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Reaction of fluoroolefins with sulfur chlorides in hydrogen fluoride–boron trifluoride system

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Dedicated to Dr. Karl Christe on the occasion of his 65th birthday

Abstract

The reaction of tetrafluoroethylene (**1**), perfluorovinyl ether (**3**), hexafluoropropene (**5**), and 2-H-pentafluoropropene (**7**) with sulfur chlorides in anhydrous HF/BF_3 system has been studied. The reaction with S_2Cl_2 at 40–100 °C produces a mixture of the corresponding di- and trisulfides along with smaller amounts of sulfenyl- and thiosulfenyl chlorides. In case of **7** the use of BF_3 catalyst results higher yields and selectivity of the process under milder conditions. The reaction of **5** and SCl_2 in HF/BF_3 at 100 °C is selective, gives $(CF_3)_2CFSCl$, isolated in 65% yield.

Keywords: Tetrafluoroethylene; Hexafluoropropene; Perfluorovinyl ether; 2-H-pentafluoropropene; Sulfur monochloride; Sulfur dichloride; Hydrogen fluoride; Boron trifluoride

1. Introduction

Polyfluoroalkyl sulphides and polysulfides is important group of fluorinated materials used for the synthesis of variety of sulfur-containing compounds. Partially fluorinated sulfides and polysulfides can be prepared by variety of methods, including the reaction of the corresponding sulfenyl chlorides with unsaturated or aromatic compounds [1], perfluoroalkyl iodides and metal salts of thiols [2,3], radical addition of polyfluorinated disulfides [4], sulfenyl- [1,5] and thiosulfenyl- [6] chlorides to olefins. Among methods for preparation of *perfluororinated* polysulfides are reaction of sulfur with perfluoroalkyl iodides [7,8], fluoroolefins [9–11], perfluorinated carbanions [12] and Lewis acid catalyzed oxidative addition of sulfur to fluoroolefins [13–15]. Thermal addition of sulfur chlorides to polyfluoroolefins [16] provides simple and direct route to perhalogenated polysulfides, however it proceeds at elevated temperature and is limited to production of sulfides containing at least two chlorine substituents in the molecule. Several years ago it was reported that the reaction of fluoroolefins with sulfur chlorides in fluorosulfonic acid as a solvent proceeds at significantly lower temperature producing a mixture of polysulfides general formulae $(FSO_2CFXCF_2)_2S_x$ [17–19]. The reaction of fluoroolefins with SF_4/HF/S_2Cl_2 system [20,21] results in the formation of the mixture of perfluoroalkyl polysulfides. Unfortunately, this process requires use of substantial amount of toxic and relatively expensive sulfur tetrafluoride. There is a growing interest in recent years in perfluorinated sulfides, since these materials has been proposed for use as components of azeotropic refrigerant compositions [22] and solvents for polymerization of fluoroolefins [23].

Perfluoroalkyl polysulfides can be also used as feedstock for the preparation of derivatives of perfluorinated sulfonic acids [21].

In search of simple and relatively inexpensive synthesis of perfluoroalkyl polysulfides the reaction of S_2Cl_2 and SCl_2 with fluoroolefins in anhydrous hydrogen fluoride as a solvent was investigated.

2. Results and discussion

Sulfur monochloride rapidly reacts with tetrafluoroethylene (**1**) in anhydrous HF as a solvent in the presence of BF_3 catalyst producing in a high yield the mixture in which sulfenyl chloride **2b**, disulfide **2c** and trisulfide **2d** are identified as major components (NMR, GC/MS). Surprisingly, crude reaction mixture contains a noticeable amount of

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Table 1
Reaction of fluoroolefins with sulfur chlorides in HF/BF_3

Entry	Reagents (g)	Temperature (°C)	Time (h)	Crude product (g)	Composition (%)
1	**1** (50), S_2Cl_2 (31), BF_3 (10), HF (100)	20	12	Trace	
2	**1** (50), S_2Cl_2 (31), BF_3 (10), HF (100)	40	12	54	**2a** (7), **2b** (2), **2c** (33), **2d** (49), **2e** (3), **2f** (4), others (2)
3	**1** (50), S_2Cl_2 (31), BF_3 (10), HF (100)	70	12	57	**2a** (12), **2b** (2), **2c** (23), **2d** (51), **2e** (3), **2f** (5), others (4)
4	**3** (66), S_2Cl_2 (26), BF_3 (10), HF (100)	100	12	70	**3** (7) **4a** (3), **4b** (9), **4c** (16), **4d** (58), others (7)
5	**4c**, **4d**[a] (36), Cl_2 (6)	10–25	8	40	**4a** (55), **4c** (30), **4b** (15)
6	**5** (50), S_2Cl_2 (26), BF_3 (10), HF (100)	100	12	77	**5** (6), **6a** (2), **6b** (33), **6c** (57), **6d** (2)
7	**5** (60), SCl_2[b] (26), BF_3 (10), HF (100)	100	12	41	**5** (6), **6a** (6), **6b** (72), **6c** (6), others (10); isolated yield of **6b**—65%
8	**7** (52), S_2Cl_2 (26), HF (100)	70	12	48	**8a** (10), **8b** (38), **8c** (37), **8d** (11), others (4)
9	**7** (52), S_2Cl_2 (26), BF_3 (10), HF (100)	50	12	71	**8a** (4), **8b** (87), **8c** (7), others (2); isolated yield of **8b**—67%

[a] Ratio 30:70, respectively.
[b] Distilled SCl_2.

monochlorodisulfide **2e** and -trisulfide **2f** (3–4%), along with smaller amount of thiosulfenyl chloride **2a** (see Table 1, entries 2 and 3)

$$\mathrm{CF_2{=}CF_2 + S_2Cl_2 \xrightarrow[BF_3,HF]{40-70^\circ} \underset{\mathbf{2a}}{C_2F_5SSCl} + \underset{\mathbf{2b}}{C_2F_5SCl} + \underset{\mathbf{2c}}{(C_2F_5)_2S_2} + \underset{\mathbf{2d}}{(C_2F_5)_2S_3} + \underset{\mathbf{2e}}{ClCF_2CF_2S_2C_2F_5} + \underset{\mathbf{2f}}{ClCF_2CF_2S_3C_2F_5}} \quad (1)$$

This result is in a sharp contrast to the data obtained for the reaction of **1** with $SF_4/HF/S_2Cl_2$ system leading to mixture of **2a**, **2b**, and **2d** in ratio 23:45:32, after 4 h at 80 °C [21]. That difference may be a result of either longer reaction time (12 h versus 4 h) or higher temperature of the work-up step of the process, which includes treatment of crude reaction mixture with water (see Section 3). The composition of crude product in the reaction of **1** and S_2Cl_2 does not change significantly at higher temperature (70 °C, 12 h), however at ambient temperature the reaction is quite slow producing only trace amount of product (see Table 1, entry 1).

The reaction between sulfur monochloride and vinyl ether **3** proceeds at higher temperature (100 °C, 12 h) leading after treatment of the reaction mixture with water to a mixture of **4a–c** and trisulfide **4d** (Table 1, entry 4).

$$\mathrm{\underset{\mathbf{3}}{CF_3OCF{=}CF_2} + S_2Cl_2 \xrightarrow[HF,BF_3]{100\,^\circ C,12\,h} \underset{\mathbf{4a}}{CF_3OCF_2CF_2SSCl} + \underset{\mathbf{4b}}{CF_3OCF_2CF_2SCl} + \underset{\mathbf{4c}}{(CF_3OCF_2CF_2)_2S_2} + \underset{\mathbf{4d}}{(CF_3OCF_2CF_2)_2S_3}} \quad (2)$$

The structures of **4a–d** were established from data ^{19}F NMR and GS/MS spectroscopy. The proposed structure of products and orientation of addition to a double bond are in good agreement with published data on the orientation of addition of electrophiles to **3** [24]. The chlorination under mild conditions of the mixture **4c** and **4d** leads to complete conversion of **4d** into a mixture of **4a** and **4b**, but surprisingly, disulfide **4c** under reaction conditions remained unchanged.

$$\mathbf{4c + 4d} + Cl_2 \xrightarrow[-5\text{ to }25\,^\circ C,8\,h]{h\nu} \mathbf{4a + 4b + 4c} \quad (3)$$

Hexafluoropropene (**5**) reacts with S_2Cl_2 at elevated temperature (Table 1, entry 6) with formation of mixture in which compounds **6b** and **6c** are major components, along with smaller amount of **6a** and **6d**

$$\mathrm{\underset{\mathbf{5}}{CF_3CF{=}CF_2} + S_2Cl_2 \xrightarrow[HF,BF_3]{100\,^\circ C,12\,h} \underset{\mathbf{6a}}{(CF_3)_2CFSSCl} + \underset{\mathbf{6b}}{(CF_3)_2CFSCl} + \underset{\mathbf{6c}}{[(CF_3)_2CF]_2S_3} + \underset{\mathbf{6d}}{[(CF_3)_2CF]_2S_4}} \quad (4)$$

Interestingly, the reaction of **5** with distilled SCl_2 is much more selective, leading to predominant formation of sulfenyl chloride **6b** isolated in 65% yield

$$\mathbf{5} + SCl_2 \xrightarrow[HF,BF_3]{100\,^\circ C,12\,h} \mathbf{6b} \quad (\text{yield } 65\%) \quad (5)$$

It should be pointed out that this result is in a good agreement with data of [18], where the formation of corresponding sulfenyl chloride as a major product was observed in the reaction of SCl_2 with **5** in $HOSO_2F$ as a solvent.

The effect of catalyst (boron trifluoride) was studied in the reaction of 2-H-pentafluoropropene (**7**) and S_2Cl_2. In the absence the reaction is slow even at 70 °C and produces a mixture of disulfide **8b**, trisulfide **8c**, tetrasulfide **8d** and $(CF_3)_2CH_2$ (**8a**) (Table 1, entry 8)

$$\mathrm{\underset{\mathbf{7}}{CF_3CH{=}CF_2} + S_2Cl_2 \xrightarrow[HF]{70\,^\circ C,12\,h} \underset{\mathbf{8a}}{(CF_3)_2CH_2} + \underset{\mathbf{8b}}{[(CF_3)_2CH]_2S_2} + \underset{\mathbf{8c}}{[(CF_3)_2CH]_2S_3} + \underset{\mathbf{8d}}{[(CF_3)_2CH]_2S_4}} \quad (6)$$

However, the same reaction in the presence of BF_3 catalyst proceeds rapidly at 50 °C leading significantly higher weight of crude product (71 g versus 46 g, respectively)

and predominant formation of disulfide **8b** (isolated in 67% yield), along with small amounts of **8a** and **8c** (Table 1, entry 9).

$$\mathbf{7} + S_2Cl_2 \xrightarrow[HF,BF_3]{50\,^\circ C,12\,h} \mathbf{8a} + \mathbf{8b} + \mathbf{8c} \quad \text{(isolated yield of } \mathbf{8b}\ 67\%) \tag{7}$$

3. Experimental

^{19}F and ^{1}H NMR spectra were recorded on a QE-300 (General Electric) instrument using $CFCl_3$ as internal standard or chloroform-*d* or acetone-d_6 as a lock solvent. Mass-spectra were recorded at 70 eV for EI using Hewlett-Packard 5985B GC/MS instrument.

3.1. Reagents

S_2Cl_2, SCl_2, BF_3 (Aldrich), tetrafluoroethylene, hexafluoropropene, perfluoromethylvinyl ether (DuPont), 2-H-pentafluoropropene (PCR) were commercially available and were used without further purification. Technical SCl_2 (Aldrich) was purified by distillation (residual amount of $S_2Cl_2 < 3\%$). Compound **8a** was identified by comparison with authentic sample. Compounds **2a–d** [14,15,21], **6a–d** [14,15,21], **8b** [25] were identified by comparison of ^{19}F and ^{1}H NMR spectra data with reported literature values. Compounds **2d**, **2f**, **4a–d**, **8c** and **8d** were not isolated, but identified in mixture by GC/MS or ^{19}F NMR spectroscopy (see below).

Caution: Hydrogen fluoride is toxic and causes severe chemical burns. It should be handled by trained personnel only.

3.1.1. Reaction of sulfur chlorides with fluoroolefins (typical procedure)

Sulfur chloride (26–31 g, 0.2–0.23 mol for S_2Cl_2; 26 g, 0.25 mol for SCl_2) was loaded in 400 ml Hastelloy shaker tube. The reactor cooled down to −50 °C and charged with 100 g of HF, 0.3–0.5 mol of the corresponding fluoroolefin and 10 g BF_3 and kept at 20–100 °C for 12 h. At ambient temperature water (200 ml) is injected into shaker tube (this step is exothermic and since the inside temperature of reactor at this step was not controlled, temperature of the reaction mixture could exceed 70–80 °C). The reactor was unloaded at 25 °C, organic layer separated, dried with $MgSO_4$ and analyzed. Reaction conditions are given in Table 1.

3.1.2. Chlorination of mixture *4c, 4d*

The mixture of 36 g of mixture **4c**, **4d** (ratio 30:70) and 15 g of chlorine was kept in a flask with dry-ice condenser under irradiation using sun lump. In 8 h temperature of the reaction mixture went from −5 to 25 °C. Reaction mixture was washed with water, dry over $MgSO_4$ and crude product (28 g) was analyzed. Reaction conditions and ratios of reactants and products are given in Table 1.

Compound **2d**: proposed structure—$ClCF_2CF_2S_2CF_2CF_3$; MS: 318 [M^+, $C_4ClF_9S_2^+$, for Cl^{35}].

Compound **2f**: proposed structure—$ClCF_2CF_2S_3CF_2CF_3$; MS: 350 [M^+, $C_4ClF_9S_3^+$, for Cl^{35}].

Compound **4a**: bp 110–112 °C; $CF_3OCF_2CF_2SSCl$; ^{19}F NMR: −55.93 (3F, t; 9 Hz), −87.38 (2F, m), −94.86 (2F, s); MS: 284 [M^+, $C_3ClF_7OS_2^+$, for Cl^{35}].

Compound **4b**: bp 58–59 °C; $CF_3OCF_2CF_2SCl$; ^{19}F NMR: −55.80 (3F, t; 9 Hz), −87.40 (2F, m), −97.67 (2F, t, 3 Hz); MS: 252 [M^+, $C_3ClF_7OS^+$, for Cl^{35}].

Compound **4c**: $(CF_3OCF_2CF_2)_2S_2$; ^{19}F NMR: −55.88 (3F), −86.41 (2F, m), −94.83 (2F); MS: 434 [M^+, $C_6F_{14}O_2S_2^+$].

Compound **4d**: $(CF_3OCF_2CF_2)_2S_3$; ^{19}F NMR: −55.88 (3F), −87.43 (2F, m), −95.76 (2F); MS: 466 [M^+, $C_6F_{14}O_2S_3^+$].

Compound **8c**: $[(CF_3)_2CH]_2S_3$; ^{19}F NMR: −66.40 (6F, d; 7 Hz); ^{1}H NMR: 4.00 (hept., 7 Hz); MS: 398 [M^+, $C_6H_2F_{12}S_3^+$].

Compound **8d**: $[(CF_3)_2CH]_2S_4$; ^{19}F NMR: −66.80 (6F, d; 7 Hz); ^{1}H NMR: 4.00 (hept., 7 Hz); MS: 430 [M^+, $C_6H_2F_{12}S_4^+$].

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