

A Lewis acid catalytic process for preparing fluorocarboxylic acid halides

Fred E. Behr^{*}, Yuri Cheburkov

3M Company, 3M Center, St. Paul, MN 55144, USA

Received 31 July 2001; accepted 31 August 2001

Dedicated to Karl Christe on the occasion of his 65th Geburtstag. Presented in part at the mini-Lewis acid symposia held in August 1997 at Whistler, BC, Canada

Abstract

Selected Group III and Group V Lewis acids were found to catalyze the isomerization and rearrangement of halosulfonyldifluoromethyl group ($R_f-CF_2SO_2X$, where X is either chlorine or fluorine) to form fluorocarboxylic acid halides (R_fCOX). Fluorodesulfoxylation of the halosulfonyldifluoromethyl group yielded SOF_2 as one of the two sulfur-containing oxides. Product analysis would suggest that both Lewis acid catalyzed and halogen exchange reactions are occurring and are dependent upon the starting halosulfonyldifluoromethyl material and Lewis acid. © 2001 Published by Elsevier Science B.V.

Keywords: Lewis acids; Halogen exchange reactions; Fluorocarboxylic acid halides

1. Introduction

Fluorinated sulfonyl fluorides and carboxylic acid halides have served as starting materials for a variety of commercially valuable products. Various commercial preparations of these valuable synthetic starting materials have been the subject of review articles [1,2]. The Simons electrochemical fluorination (ECF) process has been an industrially important method for preparing a large number of fluorinated materials such as perfluoroalkanesulfonyl fluorides as well as perfluoroalkanoyl fluorides. We report here a useful method for the functional group transformation of the sulfonyl halide materials to the useful carbonyl halides using Lewis acid catalysis.

Lewis acid chemistry has received much attention in the chemical literature. Several review articles [3,4], although somewhat outdated, provide valuable background information into the fascinating research area of Lewis acids and superacid chemistry, especially in fluorine chemistry. The early pioneering work of Gillespie [3], Olah et al. [4] used SbF_5 either alone or in an appropriate non-reactive solvent and clearly demonstrated the unique properties of liquid Lewis acids. Miller et al. [5] reported the use of the Lewis acid, aluminum chloride, to isomerize chlorofluorocarbons

such as 1,1,2-trichlorotrifluoroethane into 1,1,1-trichlorotrifluoroethane. More recent studies have demonstrated that chlorine–fluorine interchange occurred when aluminum chlorofluoride (made from aluminum chloride) was used as the Lewis acid [6,7].

We report the use of both liquid and solid Lewis acids, specifically SbF_5 and $AlCl_3$, as catalysts and halogen exchange reagents with fluorosulfonic acid halides. Olah and Ohyama [8] reported that simple fluoroalkanesulfonyl fluorides when reacted with certain Lewis acids, such as SbF_5 , produced reaction products that contained no sulfur. The chemical equation depicted in the reference mentions sulfur dioxide as the sole inorganic reaction product. Thus, it would appear that SbF_5 desulfoxylates fluorosulfonic acid fluorides. There appears to be no experimental evidence as to the exact chemical composition of the gaseous by-products in the experimental portion of the article.

We were interested whether Olah's observations were generally applicable to longer chain fluorinated sulfonyl fluorides. We set out to carefully examine the gaseous reaction products and to vary the amount and type of Lewis acid with the anticipation of better understanding the mechanistic insights in this apparently simple Lewis acid catalyzed reaction. Specifically, we were interested in the effects of Lewis acids, in general, with longer chain fluorosulfonyl fluorides that contained a difluoromethyl group, that is, $R_fCF_2SO_2F$.

^{*} Corresponding author.

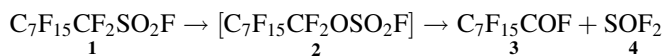
E-mail address: febehr@mmm.com (F.E. Behr).

2. Results and discussion

When catalytic amounts of distilled SbF_5 was added to base washed perfluorooctanesulfonyl fluoride and the initially homogeneous reaction mixture was heated to 100–120 °C for varying amounts of time to give gaseous, liquid and solid products. Gaseous products were collected for subsequent analysis. The fluorinated liquid phase was separated and analyzed by FT-IR, ^{19}F NMR and GC/MS. Analytical data suggested the perfluorooctanoyl fluoride was the primary functional product. Its presence was verified by the reaction of the crude reaction mixture with methanol to methyl perfluorooctanoate. The expected desulfoxylated fluorocarbon product, perfluorooctane, was observed as well as lesser amounts of perfluoroheptane. Both perfluorocarbons were identified by GC/MS.

Careful examination of the gaseous reaction products by FT-IR analysis revealed the presence of the expected sulfur dioxide, a small amount of carbon monoxide, and surprisingly, sulfur oxyfluoride, SOF_2 . The presence of a second inorganic reaction product suggests a more complicated reaction pathway than was originally outlined in [8].

Carbon monoxide was reported by Garth and Gumprecht [9] as the inorganic by-product of the reaction of perfluoroalkanoyl fluorides with SbF_5 . The presence of carbon monoxide strongly suggested the presence of an acid functionality at sometime during the reaction. The presence of sulfur oxyfluoride along with sulfur dioxide was verified by comparison of the FT-IR spectrum with the known spectrum for sulfur oxyfluoride. Simple defunctionalization of the fluorochemical sulfonyl fluoride would give only sulfur dioxide and a perfluoroalkane. The isomerization of the perfluoroalkanesulfonyl fluoride to a species such as $\text{R}_f\text{CF}_2\text{OSOF}$ may be envisioned but no spectral evidence was found by ^{19}F NMR. One can envision a transient intermediate that would be rapidly converted to the observed perfluoroalkanoyl fluoride and sulfur oxyfluoride perhaps assisted by the Lewis acid.



The acid fluoride **3** was usually observed in varying quantities (6–39%) depending upon the experimental conditions of time, temperature and molar ratios of $\text{C}_8\text{F}_{17}\text{SO}_2\text{F}:\text{SbF}_5$. The increased molar amounts of SbF_5 increase the Lewis acidity of the reaction mixture. Molecular complexes of antimony pentafluoride and sulfur dioxide, $\text{SbF}_5\cdot\text{SO}_2$ [10]; sulfur oxyfluoride, $\text{SbF}_5\cdot\text{SOF}_2$ [11] are known compounds that are thermally decomposed at the temperatures used during the experiments. Thus, the Lewis acid was regenerated when the reaction was conducted at atmospheric conditions. The Lewis acidity of the SbF_5 would be reduced due to the presence of significantly better Lewis bases, such as SO_2 , CO and SOF_2 . Perhaps, the reduced acidity of the reaction mixture may account for the formation of the desired perfluorooctanoyl fluoride.

Aluminum chloride was reacted in a similar manner with the sulfonyl fluoride **1**. Although similar conversion of the fluoride was observed, the reaction product distribution with AlCl_3 was different. The dominant reaction product was 1-chloroperfluorooctane, rather than the desired halide **3**. The formation of perfluorooctanesulfonyl chloride was probably the result of fluoride–chloride halogen exchange. The formation of 1-chloroperfluorooctane, most likely resulted from the thermolysis of the sulfonyl chloride. The presence of perfluorooctanoyl chloride rather than the fluoride suggested that chloride–fluoride exchange occurred with AlCl_3 . Halogen exchange has occurred, but the exact chemical composition of resultant Lewis acid was not determined. Whatever its composition, it was chemically different from that of aluminum chlorofluoride normally prepared and commonly used. When freshly prepared anhydrous aluminum chlorofluoride (ACF) [6,7] was reacted with the sulfonyl fluoride **1**, only perfluorooctane was observed. When ACF was used without proper handling procedure to ensure dryness, no reaction was observed with **1** at 110 °C. It would appear that freshly prepared and anhydrous ACF acted differently and was a more vigorous Lewis acid under these reaction conditions. Other commonly used Lewis acids, such as BCl_3 or BF_3 effected little, if any isomerization of or reaction with **1** even when the reaction temperatures were raised to 140 °C. Similarly, other Lewis acid fluorides, such as FeF_3 , TiF_4 , SnF_4 , TaF_5 and NbF_5 were found to be ineffective catalysts under these reaction conditions. Very little, if any, reaction occurred (<2 area%) was observed with chlorine-containing Lewis acids such as FeCl_3 , SnCl_4 or TiCl_4 . Although the Sn and Ti chlorides are liquids, the structure of these Lewis acids are more molecular than either SbF_5 or AlCl_3 . The latter Lewis acids are reported to be tetrameric or more easily dissociated [12] whilst many of the aforementioned solid and liquid Lewis acids are considerably more complex in structure.

Similarly, the reaction products from perfluorooctanesulfonyl chloride with SbF_5 showed similar reaction of the Lewis acid acting also as a halogen exchange reagent. The fluoride **3** could either have been formed by halogen exchange followed by Lewis acid catalysis on the sulfonyl chloride or from the small amount of fluoride **1** present in the crude reaction mixture. From the data, it is clear that the Lewis acid may undergo halogen exchange with the starting material to form a mixed antimony chlorofluoride compound. When the Swarts reagent was used as Lewis acid/halogen exchange reagent, no conversion of **1** was observed. Clearly, the in situ prepared antimony chlorofluoride was superior in its Lewis acid and halogen exchange reactivity as compared to the added Swarts reagent, SbCl_2F_3 .

3. Experimental

Analytical data was gathered at the Specialty Materials Manufacturing Division (SMMD) analytical service group

at 3M. Standard FT-IR, GC/MS and fluorine NMR techniques were used throughout this research. Reference spectra were available through an internal 3M reference system. Sulfonyl fluoride **1** was commercially available from 3M under the tradename FluoradTM fluorochemical FX-8. Aluminum chloride was purchased from Aldrich Chemical Company, Milwaukee, WI and was stored in a desiccator until used. Antimony pentafluoride was purchased from Allied Chemical Corporation and distilled under nitrogen and stored in fluoropolymer bottles prior to use. All glassware was dried at 110 °C and assembled hot prior to use. Dry nitrogen was used during the heating experiments. Gases were collected in dry ice–isopropanol cold trap prior to FT-IR analysis. Anhydrous chloride and fluoride salts were purchased from Aldrich Chemical Company, Ozark–Mahoning Company, Johnson Matthey Electronics or Advance Research Chemicals Inc. The anhydrous chlorides and fluorides were stored in a desiccator over P₂O₅.

3.1. Reaction of perfluorooctanesulfonyl fluoride with antimony pentafluoride

Into a round bottom flask, equipped with a reflux condenser, a –78 °C cold trap and a magnetic stirring bar was charged **1** (4.1 g, 8.2 mmol) and antimony pentafluoride (0.4 g, 1.8 mmol). The initially homogeneous mixture was heated to 100 °C for 2.5 h. As the reaction progressed, the initially homogeneous mixture formed two separate phases. The colorless, transparent upper phase (3.6 g) was separated from the darker lower inorganic phase. Gas chromatographic analysis using authentic reference compounds showed the following components: fluoride **3** (24 area%), perfluorooctane and perfluoroheptane (36 area%), and unreacted **1** (39 area%). The contents of the cold trap were analyzed by GC/FT-IR and showed the mixture to be predominately SOF₂ and SO₂ with a small amount of CO.

Using essentially the same procedure, the fluoride **1** (10.2 g, 20 mmol) and antimony pentafluoride (0.66 g, 3 mmol) were heated at 105–110 °C for 3 h. The resulting mixture was then distilled and the liquid fraction boiling up to 106 °C was collected. The analysis of the distillate showed the following components: acid fluoride **3** (24 area%), perfluorooctane (60 area%) and perfluoroheptane (5 area%) and unreacted **1** (9 area%).

3.2. Reaction of (excess) perfluorooctanesulfonyl fluoride with SbF₅

Using essentially the same procedure as in Section 3.1, the fluoride **1** (5.0 g, 9.9 mmol) and antimony pentafluoride (0.64 g, 2.9 mmol) were heated at 98 °C for 1 h. Gas chromatographic analysis of the resulting mixture showed the following components: acid fluoride **3** (27 area%), perfluorooctane and perfluoroheptane (56 area%) and unreacted **1** (9 area%). An additional 5 g of the sulfonyl fluoride **1** was

added to the mixture and the resulting mixture was reheated at 110 °C for 4 h. GC analysis showed the mixture contained 18 area% of the starting material. Additional 5 g of **1** was added and the resulting mixture was heated at reflux temperature of 125 °C for 16 h. The resulting upper layer (12.6 g) was separated from the lower dark viscous layer and was distilled with dry sodium fluoride (0.2 g). The fraction (10.3 g) boiling at 102–108 °C was collected and showed the following components: **3** (27 area%), perfluorooctane and perfluoroheptane (67 area%) and unreacted **1** (6 area%).

3.3. Reaction of perfluorooctanesulfonyl fluoride with aluminum chloride

While using essentially the same experimental procedure as in Section 3.1, the sulfonyl fluoride **1** (4 g, 8 mmol) and aluminum chloride (1 g, 8 mmol) were combined and the heterogeneous mixture was heated to 100–110 °C in a hot oil bath for 5 h. The resulting mixture was distilled and the fraction boiling at 50–86 °C at 30 Torr was collected. GC/FT-IR analysis showed the following components: perfluorooctanoyl chloride (13 area%), perfluorooctane and perfluoroheptane (9 area%), 1-chloroperfluorooctane (23 area%) and perfluorooctanesulfonyl chloride (56 area%).

3.4. Reaction of perfluorooctanesulfonyl fluoride with boron trifluoride

Into a dry 180 ml HastelloyTM pressure vessel equipped with a mechanical stirrer was charged **1** (51 g, 0.11 mol). The reactor was sealed, cooled with dry ice and attached to a vacuum pump to further reduce the internal pressure. Anhydrous gaseous boron trifluoride (8 g, 0.12 mol) was added to the reactor that was heated to 140 °C for 16 h. The reaction vessel was cooled, the excess pressure was vented through a scrubber filled with potassium hydroxide. The clear fuming liquid was analyzed by GC. No low boiling components were detected, only unreacted starting material.

3.5. Reaction of perfluorooctanesulfonyl fluoride with other solid and liquid Lewis acids

The following Lewis acids were mixed in equal molar amounts with **1**: BCl₃, SnCl₄, TiCl₄, FeCl₃, SbCl₅, TiF₄, FeF₃, SbF₅, TaF₅, CoF₃ and SbCl₂F₃. The experiments with the liquid Lewis acid chlorides were conducted in a similar manner as in Section 3.4. The experiments utilizing the solid Lewis acids were conducted in a glass reactor similar to that used in Section 3.1. Higher reaction temperatures (140–150 °C) and longer reaction times (12–16 h) were generally used to maximize the reaction parameters. The workup of the solid Lewis acid experiments entailed separation of the solids by filtration from the liquid fluoride **1**. Only trace amounts of unidentified low boiling materials were observed. Separation of the immiscible

fluorochemical phase from the liquid Lewis acids was done prior to GC analysis. No lower boiling components were detected.

3.6. Reaction of perfluorooctanesulfonyl chloride with antimony pentafluoride

Perfluorooctanesulfonyl chloride (5.74 g, 0.11 mmol), prepared by the method described by Brown and Coon [13], and antimony pentafluoride (0.47 g, 2 mmol) were heated at 100–110 °C in a hot oil bath for 4 h. The resulting upper layer (4.96 g) was separated from the precipitated antimony halides on the bottom. GC analysis of the upper liquid phase showed the following components: acid fluoride **3** (27 area%), perfluorooctane (37 area%), sulfonyl fluoride **1** (16 area%) and unreacted perfluorooctanesulfonyl chloride starting material (18 area%). No 1-chloroperfluorooctane was detected.

References

- [1] T. Abe, et al., in: R.E. Banks (Ed.), Preparation, Properties and Industrial Applications of Organofluorine Compounds, Wiley, New York, 1982.
- [2] M. Hudlicky, Chemistry of Organic Fluorine Compounds, 2nd Edition, Ellis Horwood, Chichester, 1976.
- [3] R.J. Gillespie, Acc. Chem. Res. 1 (1968) 202.
- [4] G.A. Olah, A.M. White, D.H. O'Brien, Chem. Rev. 70 (1970) 561.
- [5] W.T. Miller Jr., E.W. Fager, P.H. Griswald, J. Am. Chem. Soc. 72 (1950) 705.
- [6] V.A. Petrov, C.G. Krespan, B.E. Smart, J. Fluorine Chem. 77 (1996) 139.
- [7] V.A. Petrov, C.G. Krespan, B.E. Smart, J. Fluorine Chem. 89 (1998) 125.
- [8] G.A. Olah, T. Ohyama, Synthesis (1976) 319.
- [9] B.H. Garth, W.H. Gumprecht, US Patent 3555100 (1971).
- [10] G.S.H. Chen, J. Passmore, J. Chem. Soc., Dalton Trans. (1979) 1257.
- [11] J.W. Moore, H.W. Baird, H.B. Miller, J. Am. Chem. Soc. 90 (1968) 1358.
- [12] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.
- [13] H.A. Brown, R.I. Coon, US Patent 2950317 (1960).