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Electrochemical Fluorination of Ethanethiol

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Synopsis. The electrochemical fluorination of ethanethiol has been carried out. A number of new fluoroalkyl sulfur compounds have been isolated and characterized.

With bivalent sulfur compounds, the electrochemical fluorination of alkyl sulfides has frequently been carried out,[1)] but little work has been reported on the electrochemical fluorination of thiols.[2)] The present paper will describe the results of a study of the electrochemical fluorination of ethanethiol, a study initiated in order to examine the possible use of this method for the preparation of partially-fluorinated alkyl sulfur compounds.

The results turned out to be very complex, yielding almost all possibly producible fluoroethyl derivatives of sulfur hexafluoride, most of them new. However, their yields were quite small ($<13\%$). The extensive cleavage of the carbon-sulfur bond of the thiol was observed giving fluorocarbons and sulfur hexafluoride. There were also formed dialkyl sulfur tetrafluoride compounds, that may be yielded as a consequence of the fragmentation of the thiol and the combination of the fragments, showing the complexity of the nature of the electrochemical fluorination of sulfur compounds.[1c,f)] The low yields of the fluorinated products may be ascribed partly to the instability of the thiols in hydrogen fluoride[3)] and also to the formation of tar-like materials during fluorination.

Table 1. Fluoroalkyl sulfur compounds

Compound	Bp[a)] (°C)	n_D^{20}	Elemental analysis[b)] C (%)	H (%)	F (%)
$CHF_2CF_2SF_5$	31.6	<1.28	10.63 (10.53)	0.70 (0.44)	74.6 (75.0)
$CF_3CH_2SF_5$	39.5	<1.28	11.55 (11.43)	0.95 (0.96)	72.4 (72.4)
CHF_2CHFSF_5	48.0	1.2866	11.57 (11.43)	1.16 (0.96)	72.9 (72.4)
$CHF_2CH_2SF_5$	56.0	1.2967	12.25 (12.50)	1.75 (1.58)	69.0 (69.2)
$C_2H_5SF_5$	59.6	1.3114	15.56 (15.38)	3.67 (3.23)	60.5 (60.9)
$CH_2FCHFSF_5$	62.2	1.3048	12.72 (12.50)	1.77 (1.58)	69.1 (69.2)
cis-$(C_2F_5)_2SF_4$	71.7	1.2832	13.81 (13.88)		76.4 (76.9)
$CF_3CHFSF_4C_2F_5$	81.4	1.2870	14.63 (14.64)	0.50 (0.31)	74.7 (75.3)
$CF_3CH_2SF_4C_2F_5$	88.6	1.2941	15.26 (15.49)	0.85 (0.65)	73.0 (73.5)
$C_2F_5SF_4C_2F_4SF_5$	132.0	1.3057	10.77 (10.58)		75.2 (75.3)

a) Recorded, uncorrected, at atmospheric pressure.
b) The calculated values are given in parentheses.

The physcial constants and elemental analyses of the new sulfur-containing compounds are listed in Table 1. From the kinds of the products, such as $CF_3CH_2SF_5$, $CHF_2CH_2SF_5$, and $C_2H_5SF_5$, it may be said that, during the fluorination, the sulfur atom in the thiols is oxidized to the sexivalent state, mainly in the initial stage of the fluorination, before the fluorination of the alkyl group is complete, as has been shown in the fluorination of alkyl sulfides.[1b,c,f)]

The ^{19}F NMR spectroscopy was particularly useful in the structure determination of these kinds of compounds.[4,5)] For example, fluoroethylsulfur pentafluorides could be confirmed by indicating the presence of two differently shielded types of fluorine nucleus bonded to the sulfur in the correct intensity ratio of 1 : 4 in the regions expected. The axial fluorine nuclei are more shielded than the equatorial fluorine nuclei. The ^{19}F and ^1H NMR data are shown in Table 2. Except for the case of bis(pentafluoroethyl)sulfur tetrafluoride, the *trans* configuration of the dialkyl groups of disubstituted derivatives of sulfur hexafluoride was confirmed: all of the $-SF_4-$ fluorine atoms are equivalent, showing a single multiplet expected for only the *trans*-isomer.

The bis(pentafluoroethyl)sulfur tetrafluoride obtained was found to be a mixture of *cis* ($A_2B_2X_4Y_6$ system)- and *trans* ($A_4X_4Y_6$ system)-isomers in an approximate ratio of 1 : 6, which could be resolved by gas chromatography. For the *trans*-isomer, the $-SF_4-$ signals are a multiplet centered at -26.7 ppm (in CCl_4, with respect to internal CCl_3F). In the case of the *cis*-isomer, in the sulfur-fluorine regions, two triplets of multiplets of an equal intensity, centered at -21.8 and -61.4 ppm, are exhibited. The coupling interaction between SF_{ax} and SF_{eq} is 89.5 Hz. This is the first example of the formation and identification of the *cis*-isomer of bis(perfluoroalkyl)sulfur tetrafluoride in the electrochemical fluorination. Only the *trans*-isomers have been yielded *via* the electrochemical fluorination of the sulfides.[1b-d,4,5)]

Experimental

The electrolytic fluorination apparatus and operating procedures were similar to those described previously.[6)] The mass spectra were recorded on a Hitachi RMU-7 instrument at 70 eV, the ^{19}F NMR spectra, on a Hitachi R-20B instrument at 56.4 MHz, and the ^1H NMR spectra, on a Hitachi R-22 instrument at 90 MHz.

A representative run and the results obtained will be described below. The sample (25.5 g, 0.410 mol) was dissolved in anhydrous hydrogen fluoride (400 ml) in the cell and fluorinated under the following conditions: sodium fluoride, 20.0 g; anodic current density, 3.5 A/dm^2 (the effective surface areas of the anodes and the cathodes were both 7.7 dm^2); cell voltage, 5.5—6.5 V; cell temperature, 17—18 °C; electricity supplied, 312 A h (690 min); helium, 100 ml/min. (Though this flouorination could be carried out without using a conductivity additive, the use of sodium fluoride increased the yields of partially-fluorinated ethylsulfur pentafluorides). The products (75.5 g) obtained were rectified into four fractions by means of a low-temperature rectification column, and each fraction was then subjected to gas-chromatographic analysis using the following stainless-steel column, 2 m × 3 mm, silica gel; 4 m × 3 mm, Daifl oil 3 (20%) on Chromosorb P-AW, 4 m × 3 mm, Silicone DC QF-1 (15%) on Chromosorb P-AW.

The following compounds were obtained (the compositions were calculated on the basis of the chromatographic peak

TABLE 2. ^{19}F AND ^1H NMR SPECTRAL DATA[a,b,c)]

Compound	Chemical shifts, ppm	Coupling constants, Hz
$CHF_2{}^aCF_2{}^bSF_5$	F^a 135.1, F^b 101.2, SF_{eq} -41.5, SF_{ax} -64.9 H 6.1	F^a–H 52.2, F^a–F^b 8.1, F^a–SF_{eq} 8.1, F^b–SF_{eq} 13.0, F^b–H 5.2, F^b–SF_{ax} 5.0, SF_{ax}–SF_{eq} 147.2 H–F^a 52.1, H–F^b 5.2, H–SF_{eq} 0.9
$CF_3{}^aCH_2SF_5$	F^a 65.5, SF_{eq} -70.0, SF_{ax} -76.5 H 4.0	F^a–SF_{eq} 10.5, F^a–H 8.7, SF_{ax}–F^a 2.1, $SF^a{}_x$–SF_{eq} 143.9 H–F^a 8.9, H–SF_{eq} 7.3
$CH^aF_2{}^aCH^bF^bSF_5$	F^a_A 128.8, F^a_B 132.4, F^b 175.1, SF_{eq} -49.8, SF_{ax} -70.9 H^a 6.0, H^b 5.4	F^a_{A-B} 306.3, F^a–H^a 52.2, F^a_A–F^b 12.4, F^a_A–SF_{eq} 9.4, F^a_A–H^b 6.6, F^a_B–F^b 9.4, F^a_B–SF_{eq} 8.1, F^a_B–H^b 8.7, F^b–H^b 44.2, F^b–H^a 6.5, F^b–SF_{eq} 2.3, F^b–SF_{ax} 1.8, SF_{ax}–SF_{eq} 147.5 H^a–H^b 3.9, H^b–SF_{eq} 5.2
$CH^aF_2{}^aCH_2{}^bSF_5$	F^a 117.3, SF_{eq} -68.5, SF_{ax} -79.1 H^a 6.2, H^b 3.9	F^a–H^a 54.5, F^a–H^b 13.9, F^a–SF_{eq} 9.6, F^a–SF_{ax} 1.5, SF_{ax}–SF_{eq} 146.8 H^a–H^b 4.5, H^b–SF_{eq} 8.0
$CH_3{}^aCH_2{}^bSF_5$	SF_{eq} -61.3, SF_{ax} -84.2 H^a 1.5, H^b 3.7	SF_{ax}–SF_{eq} 143.9 H^a–H^b 7.6, H^a–SF_{eq} 1.5, H^b–SF_{eq} 7.7
$CH_2{}^aF^aCH^bF^bSF_5$	F^a 232.1, F^b 164.0, SF_{eq} -49.1, SF_{ax} -73.6 H^a 4.8, H^b 5.6	SF_{ax}–SF_{eq} 145.7, others unresolved H^a–F^a 46, H^b–F^b 46.2, H^b–F^a 25
cis-$(CF_3{}^aCF_2{}^b)_2SF_4$	F^a 81.1, F^b 97.4, SF_{ax} -21.8, SF_{eq} -61.4	F^a–SF_{ax} 8.8, F^a–SF_{eq} 8.6, F^a–F^b 2.2, F^b–SF_{ax} 12.0, F^b–SF_{eq} 9.9, SF_{ax}–SF_{eq} 89.5
$CF_3{}^aCHF^bSF_4CF_2{}^c$-$CF_3{}^d$	F^a 76.1, F^b 170.1, F^c 97.7, F^d 81.2, SF_{eq} -34.7 H 5.6	F^a–SF_{eq} 10.0, F^a–H 5.3, F^b–H 43.3, F^b–F^a 9.3, F^b–SF_{eq} 1.0, F^c–SF_{eq} 15.7, F_d–SF_{eq} 9.0 H–F^b 43.2, H–F^a 5.2, H–SF_{eq} 5.0
$CF_3{}^aCH_2SF_4CF_2{}^b$-$CF_3{}^c$	F^a 65.1, F^b 97.5, F^c 81.2, SF_{eq} -53.1 H 4.1	F^a–SF_{eq} 10.9, F^a–H 8.6, F^b–SF_{eq} 16.3, F^c–SF_{eq} 9.0 H–F^a 8.7, H–SF_{eq} 7.7
$CF_3{}^aCF_2{}^bSF_4CF_2{}^c$-$CF_2{}^dS'F_5$	F^a 79.8, F^b 96.6, SF_{eq} -28.5, F^c 91.8, F^d 93.6, $S'F_{eq}$ -44.7, $S'F_{ax}$ -62.4	F^a–SF_{eq} 8.8, F^b–SF_{eq} 15.3, F^c–SF_{eq} 16.1, F^c–$S'F_{eq}$ 13.3, F^d–$S'F_{eq}$ 16.1, F^d–SF_{eq} 13.5, F^d–$S'F_{ax}$ 4.8, F^d–F^c 2.3, $S'F_{ax}$–$S'F_{eq}$ 145.7, $S'F_{ax}$–F^d 4.9, $S'F_{ax}$–F^c 1.4

a) CCl_4 solution. b) The chemical shifts are in δ values with respect to CCl_3F for ^{19}F, and to TMS for ^1H as internal references. c) SF_{eq} and SF_{ax} indicate equatorial (basal) and axial (apical) fluorine atoms respectively.

areas): C_1 and C_2 fluorocarbons (29.4 g), SF_6 (12.7 g), *n*-C_4F_{10} (0.2 g), $C_2H_5C_2F_5$ (0.3 g), $C_2F_5SF_5$[1b,c)] (12.9 g, 12.8%), *trans*-$(C_2F_5)_2SF_4$[1b)] (1.2 g), *cis*-$(C_2F_5)_2SF_4$ (0.2 g), CF_3CHFSF_5[7)] (2.9 g), $CHF_2CF_2SF_5$ (0.5 g), $SF_5C_2F_4SF_5$[2c)] (0.4 g), $CF_3CH_2SF_5$ (9.8 g, 11.3%), CHF_2CHFSF_5 (1.1 g), $CF_3CHFSF_4C_2F_5$ (0.03 g), $CHF_2CH_2SF_5$ (1.5 g), $C_2H_5SF_5$ (0.3 g), $CH_2FCHFSF_5$ (0.1 g), $C_2F_5SF_4C_2F_4SF_5$ (0.04 g), $CF_3CH_2SF_4C_2F_5$ (0.02 g), others (1.6 g).

trans-$(C_2F_5)_2SF_4$ had bp 70.0 °C (lit,[1b)] bp 70.0 °C) and n_D^{20} <1.28. ^{19}F NMR:[4,5)] $(CF_3{}^aCF_2{}^b)_2SF_4$; F^a 80.5, F^b 97.7, SF_{eq} -26.7 ppm; F^a–SF_{eq} 8.9. F^b–SF_{eq} 14.9, F^a–F^b 0.6 Hz,

The significant ions from the mass cracking patterns are as follows: *cis*-$(C_2F_5)_2SF_4$; (*m/e*) 189 [$C_2F_5SF_2$], 119 [C_2F_5], 89 [SF_3], 69 [CF_3]. $CHF_2CF_2SF_5$: (*m/e*) 127 [SF_5], 101 [M$-SF_5$], 89 [SF_3]. $CF_3CH_2SF_5$: (*m/e*) 191 [M$-$F], 127 [SF_5], 89 [SF_3], 83 [M$-SF_5$], 69 [CF_3]. CHF_2CHFSF_5: (*m/e*) 127 [SF_5], 122 [CH_2SF_4], 89 [SF_3], 83 [M$-SF_5$]. $CF_3CHFSF_4C_2F_5$: (*m/e*) 119 [C_2F_5], 101 [C_2HF_4], 89 [SF_3], 82 [C_2HF_3], 69 [CF_3]. $CHF_2CH_2SF_5$: (*m/e*) 127 [SF_5], 89 [SF_3], 65 [M$-SF_5$]. $C_2H_5SF_5$: (*m/e*) 127 [SF_5], 89 [SF_3], 70 [SF_2]. 51 [SF], 29 [M$-SF_5$], 28 [C_2H_4]. $CH_2FCHFSF_5$: (*m/e*) 127 [SF_5], 89 [SF_3], 65 [M$-SF_5$], 64 [$C_2H_2F_2$]. $C_2F_5SF_4C_2F_5SF_5$: (*m/e*) 189 [$C_2F_5SF_2$], 119 [C_2F_5], 100 [C_2F_4], 89 [SF_3], 69 [CF_3]. $CF_3CH_2SF_4C_2F_5$: (*m/e*) 191 [$C_2H_2F_3SF_4$], 153 [$C_2H_2F_5S$], 119 [C_2F_5], 89 [SF_3], 84 [CH_2F_2S], 83 [$C_2H_2F_3$], 70 [SF_2], 69 [CF_3].

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