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SHORT COMMUNICATION

A Simple Method for the Purification of Fluorine

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A simple method for the purification of fluorine gas is described. With the exception of nitrogen and argon, all impurities usually present in commercial fluorine can be readily removed by 1) conversion of O_2 to non-volatile O_2^+ salts, and 2) a 70 to 63°K trap-to-trap distillation.

Commercial fluorine gas contains 1-2% of impurities, primarily O_2, N_2 and HF with trace amounts of Ar, CO_2, CF_4, C_2F_6, C_3F_8, COF_2, NF_3, OF_2, SiF_4, SF_6, SO_2F_2, and others [1-5]. For most preparative purposes the O_2 content of fluorine does not interfere with the desired reactions, and the purification of F_2 can be limited to the removal of HF by a NaF scrubber. For example, a nearly quantitative synthesis of IrF_6 is possible by heating Ir metal in an atmosphere of 20% F_2 and 80% O_2 [6]. However, there are applications, where oxygen free fluorine is needed. A typical example is the HF-DF chemical laser. It is known [7,8] that molecular oxygen acts as an inhibitor for the chain branching reaction of H_2 and F_2. In addition, the presence of O_2 causes the formation of water which is a very strong deactivator for vibrationally excited HF or DF [9]. In order to obtain meaningful baseline data, oxygen free fluorine is required. Furthermore, in the syntheses of the very expensive platinum metal hexafluorides RuF_6, RhF_6, and PtF_6 the yield of the products is decreased by the formation of the undesired and volatile [10] $O_2^+MF_6^-$ salts. Similarly, in the syntheses of ReF_7 and OsF_6 the presence of O_2 results in the formation of the corresponding oxide pentafluorides. Other applications requiring high purity fluorine include calorimetry [1], and spectroscopic [11, 12] and analytical [3] studies.

Previously described methods for the purification of fluorine involved either low-temperature distillation [2-4], low-temperature uv-photolysis [13], or the pyrolysis of K_2NiF_6 in the presence of KF [4]. These methods have the following shortcomings. The low-temperature distillations require rather complex and expensive equipment which is beyond the reach of most laboratories. The low-temperature uv-photolysis involves the irradiation of liquid fluorine in a glass apparatus to convert O_2 to the less volatile O_2F_2, followed by a distillation at 90°K. This method is not suitable for scale-up, and the handling of larger amounts of liquid fluorine in a glass apparatus presents a potential hazard. The pyrolysis of K_2NiF_6-KF mixtures is somewhat cumbersome, because the bulk of the material and not the impurity must be converted to a nonvolatile compound. In this paper, we describe an alternate method which we have found to be more convenient than those previously reported.

(1) Removal of Oxygen

We have found that the well known [14-16] reaction

$$O_2 + F_2 + nSbF_5 \xrightarrow{\Delta E} O_2^+SbF_6^- \cdot (n-1)SbF_5$$

is ideally suited for the removal of oxygen impurities from fluorine. Either heating [14] or uv-photolysis [15] can be used for activation of the reaction. Of these two activation energy sources, thermal activation is preferred owing to its scalability and simplicity.

In a typical example, crude F_2 (17 g, 500 mmol) [17] and SbF_5 (2.1 g, 10 mmol) [18] in a 1.2 ℓ Monel reactor were heated for 2 h to 460°K. The vessel was cooled to 90°K and the F_2 was distilled into a container kept at 77°K. The excess of unreacted SbF_5 was removed from the Monel vessel by pumping at room temperature. The vessel was opened in a dry box and contained 1.1 g of a white solid which was identified by its vibrational spectra [16] as $O_2^+Sb_2F_{11}^-$. The above procedure was repeated with pretreated F_2. In this case, no evidence for the formation of any O_2^+ salt was obtained and the reaction vessel showed clean inner surfaces. It can therefore be assumed that the oxygen was quantitatively removed by a single heating cycle.

(2) Removal of Trace Impurities

It is known that impurities which have no measurable vapor pressure at 90°K can be removed from F_2 by a 90 to 77°K trap-to-trap distillation. For the removal of the more volatile impurities CF_4, NF_3, and OF_2, however, lower temperatures are required. In our experience, a 70 to 63°K trap-to-trap distillation can be carried out with relative ease and removes all remaining impurities, except for N_2 and Ar which usually do not interfere with most applications. Since the amount of N_2 present in commercial F_2 can vary strongly depending on the batch and supplier, no meaningful number can be quoted for the overall purity of the F_2 obtained by our method. The temperature of 63°K (nitrogen slush bath) is easily obtained by either pumping on liquid N_2 or by passing a stream of helium, precooled to 77°K, through liquid N_2. The temperature of 70°K is obtained either by passing He through liquid N_2 or by allowing a 63°K trap to gradually warm towards 70°K. The purity of F_2 after two 70 to 63°K trap-to-trap distillations was tested by recording its infrared spectrum as a solid [12] at 12°K. No detectable impurities were observed. The absence of impurities volatile at 70°K but nonvolatile at 63°K in the purified fluorine was established by mass spectroscopy.

Thus, a 70 to 63°K trap-to-trap distillation combined with the O_2 scavenging method using SbF_5 provides a convenient purification method for fluorine.

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