Fluorsulfonylmethylidene Sulfur Difluoride Oxide, FSO_2–$CH=SF_2=O$

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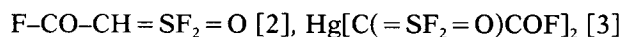## ABSTRACT

SO_3 adds across the CS double bond of $H_2C=SF_4$ with formation of 2-tetrafluoro-4-dioxo-1,2,4-oxadithietane, which rearranges to fluorsulfonylmethylidene sulfur difluoride oxide, F–SO_2–$CH=SF_2=O$ in the presence of CsF. © 1996 John Wiley & Sons, Inc.
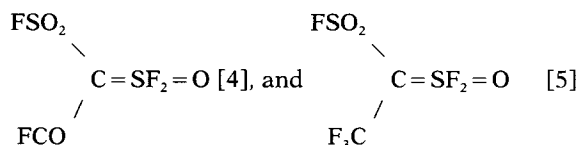
INTRODUCTION

Alkylidene sulfur tetrafluorides ($R_2C=SF_4$) are known to react in two ways: addition across the CS double bond, or cleavage of the CS double bond under formation of an intermediate carbene and SF_4 [1]. While there are only a few examples for the latter reaction, the addition reaction is well understood. The reactions occur often at very low temperature and with quantitative yields. Polar molecules add particularly smoothly and in a regiospecific manner: the negative part adds to the sulfur atom. This reaction principle made it possible to produce the first alkylidene sulfur difluoride oxides, a class of compounds related to the alkylidene sulfur tetrafluorides.

FCO–$CH=SF_2=O$ was first prepared in 1988 by Krügerke and Seppelt, and by now a total of four such compounds are known.

F–CO–$CH=SF_2=O$ [2], $Hg[C(=SF_2=O)COF]_2$ [3]

$$\begin{array}{cc} FSO_2 & FSO_2 \\ \diagdown & \diagdown \\ \quad C=SF_2=O \text{ [4], and} & \quad C=SF_2=O \quad \text{[5]} \\ \diagup & \diagup \\ FCO & F_3C \end{array}$$

The parent molecule $H_2C=SF_2=O$ is still missing, however.

The structural principle of sulfur in these compounds is of course the tetrahedron. Of special interest is the nature of the CS double bond. F–CO–$CH=SF_2=O$ exists, according to NMR measurements at low temperatures, in three isomeric forms [2]. If one assumes that there is hindered rotation around the CS double bond *and* the CC single bond, then four isomers can exist. These isomers should have slightly different energies, and indeed they appear in different intensities in the NMR spectra under the assumption that the missing isomer has too little intensity to be observed. According to ab initio calculations, the isomer with double cis configuration of the O...H...O atoms is the most stable one, possibly as a result of the weak intramolecular electrostatic attraction of these differently charged atoms [6]. Free rotation around the CC bond is frozen in, at first, and around the CS bond only at very low temperatures. The model given in Ref. [2] has been revised, the assignment now being based on comparison with calculated relative intensities and trends in coupling constants [6].

None of the other three known alkylidene sulfur difluoride oxides show similar behavior. Full structural information is available for $Hg[C=SF_2=O(CF_3)]_2$ [3]. Here, the Hg–$C=S=O$ atoms lie practically in one plane having a *cis* orientation, the same geometry that is predicted to be most stable for COF–$CH=SF_2=O$ by calculations [6].

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RESULTS

In order to arrive at another more simple alkylidene sulfur difluoride oxide, we started out with $H_2C = SF_4$ and added SO_3 across the CS double bond in a manner analogous to Ref. [5]. The resulting 1,2,4-oxadithietane can be isolated as a colorless solid that is moderately stable in the absence of bases. Its full structural characterization is based on NMR spectroscopy and a single-crystal structure determination. The ^{19}F NMR shows a spectrum that can, in simplified form, be described as an A_2BC spectrum because ^1H–^{19}F couplings are quite small, as was shown by simulation, (see Figure 1).

A clear picture of the structure results from the single-crystal structure determination at low temperatures (see Figure 2 and Table 1). The four-membered ring is found to be planar, and bonds within the ring to the four coordinated sulfur atom are clearly shorter than those to six coordinated sulfur, as can be rationalized by the different hybridizations of the two sulfur atoms. Intermolecular contacts between hydrogen and terminal oxygen atoms of 248.3 pm (C-H. . .O) lengths are important for the packing.

The 1,2,4-oxadithietane undergoes a ring-cleavage reaction with CsF. It can be assumed that there is at first an HF elimination step occurring, because the postulated intermediate 1,2,4-oxadithiet has previously been observed in a similar reaction [5]. There, however, CF_3 substitution on carbon might have protected the intermediate oxadithiet from further reaction. The unsaturated ring is then opened in the presence of CsF, resulting in fluorosulfonylmethylidene sulfurdifluoride oxide. An excess of SO_3, $K^+(t)C_4H_9O^-$, DBO, or DBU can replace CsF in bringing about this transformation.
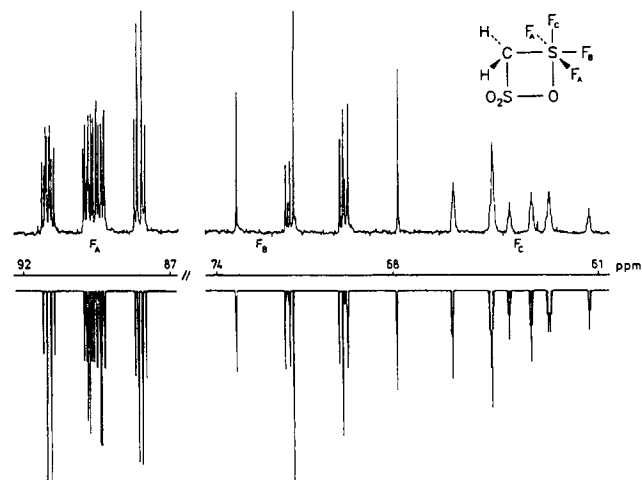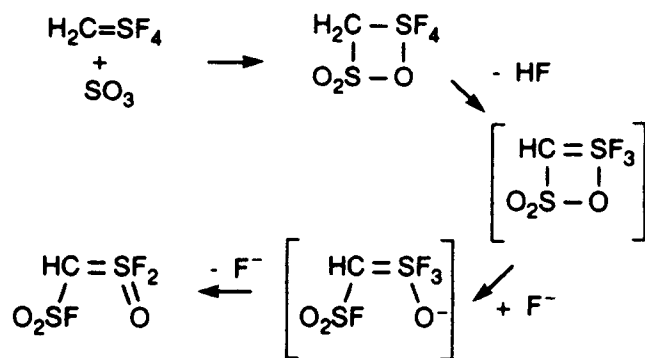

The identity of FSO_2–$CH = SF_2 = O$ is proven by the usual physical data. IR and Raman spectra are comparatively simple, a partial assignment of bands being possible. The ^{19}F, ^1H, and ^{13}C NMR spectra are in accord with the structure; the AB_2 type of the ^{19}F NMR spectrum is especially structurally meaningful. Cooling to $-95°$ (melting point of CF_2Cl_2) does not bring about any change in the spectrum. This can be interpreted in two ways: either the CS double bond can rotate freely, or it is fixed in one preferred orientation over the entire temperature range. In the light of the most recent assignment of the dynamic behavior of $FCO–CH = SF_2 = O$, namely that the SC double bond is the one that is frozen in place only at $-135°C$, [2,6] we assume that, in FSO_2–$CH_2 = SF_2 = O$, the SC double bond rotates freely

FIGURE 1 ^{19}F NMR spectrum of $O_2S\diagup^{CH_2}\diagdown SF_4$ at 84.25 $\diagdown \diagup$ O MHz, above: experimental, lower line: simulated spectrum [7].
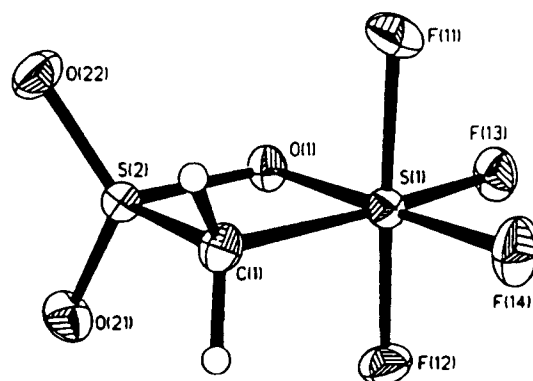
FIGURE 2 $O_2S\diagup^{CH_2}\diagdown SF_4$, crystal structure at $-140°C$, $\diagdown \diagup$ O Ortep plot, 50% probability.

TABLE 1 Important Bond Lengths (pm) and Angles (°) of 4,4-dioxo-2,2,2-tetrafluoro-1,2,4-oxadithiethane

C1–S1	181.0(2)	O1–S1–C1	83.8(1)
O1–S1	169.8(2)	O1–S2–C1	87.1(1)
C1–S2	178.0(2)	S1–O1–S2	99.4(1)
O1–S2	162.0(2)	S1–C1–S2	89.7(1)

even at −95°C. Since, at this temperature, no indication of line broadening was observed, we did not try to cool the compound down further in a more suitable solvent. If this interpretation remains true, the alkylidene sulfur difluoride oxides are intermediate between alkylidensulfurtetrafluorides ($R_2C = SF_4$) or difluorides ($R_2C = SF_2$) that have torsionally stable CS double bonds, and the sulfur ylides ($R_2\bar{C}\overset{+}{S}R_2$ and/or oxy sulfur ylides ($R_2\bar{C}-\overset{+}{S}OR_2$) always show a free rotation around the CS bond. In the latter case, the CS bond is always written in the ylidic form, not only because of free rotation, but also because of their comparatively large lengths of 171–174 pm [8] as compared with $R_2C = SF_4$ (155–160 pm) [1] and $R_2C = SF_2$ (160 pm) [1,9]. The ¹³C chemical shift at δ 42.9 and the coupling constant $^1J_{H-C}$ = 200.2 Hz are very similar to the values found for $CH_2 = SF_4$ (δ 47.0, 190.4 Hz) and $CF_3–CH = SF_4$ (δ 55.6, 192.4 Hz) [10], so the carbon binding state should be similar, but is obviously different from the sulfur ylids (δ 10–20, 150–180 Hz) [11].

A crystal structure of $FSO_2–CH = SF_2 = O$ revealed that the CS bond is of similar length (157.9 pm), as in $R_2C = SF_4$ and $R_2C = SF_2$ (see Figure 3, and Table 1).

Also the CS "single" bond directed towards the fluorosulfonyl group is much shorter 167.2(4) pm than a typical CS single bond. To account for this partial double-bond character, numerous resonance formulations can be taken into consideration; especially all SO and SF bonds are of course far from being purely covalent. In the solid state, the −CH = SF₂ = O part of the molecule is fixed in the cis H–C = S = O orientation, as also proposed for COF–CH = SF₂ = O, as the most stable configuration [2]. Weak electrostatic intramolecular interaction between H and O could account for this. Concerning the packing, there is a hydrogen bridge observed, CH. . .OS, of 247 pm length (C. . .O). These bridge bonds may be responsible for the asymmetric orientation of the FSO₂ group, preventing the molecule from having mirror symmetry.
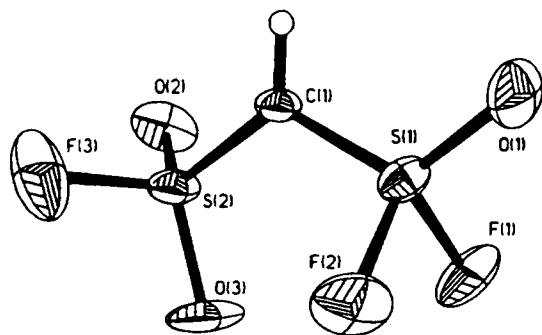
$FSO_2–CH = SF_2 = O$ undergoes hydrolysis to

FIGURE 3 FSO₂–CH = SF₂ = O, crystal structure at −143°C, Ortep plot, 50% probability.

$CH_2(SO_2F)_2$. This material is known and has originally been prepared by chlorine fluorine exchange [12].

EXPERIMENTAL

Moisture-sensitive compounds were handled in a dry box with an automatically dried argon atmosphere that has a water content of <1 ppm. Gases and volatile materials were handled in glass vacuum lines. NMR spectra were recorded on a FX 90Q spectrometer of JEOL Ltd., Tokyo, Japan. Frequencies are 89.55 MHz (¹H), 84.25 MHz (¹⁹F), and 22.49 MHz (¹³C). Spectra are recorded against TMS and CFCl₃ as external or internal standards, and chemical shifts are given according to IUPAC rules. Mass spectra were recorded on a MAT 711 Spectrometer (Varian Co., Bremen, Germany) EI excitation, 80 EV. IR spectra were recorded in gas cells of 10 cm lengths on a Perkin-Elmer 883 instrument. Raman spectra were recorded on an SPEX Industries Instrument, type 1403 (Edison, NY), and with Ar laser excitation of 488 nm wave lengths. Crystal-structure measurements were done on an Enraf Nonius CAD 4 four-cycle diffractometer (Delft, Netherlands).

Starting materials: $H_2C = SF_4$ was prepared according to Ref. [13]; SO_3 was pumped out of disulfuric acid in vacuum and used immediately. CsF was briefly melted in a platinum crucible, emptied on a stainless plate, and broken and powderized under dry argon in a ball mill.

2,2,2,2-Tetrafluoro-4,4-dioxo-1,2,4-oxadithietane, $CH_2-SF_4-O-SO_2$

0.55 g (6.9 mmol) of SO_3 was condensed in vacuum out of disulfuric acid into a 10 mm glass ampule, and then 1.1 g (9.0) mmol $H_2C = SF_4$ was added by condensation. The ampule was sealed. Upon warming to room temperature, an exothermic reaction took place, and most of the content solidified. Shaking for 5 minutes at room temperature completed the reaction; then the cooled ampule was opened and the content was pumped in vacuum through −78 and −196°C cold traps. The −196° trap contained unreacted $H_2C = SF_4$. The oxadithietane in the −78°C cold trap was sublimed by heating under vacuum

TABLE 2 Important Bond Lengths (pm) and Angles (°) of Fluorosulfonyl Methylidene Sulfur Oxide Difluoride

S1–F1	152.7(2)	F1–S1–F2	92.8(2)
S1–F2	151.8(3)	O1–S1–C1	118.9(2)
S1–O1	139.1(3)	S1–C1–S2	122.6(3)
S1–C1	157.9(4)	O2–S2–O3	118.6(2)
S2–F3	150.2(3)		
S2–O2	140.3(3)		
S2–O3	141.7(3)		
S2–C1	167.2(4)		

TABLE 3 Experimental Details of the Crystal Structures

Compound	CH_2SF_4–O–SO_2	FSO_2–CH=SF_2=O
Formula	$CH_2S_2O_3F_4$	$CHS_2O_3F_3$
Size (mm)	0.4 × 0.4 × 0.3	0.5 × 0.3 × 0.2
Color	colorless	colorless
a (pm)	220.8(1)	571.1(2)
b (pm)	502.5(2)	684.6(2)
c (pm)	1039.4(8)	1438.0(4)
a (°)	90.	90.
β (°)	97.00(5)	100.03(3)
γ (°)	90.	90.
V (10^6 pm^3)	1145.0(6)	556.4(4)
T (°C)	−140	−143
Space group	C2/c	P2₁/n
Z	8	4
ρ_{calc} (Mg m^{-3})	2.337	2.17
μ (mm^{-1})	0.92	0.92
$2\Theta_{max}$ (°)	56	60
F(000)	800	356
Measured reflexes	1584	1504
Independent reflexes	1379	1275
F ≥ 3σ(I)	1140	1062
R_{int}	0.03	0.019
Parameters	99	85
R	0.058	0.083
Rw	0.033	0.048
Largest residual electron density (e$^-$10^{-6} pm^{-3})	0.49	1.214

into another trap, a yield of 1.33 (95%) as a colorless solid being obtained. This compound dissolved well in CH_2Cl_2, and only very slightly in $CFCl_3$.

^{19}F NMR (CH_2Cl_2): δ_A = 89.53, δ_B = 70.50, δ_C = 63.76, $^2J_{AB}$ = 148.1, $^2J_{AC}$ = 114.7, $^2J_{BC}$ = 164.7 Hz, ^{1}H NMR ($CHCl_3$): δ = 6.70, $^3J_{A-H}$ = 10.0, $^3J_{C-H}$ = 3.7 Hz.

Mass spectrum (60°C), m/z = 202 (M$^+$, 1.8%), 182 (M$^+$–HF, 1.4%), 122 ($CH_2SF_4^+$, 100%), 105 (SOF_3^+, 46%), 89 (SF_3^+, 78%), 78 (CH_2SO^+, 11%), and smaller fragments.

Crystal structure, see Table 3: colorless single crystals were obtained by sublimation at −78°C in a sealed glass ampule. A suitable crystal was mounted under cold, dry nitrogen on a glass needle and transferred to the diffractometer. Lattice constants were obtained by fine orientation of 25 reflexes with $\theta \approx$ 20°. Intensities were measured in the $\omega2\theta$ scan mode, with maximum time of 60 seconds, depending on the intensity, and allowing at the beginning and end of scan 25% for background measurement. After Lorentz polarization correction, the structure was solved with direct methods [14], and refined with the full-matrix least-square method [15]. All atoms except hydrogen were refined anisotropically, hydrogen being refined with a fixed isotropic vibrational parameter. No absorption or extinction correction was applied. Further experimental data are given in Table 2.

Fluorosulfonyl methylidene sulfur difluoride ox-

ide, FSO_2–CH=SF_2=O. 37.5 mmol oxadithietane was dissolved in 10 mL of CH_2Cl_2 and added dropwise into a $CFCl_3$ suspension of powdered CsF at −20°C. The mixture was stirred for 1 hour at room temperature and pumped through −60 and −196°C cold traps, 4.78 mg (25.8 mmol, 69% yield) FSO_2–CH=SF_2=O being collected in the −60°C trap as a colorless ligand, mp −35°C. It is stable at room temperature and dissolves well in CH_3CN, CH_2Cl_2, and $CFCl_3$.

^{19}F NMR (CD_2Cl_2), δ_A = 77.78 (SO_2F), δ_B = 61.81 (SOF_2), J_{AB} = 12 Hz. ^{1}H NMR (CD_2Cl_2), δ = 6.08, $^3J_{A-H}$ = 5, $^3J_{B-H}$ = 1.2 Hz, ^{13}C NMR (neat liquid), δ = 49.17, $^1J_{CH}$ = 200.2, $^2J_{C-A}$ = 35.4, $^2J_{C-B}$ = 12.2 Hz.

Mass spectrum (40°C): m/z = 182 (M$^+$, 100%), 163 (M$^+$–F, 3.2%), 96 ($CHSO_2F^+$, 6.4%), and smaller fragments. IR (gas [cm^{-1}]): $\tilde{v}$ = 3115 (m), 1448 vs, $v_{as}SO_2$, 1400 vs, vSO, 1238 s, $v_{C=S}$, 1212 s, v_sSO_2, 1051 s, 896 m, 855 s, 789 s, 614 m, 544 s. Raman (liquid [cm^{-1}]): $\tilde{v}$ = 3081.5, m, p, CH, 2950 w, p, 2267.5 m, p, 2213 vw, p, 2121.5 m, p, 1427 w, dp $v_{as}SO_2$, 1398.5 m, p, vSO, 1235.5 m, p, $v_{C=S}$, 1201.55, p, v_sSO_2, 1053, m, p, 1026.5 w, p, 899.5 m, dp, v_{as} SF_2, 833.5 w, p, 773 vs, p, v_sSF_2, 737 w, p, 616.5 m, p, 541.5 w, dp, 528.5 w, dp, 461 m, dp, 453 m, p, 388 vw, dp, 346 vw, dp, 311 vs, dp, 304.5 m, p, 276.5 m, dp, 233 m, dp, 145.5 m, p. Crystal structure, see Table 3: sublimation in a sealed glass ampule at −60°C afforded colorless single crystals. Treatment of the crystal and crystal-structure solution was done as described be-

fore. Further experimental details are given in Table 2.

Methane disulfonylfluoride, $CH_2(SO_2F)_2$. 1.0 g (5.5 mmol) $FSO_2-CH=SF_2=O$ was added to 5 mL of H_2O and stirred for 10 hours. When cooled to 2°C, the lower organic phase solidified, and the water was poured off. The product was dissolved in CH_2Cl_2, dried with Na_2CO_3, and, after evaporation of the solvent, 0.9 g (5 mmol, 91%) $CH(SO_2F)_2$ was obtained.

NMR spectra, see Ref. [16].

Mass spectrum (40°C): m/z = 180 (M^+, 20%), 161 (M–F, 0.1%), 97 (CH_2SO_2F, 100%), and smaller fragment.

Further details of the crystal-structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein Leopoldshafen (FRG) on quoting the depository number CSD 58928.

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