A Simple Method for the Preparation of Nitrosyl Fluoride

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AN easy, straightforward method for the synthesis of nitrosyl fluoride has been discovered which requires only simple laboratory entities compared to more difficult methods previously reported.[1]

The preparation consists of the reaction of nitrogen dioxide with either KF or CsF to give essentially pure ONF as the only volatile product. The solid residue remaining is the alkali-metal nitrate. The reaction proceeds smoothly at room temperature in either a Pyrex glass or metal reaction vessel. Temporary storage of the product in the reaction vessel without noticeable decomposition is possible.

In a typical run, 5 g. (33 mmoles) of 99% CsF was dried at 300° for 2 hr., powdered under vacuum conditions, and placed in a 150 ml. prefluorinated Monel vessel. 2·85 mmoles of NO_2 were condensed into the vessel at −78° and allowed to warm to ambient temperature. The volatile material was removed after 5 days and found to contain 1·37 mmoles of nitrosyl fluoride as the only gaseous product. The reaction time varied from 1—5 days in several runs and is dependent on the particle size and anhydrous nature of the salt.

The rate of preparation of ONF can be enhanced by allowing the reaction to occur in a prefluorinated metal vessel above 90°. 2·47 mmoles of NO_2 and an excess of KF were heated to 90° for 2·5 hr. Total reaction had occurred and 1·19 mmoles of ONF were recovered corresponding to 48·2% conversion based on the NO_2 added. At 300° the reaction occurred within 15 min. with a slightly lower yield of ONF. Both metal fluorides react to give only ONF in about the same yield.

Identification of the volatile product was carried out by molecular-weight determination and infrared spectra.[2] Gravimetric determination and *X*-ray powder pattern analysis were used to identify the solid residue as the alkali-metal nitrate.

The reaction can be carried out in all Pyrex equipment with similar experimental results as listed above. Storage of the ONF in a Pyrex bulb over CsF was found satisfactory for at least a week, with no SiF_4 observed in any of the preparations of the product.

The reactivity of CsF and KF has been found to be greatly enhanced by first forming the hexafluoroacetone adduct of the metal fluoride in acetonitrile solution.[3] The compound $MF{\cdot}OC_3F_6$ can then be decomposed by removing the solvent and hexafluoroacetone at 100° under dynamic vacuum.

When mmole samples of NO_2 were condensed on the salt at $-78°$, the reaction was found to go to completion upon warming to room temperature with quantitative yields of ONF as the only volatile product. It was found that the metal fluoride must be present in excess to allow complete reaction to occur, and attempts to react NO_2 and CsF in stoicheiometric amounts gave a mixture of NO_2 and ONF.

If an excess of hexafluoroacetone is added to CsF in acetonitrile to give a clear solution and the solvent is removed under vacuum at room temperature, the salt, $CsF{\cdot}OC_3F_6$ is found to be stable. Addition of NO_2 to the latter causes an immediate reaction to occur giving $CF(CF_3)_2ONO$ as the major product with ONF present in only minor amounts.[4]

Based on the above evidence the reaction appears to proceed according to

$$2NO_2 + MF \rightarrow ONF + MNO_3$$

$$(M = K \text{ or } Cs)$$

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