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A convenient preparation of sulfuryl chloride fluoride

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Abstract

The reaction of either ammonium fluoride or potassium fluoride with sulfuryl chloride in the presence of trifluoroacetic acid at ambient temperature gave sulfuryl chloride fluoride in good to moderate yields.

Introduction

Sulfuryl chloride fluoride is a useful solvent owing to its low nucleophilicity, high dielectric constant and wide liquid range (−120 °C to +7 °C). In spite of its numerous applications in the preparation of carbocations at low temperatures [1], and its synthetic applications [2], there are only a few convenient methods available for its synthesis. Although commercially available, it is expensive. It has been prepared by reacting sulfuryl chloride with nitrogen trifluoride [3], antimony trifluoride [4], sodium fluoride [5], ammonium fluoride [6] and lead fluoride [7] in boiling acetonitrile. Olah and coworkers introduced a method involving the reaction of sulfuryl chloride with pyridinium polyhydrogen fluoride [8]. Most of these methods suffer from harsh reaction conditions, or use special apparatus. We now describe a convenient method for the preparation of sulfuryl chloride fluoride by reacting either ammonium fluoride or potassium fluoride with sulfuryl chloride in the presence of trifluoroacetic acid at ambient temperature.

Experimental

Sulfuryl chloride, ammonium fluoride, potassium fluoride and trifluoroacetic acid were highest purity materials available from Aldrich and used as received. ^{19}F NMR spectra were obtained on a Variah Associates model VXR-200 NMR spectrometer equipped with a 5 mm switchable ^{1}H, ^{19}F-broad

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band probe with $CFCl_3$ as the reference. All glass apparatus were used with no etching problems.

Sulfuryl chloride fluoride

A 100-ml three-necked round-bottom glass flask was equipped with a magnetic stirrer, a serum cap, a reflux condenser and an exit tube connected through Tygon tubing into an efficient condenser kept at −78 °C. A small, positive flow of nitrogen was maintained through a hypodermic needle attached to the serum cap. Ammonium fluoride (8.2 g, 0.22 mol), and excess sulfuryl chloride (30 ml, 0.37 mol) were placed in the flask, and trifluoroacetic acid (16.9 g, 11.2 ml, 0.15 mol) was then injected dropwise to the contents, over a period of 10 min. An exothermic reaction ensued during the addition of the trifluoroacetic acid, and sulfuryl chloride fluoride distilled into the receiver flask upon addition of the trifluoroacetic acid. After the addition of the acid, the reaction flask was warmed to 50 °C for 10 min to drive out all the product. The distillate in the receiver flask was treated with 1 ml of antimony pentafluoride (to complex any unwanted sulfur dioxide) and redistilled into a precooled flask. The sulfuryl chloride fluoride (10 g, 57%), b.p., +7 °C, thus obtained was found to be identical with an authentic sample (^{19}F NMR, δ 100.7). A similar reaction with potassium fluoride gave the product in 30% isolated yield.

Results and discussion

The present procedure is based on a modification of Woyski's [6] method wherein ammonium fluoride was used. While the reaction of fluoride salts, such as ammonium fluoride, lead fluoride, or sodium fluoride with sulfuryl choride, as reported [4–7], is slow, and occurs only at elevated temperatures, such as refluxing acetonitrile, we have found that in trifluoroacetic acid the reaction is extremely fast and pure sulfuryl chloride fluoride can be obtained in moderate to good yields at ambient temperature.

$$SO_2Cl_2 \xrightarrow[CF_3COOH]{NH_4F \text{ or } KF} SO_2ClF$$

The mechanism of the action of trifluoroacetic acid is not clear. It seems that the acid and ammonium fluoride or potassium fluoride may exist in equilibrium with hydrogen fluoride or bifluoride (HF_2^-), and the trifluoroacetate salts ($TFAHF^-$). Thus formed, hydrofluoric acid or the bifluoride ion (or $TFAHF^-$) readily reacts with sulfuryl chloride to give the sulfuryl chloride fluoride. Thus, trifluoroacetic acid assists in the *in-situ* generation of reactive hydrogen fluoride or bifluoride (or $TFAHF^-$). The advantage of this reaction over the use of pyridinium polyhydrogen fluoride [8] lies in the fact that the reaction can be carried out in ordinary glass equipment, whereas polyethylene apparatus is required for the latter. Furthermore, under these conditions the formation of sulfuryl fluoride was not observed.

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