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Experimental and theoretical research towards $R_fNCl_3^+$ cations, where $R_f = CF_3$, SF_5, FC(O) and F

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1. Introduction

Our group first proposed the synthesis of the $R_fNCl_3^+$ MF_6^- salts (M = As, Sb) from the reaction of the dichloroamines R_fNCl_2 with ClF and MF_5 several years ago. While our studies were underway, Minkwitz and coworkers reported the synthesis of the salts NCl_4^+ AsF_6^- [1] and $(CH_3)_nNCl_{4-n}^+$ MF_6^- (n = 1–3; M = As, Sb) [2] from the chlorination of NCl_3 and $(CH_3)_nNCl_{3-n}$ with Cl_2/AsF_5 (or SbF_5). We have subsequently synthesized $CF_3NCl_3^+$ AsF_6^- by both routes [3]. More recently, Minkwitz and coworkers have stated that the reaction between CF_3NCl_2, Cl_2, and AsF_5 does not yield $CF_3NCl_3^+$ AsF_6^-; however, one is led to believe that these workers used SO_2 as a solvent in their reaction, although little detail about reaction conditions was given [4].

2. Experimental details

Caution! Many *N*-halo compounds are known to be powerful explosives; therefore, suitable safety precautions should be kept in mind. We advise that the preparations and reactions of these materials be undertaken on a small scale.

In a typical reaction, AsF_5 and the respective dichloroamine R_fNCl_2 were reacted stoichiometrically with either Cl_2 (0.5 mmol) or ClF (3 mmol). The starting materials were condensed in an FEP tube reactor in the order given by successively lowering the level of the reactor in a Dewar containing liquid nitrogen. The reaction mixture was slowly warmed to −78 °C and placed in a slush bath at −78 °C for either 24 h (Cl_2 oxidant) or 12 h (ClF oxidant). The component volatile at −78 °C was then dynamically pumped from the reactor to a cold trap (−196 °C) until a constant weight was achieved. Fine white solids (70%–96% yield) remained in the reactor.

3. Results and discussion

The formation of the $R_fNCl_3^+$ AsF_6^- [$R_f = CF_3$, SF_5, FC(O)] salts occurs in high yield by reaction of the dichloroamine R_fNCl_2 with either Cl_2/AsF_5 or ClF/AsF_5 as shown in Eqs. (1) and (2).

$$2R_fNCl_2 + Cl_2 + 3AsF_5 \xrightarrow{-78\ ^\circ C} 2R_fNCl_3^+\ AsF_6^- + AsF_3 \quad (1)$$

$$R_fNCl_2 + ClF + AsF_5 \xrightarrow{-78\ ^\circ C} R_fNCl_3^+\ AsF_6^- \quad (2)$$

Support for the production of the same salts via the different chlorination routes came from identical Raman and ^{19}F NMR spectra. Longer reaction times were required for the reactions with Cl_2/AsF_5 and the yields were somewhat higher. Excess Cl_2 and/or higher reaction temperatures for reaction (1) led to the impurity $AsCl_4^+$ AsF_6^-. The existence of AsF_3 as a by-product in reaction (1) was supported by infrared spectroscopy.

All of the $R_fNCl_3^+$ AsF_6^- [$R_f = CF_3$, SF_5, FC(O)] salts are sensitive to moisture, while the $SF_5NCl_3^+$ AsF_6^- salt is the most thermally stable. It decomposed slowly at room temperature over a few days (Raman). To date, our attempts to prepare $FNCl_3^+$ AsF_6^- have resulted only in explosions. The ^{19}F NMR spectra of the $R_fNCl_3^+$ AsF_6^- [$R_f = CF_3$, SF_5, FC(O)] salts were consistent with the proposed structures; CD_3CN was used as solvent and CCl_3F as external reference. A comparison of these spectra with those of the starting dichloroamines was informative. Although we were unsuccessful in obtaining a ^{13}C NMR spectrum of the $CF_3NCl_3^+$ AsF_6^- salt, the J_{C-F} coupling constant was determined as 264 Hz from ^{13}C satellites in the ^{19}F

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NMR spectrum. In contrast, the ^{13}C NMR spectrum of $FC(O)NCl_3^+$ AsF_6^- could be recorded and the J_{C-F} coupling constant measured as 300 Hz. The $CF_3NCl_3^+$ AsF_6^- salt was also found to decompose in SO_2, either when monitored by ^{19}F NMR spectroscopy or when attempts were made to grow single crystals. The observed instability of $CF_3NCl_3^+$ AsF_6^- in SO_2 certainly explains the inability of Minkwitz and coworkers to observe the same product in their reaction [4].

The calculated vibrational frequencies (MP2/6-31G*) of the dichloroamines R_fNCl_2 [$R_f = CF_3$, FC(O) and F] matched the infrared and Raman data very well when a scaling factor of 0.95 was used; for SF_5NCl_2 a scaling factor of 0.88 was appropriate at the HF/6-31G* level. The calculated vibrational frequencies (MP2/6-31G*) of the $R_fNCl_3^+$ cations [$R_f = CF_3$, FC(O)] matched the infrared and Raman spectra quite well when scaled appropriately, as did the calculated vibrational frequencies of the $SF_5NCl_3^+$ cation at the HF/6-31G* level.

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