CHAPTER 1

Preparation of Elemental Fluorine

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Although the syntheses of fluorinated compounds usually do not involve the use of elemental fluorine (F_2), F_2 can be considered to be the mother of all fluorine compounds. Because fluorine is the most electronegative element, its synthesis presented an enormous challenge and had been pursued unsuccessfully for almost a century, until finally in 1886 Moissan succeeded to prepare it electrochemically [1]. For the next 100 years, every major chemistry textbook stated that for the above reasons F_2 cannot be prepared by purely chemical means. This dogma was shattered in 1986 by Christe who prepared and isolated in a 3-day tour de force [2] F_2 in high yield from potassium hexafluoromanganate (K_2MnF_6) and antimony pentafluoride (SbF_5), two compounds that had already been known in the days of Moissan. He used a combination of two very simple and well-known principles for his synthesis: (1) that stronger acids can displace weaker acids from their salts and (2) that high oxidation states are stabilized by formal negative charges. Thus, a high oxidation state complex fluoro anion can be prepared with relative ease and when converted by the acid displacement reaction to its neutral parent molecule, the latter, if thermodynamically unstable, might spontaneously decompose to a lower oxidation state and thereby liberate F_2.

$$K_2MnF_6 + 2\,SbF_5 \rightarrow 2\,KSbF_6 + [MnF_4]$$

$$2\,[MnF_4] \rightarrow 2\,MnF_3 + F_2$$

In view of the relative ease, simplicity, and historical significance of this synthesis, it has been included in this book. It might be attractive for demonstration purposes or when only smaller amounts of fluorine are desired and the costs of either setting up an electrochemical cell or a compressed F_2 gas-handling system are prohibitive. Since SbF_5 is commercially readily available from at least 38 global and 14 U.S.

Efficient Preparations of Fluorine Compounds, First Edition. Edited by Herbert W. Roesky.

suppliers, its synthesis is not described in this chapter. However, if desired, it can be prepared in high yield by purely chemical means from $SbCl_5$ and HF [3]. The other starting material, K_2MnF_6, is more difficult to buy commercially and, therefore, its one-step, one-pot synthesis [2,4,5] from $KMnO_4$, KF, H_2O_2, and aqueous HF is described here.

$$2\,KMnO_4 + KF + 10\,HF + 3\,H_2O_2 \rightarrow 2\,K_2MnF_6 \downarrow + 8\,H_2O + 3\,O_2$$

1.1 PREPARATION OF K_2MNF_6

Apparatus Two 4-L polyethylene beakers, Teflon-coated magnetic stirrer, polyethylene Buchner funnel with Teflon filter paper, safety glasses, laboratory coat, and protective gloves.

Chemicals $KMnO_4$, KF, 48–50% reagent grade aqueous HF (caution: technical grade HF should be avoided because it contains a significant amount of H_2SiF_6, resulting in a product containing significant amounts of K_2SiF_6 as impurity), and 30% aqueous H_2O_2.

Attention! Safety glasses and protective gloves must be used at all times because HF and H_2O_2 can cause skin burns.

Experimental Procedure A 4-L polyethylene beaker, equipped with a Teflon-coated magnetic stirring bar, is charged with 50% aqueous HF (1 L) and cooled with an ice bath. Then KF (240 g, 4.13 mol) and finely powdered $KMnO_4$ (15 g, 94.9 mmol) are added and the mixture is vigorously stirred for 15 min. The stirring is stopped and any undissolved material is allowed to settle. The supernatant solution is decanted into a second beaker to assure the absence of any undissolved $KMnO_4$, which could make the endpoint recognition in the subsequent titration step difficult. To the cold dark purple solution, 30% aqueous H_2O_2 is slowly added with an eyedropper. After the addition of each 5–10 drops, further additions are halted until O_2 evolution has ceased. After the addition of about 20 mL of H_2O_2, the endpoint is being approached. A brownish golden precipitate is formed and the endpoint can be judged by stopping the stirring and observing the color of the supernatant solution. The reaction is complete when the color of the solution has changed from purple to medium reddish brown. The golden yellow K_2MnF_6 precipitate is collected using a plastic Buchner funnel with Teflon filter paper. The precipitate is washed twice with cold acetone (10 mL each) and pumped to dryness to yield 18.44 g (78.6% based on $KMnO_4$) of yellow K_2MnF_6.

Characterization Data Yellow, non-hygroscopic, crystalline solid. IR (AgCl, cm^{-1}): $\bar{\upsilon}$ 620 vs, 340 s. RA (glass melting point (mp) capillary): $\bar{\upsilon}$ 601 vs, 512 m, 307 ms. Crystal data: hexagonal, $P6_3mc$, $a = 5.719(1)$ Å, $c = 9.330(3)$ Å [6].

Application In addition to serving as convenient starting materials for the chemical synthesis of F_2, alkali metal hexafluoromanganates can be used in acidified HF solutions as fluorinating agents or as starting materials for the synthesis of $(NF_4)_2MnF_6$ for solid propellant NF_3/F_2 gas generators for chemical HF/DF lasers [7,8].

1.2 PREPARATION OF F_2

Apparatus The apparatus used in Christe's original synthesis of F_2 is shown in Figure 1.1, which shows a typical set up for the transfer of a compound of relatively low volatility, such as SbF_5, in a dynamic vacuum from a storage vessel into a reaction U-tube. The reactor can be a $^1/_2$-in. or $^3/_4$-in. o.d. Teflon-FEP (perfluoroethylene/perfluoropropylene copolymer) or metal (Monel, nickel, copper, or stainless steel) U-tube reactor, closed at both ends with Hoke stainless steel valves. Since Teflon-FEP starts softening and being attacked by the nascent fluorine at about 200 °C, the use of a Monel U-tube is preferred, unless the visual observation of the reaction is desired. The connections can be made with either Teflon or preferentially metal tubing. The T-piece connector between the SbF_5 vessel and the reactor allows evacuation and passivation of the connection. The

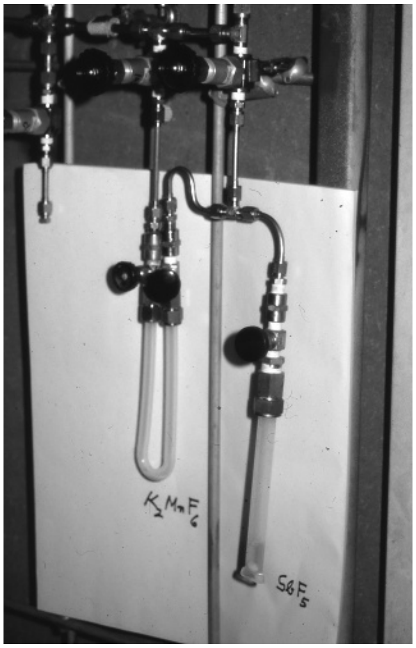

FIGURE 1.1 The original apparatus used by Christe in 1986 for the first chemical synthesis of F_2. (For a color version of the figure, please see color plates.)

exit side of the U-tube reactor is also connected to the vacuum manifold. The Teflon U-tube can be prepared by tightly packing a desired length of straight Teflon tubing with crystalline NaCl, closing both ends with rubber stoppers, heating the central part of the tube with a heat gun to the softening point of the Teflon, wrapping it 180° around an approximately 2-in. o.d. metal cylinder, allowing it to cool and removing the NaCl by pouring it out, and washing out any imbedded salt with water. The metal U-tubes are easily prepared with a tube bender. Safety requirements include face shield, safety glasses, laboratory coat, and protective gloves.

Chemicals Silicon-free $K_2[MnF_6]$, distilled SbF_5.

Attention! F_2 is a highly reactive gas with a very intense halogen odor and is easily detected already at very low concentrations (0.02 ppb) by its characteristic smell. Inhalation or contact with the skin must be strictly avoided. Laboratory coat, face shield, safety glasses, and protective gloves must be used at all times.

Experimental Procedure A passivated (with F_2 or preferentially ClF_3) $^3/_4$-in. o.d. Teflon-FEP ampoule, equipped with a valve, and a passivated $^1/_2$-in. o.d. Monel U-tube, closed at each end by a valve, are loaded in the dry box with distilled SbF_5 (~7 g or 32 mmol) and silicon-free K_2MnF_6 (1.912 g, 7.744 mmol), respectively, and are then connected to the vacuum manifold as shown in Figure 1.1. The connections are leak-checked and passivated. The Monel U-tube is cooled to −196 °C, and the SbF_5 is transferred in a dynamic vacuum from the Teflon ampoule to the Monel U-tube. After closing the valves, the Monel reactor is heated with an oil bath to 180 °C for 1 h and then cooled to −78 °C. The only product volatile at this temperature is the desired F_2 (56 mg, 1.47 mmol) in 38% yield, based on the limiting reagent K_2MnF_6.

Assay of the F_2 The formation, purity, and exact amount of fluorine formed in the above experiment can be verified easily by reacting the gas with mercury (Hg) and measuring the change in the volume of the gas by standard pressure–volume–temperature (PVT) techniques and monitoring the weight uptake of Hg. A typical experimental setup for this step is shown in Figure 1.2. Care must be taken to pump on Hg only at low temperatures (–78 °C or −196 °C), because Hg has some volatility at ambient temperature and even small losses will severely impact this analysis due to the high atomic weight of Hg.

Characterization Data Faint yellow-green, highly toxic, corrosive gas, mp −219.62 °C, boiling point (bp) −188.12 °C, standard atomic weight, 18.9984032 g/mol, first ionization energy, 1681.0 kJ/mol [9].

Waste Disposal The aqueous HF solution from the K_2MnF_6 preparation can be disposed of as NaF after neutralization with sodium bicarbonate. The $KSbF_6 \cdot nSbF_5$ and Mn-containing by-products from the chemical synthesis of F_2 have to be collected and properly deposited in a labeled container for toxic metal waste.

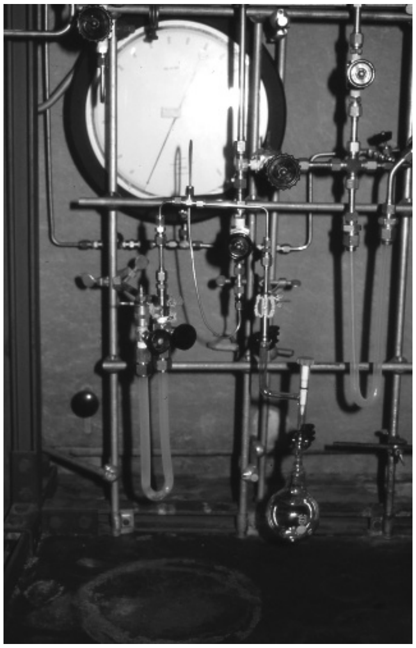

FIGURE 1.2 The original apparatus used by Christe in 1986 for the assay of F_2. On the left is the Teflon-FEP U-tube reactor containing the F_2 gas. It is connected to a glass bulb containing the mercury, and the whole system is connected to the Heise gauge for the pressure measurements. (For a color version of the figure, please see color plates.)

Application Due to its high reactivity and toxicity, F_2 is rarely used as a fluorinating agent in industrial processes. The major applications are the preparations of UF_6 for uranium isotope separation and SF_6 as a dielectric medium in transformers, and its use in the electronics industry for plasma etching and chamber cleaning.

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