution of CO_2 has ceased the reaction is finished by heating for thirty minutes on a steam-bath. The AgF-solution is separated from excess Ag_2CO_3 by filtering through ash-free filter-paper on a paraffined funnel into a paraffined beaker and afterwards placed in the (weighed) platinum dish again. The water is evaporated on a steam-bath under continued stirring until the weight of the sample is 115 g. The contents of the dish are now a mixture of about 90 g AgF (partly separated as crystals) and about 25 g water. In order to remove the water rapidly and completely 100 ml anhydrous methanol is added and, after thourough stirring, removed by decantation together with most of the water. The treatment with methanol is repeated twice and followed by a similar treatment with 100 ml anhydrous ethyl ether three times. The silver fluoride (moist with ether) is now quickly transferred to a round-bottomed glass flask with a side tube through which most of the ether is removed by a water aspirator. The last trace is evaporated by heating to 60—70° C in a water-bath and applying an oil pump. Yield: 75 g (70—80 g) of a light-brown powder.

The ether, used at the decantation, is added to the methanol together with 300 ml extra ether. A nice, yellow precipitate is separated from the mother liquor by decantation and washed twice with 25 ml anhydrous methanol and three times with 50 ml anhydrous ether. The last ether is removed as above. Yield: 15 g (14—16 g). The two crops are almost of the same quality although they differ in colour. Total yield: 90 g (0.72 mole) or 89 %.

Properties. AgF is highly hygroscopic and very sensitive to day-light. It attacks glass only very slowly at room temperature. It is stored in dark, paraffined vessels. The purity of the preparation was checked by determining the silver and the fluorine equivalent weights. For the brown and the yellow sample the silver equivalent weight was 126.4 and 127.3, respectively, (theory 126.9) while the fluorine determinations gave 124.4 and 122.0. 1 000 ml anhydrous methanol dissolves 14.5—15 g AgF at room temperature. In the dark and stored on a platinum container the solution is stable for at least 24 hours.

The method for the preparation of AgF here indicated is preferable to removing the water from an aqueous solution in a desiccator, a procedure which does not result in a well-defined product within a reasonable period.

Received January 8, 1953.

The Question of Furanosidic Bonds in Starch

BENGT LINDBERG

Organisk-kemiska Institutionen, Kungl. Tekniska Högskolan, Stockholm, Sweden

In a recent study of the hydrolysis of starch with acids and with β-amylase, Blom and Schwartz [1] find that the change in specific rotation per mole hydrolysed bond, $[S_p]_D$, is 166—187° at the beginning of hydrolysis, the mean value for total hydrolysis 232° and the values for maltose and isomaltose 280° and 221°, respectively. They conclude that as the value for the first bonds hydrolysed is much lower than the value for maltose, these bonds must be of a quite different type, and assume, therefore, that they are furanosidic (1 : 4), and that the next glucose unit in the starch molecule is linked by a 1 : 5-bond.

The authors appear, however, to have overlooked the great differences between terminal and central bonds with respect to their contribution to the rotation. If, in a linear polysaccharide containing uniform bonds every second bond (n/2 bonds) is