705. *Silyl Trifluoromethyl Sulphide.*

By A. J. Downs and E. A. V. Ebsworth.

Silyl trifluoromethyl sulphide has been prepared by reaction between silyl iodide vapour and solid bis(trifluoromethylthio)mercury, and some of its physical properties have been determined. The compound decomposed at room temperature in the presence of impurity into silyl fluoride and (probably) thiocarbonyl fluoride. Hydrogen iodide and mercuric chloride broke the silicon–sulphur bond almost quantitatively; the reactions with certain other mercuric and silver salts, and with boron trifluoride and trimethylamine, have also been investigated.

Many silver and mercuric salts react with silyl iodide to form the iodide of the heavy metal and the silyl derivative of the original anion.[1] Moreover, bis(trifluoromethylthio)mercury has been found to react with a number of inorganic and organic chlorides, forming the corresponding trifluoromethylthio-derivatives.[2] We have prepared silyl trifluoromethyl sulphide, $SiH_3{\cdot}S{\cdot}CF_3$, by passing silyl iodide vapour over solid bis(trifluoromethylthio)mercury suspended on glass wool, and have investigated some of its physical and chemical properties.

The reaction is smooth at room temperature, giving yields up to 90%, but the product is very sensitive to the presence of impurity. Some more volatile material is always produced at the same time; this must consist of decomposition products of silyl trifluoromethyl sulphide, since it is also formed when crude samples of this compound are allowed to stand at room temperature. It is not homogeneous, but attempts to separate its components have been partly successful. It has been identified on the basis of vapour density and infrared and nuclear resonance measurements as an equimolar mixture of silyl fluoride and thiocarbonyl fluoride—the latter compound has not yet been characterised, but the infrared[3] and nuclear resonance[4] spectra of the former compound have been recorded. It follows that silyl trifluoromethyl sulphide decomposes according to the reaction: $SiH_3{\cdot}S{\cdot}CF_3 \longrightarrow SiH_3F + SCF_2$. Disilyl sulphide has been observed to decompose in an analogous way, giving monosilane and a solid material believed to be polymeric $({\cdot}SiH_2{\cdot}S{\cdot})_x$.[5]

Silyl trifluoromethyl sulphide is stable when pure in the liquid or vapour phase at room temperature in clean glass apparatus. The decomposition is, however, catalysed by bis(trifluoromethylthio)mercury, and in a dirty vacuum-line it was rapid even at $-46°$. Satisfactory vibrational assignments for the infrared spectrum of the pure compound can be made by using the spectra of disilyl sulphide[6] and of trifluoromethanesulphenyl chloride[7] as analogues. In the nuclear resonance spectra, the proton resonance appears at slightly lower field than in disilyl sulphide,[4] suggesting that the sulphur atom is rather more electron-withdrawing in the trifluoromethyl derivative. The small change in chemical shift, however, does not necessarily mean that this increase in electron-withdrawing power is slight; the resonant magnetic field values for protons bound to silicon are not very sensitive to the nature of the rest of the molecule.[4] The change in $J(^{29}Si{-}H)$ is also small but may be significant; the value of $J(^{19}F{-}H)$, however, is considerably greater than in methyl trifluoromethyl sulphide[8] where the observed

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[1] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194; MacDiarmid, *J. Inorg. Nuclear Chem.*, 1956, **2**, 88.

[2] Emeléus and Pugh, *J.*, 1960, 1108; Man, Coffman, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

[3] Newman, O'Loane, Polo, and Wilson, *J. Chem. Phys.*, 1956, **25**, 855; Onyszchuck, Ph.D. Thesis, Cambridge, 1956.

[4] Ebsworth, Sheppard, and Turner, unpublished work.

[5] Ebsworth, unpublished observations.

[6] Ebsworth, Taylor, and Woodward, *Trans. Faraday Soc.*, 1959, **55**, 211.

[7] Nabi and Sheppard, *J.*, 1959, 3439.

[8] Downs and Emeléus, unpublished work.

splitting is $\sim$0·4 c./sec. as against 1·7 c./sec. for the silyl compound. The increased F–H coupling in the silicon compound may be brought about by ($p \rightarrow d$) π-type bonding between silicon and sulphur. So few values for $\phi(^{19}F)$ in analogous compounds [9] are available that no comparison is possible.

The compound did not react with boron trifluoride or with mercuric sulphide. Hydrogen iodide broke the silicon–sulphur bond, giving silyl iodide and trifluoromethanethiol: $SiH_3{\cdot}S{\cdot}CF_3 + HI \longrightarrow SiH_3I + CF_3{\cdot}SH$. Mercuric chloride also broke the silicon–sulphur bond; the complex mixture of products obtained with mercuric bromide at room temperature suggests that an equilibrium mixture was set up in which appreciable amounts of both silyl bromide and silyl trifluoromethyl sulphide were present; mercuric iodide and the sulphide did not react. The order of reactivity of the mercuric halides is that expected from a consideration of the relevant bond energies, and is consistent with MacDiarmid's conversion series (though this predicts complete reaction with mercuric bromide); [10] the complete reaction with mercuric chloride at −78° suggests that the differences involve equilibria rather than reaction rates. With silver chloride, no silyl chloride was formed at −78°, and reaction at room temperature was far from quantitative; moreover, the reaction with silver cyanide was similarly incomplete. The difference in behaviour between silver and mercuric chlorides is unusual, since they have in the past been found to react similarly with silyl compounds; [10] it may indicate that the expected trifluoromethylthio-derivative of silver is relatively unstable. A remarkable feature of the reactions with mercuric bromide and with the two silver salts is the extent to which decomposition products of the starting material were recovered.

Trimethylamine reacted with silyl trifluoromethyl sulphide in a 2 : 1 molar ratio to give two solid products. One of these, readily volatile at room temperature, was identified as the adduct SiH_3F,NMe_3, which has not previously been described. As with the monomethylsilyl compounds,[11] it was appreciably more volatile than the corresponding adduct of silyl chloride.[12] The other solid product was brown, and decomposed when attempts were made to investigate its physical properties. On this basis, the reaction may be represented: $SiH_3{\cdot}S{\cdot}CF_3 + 2NMe_3 \longrightarrow SiH_3F,NMe_3 + (SCF_2,NMe_3)$. The involatile solid is regarded as a polymeric adduct of trimethylamine and thiocarbonyl fluoride. This reaction is very similar both to the other decompositions of silyl trifluoromethyl sulphide and to the reaction between disilyl sulphide and trimethylamine: [10] $(SiH_3)_2S + NMe_3 \longrightarrow SiH_4 + (SiH_2S,NMe_3)$. The trifluoromethyl compound reacted very much the more rapidly, in keeping with its greater tendency to decompose.

EXPERIMENTAL

Preparation.—In a typical experiment, silyl iodide (1·33 g.) distilled slowly through a U-tube packed with bis(trifluoromethylthio)mercury (9·7 g.) sublimed on to glass wool. The formation of a red solid was observed; the volatile products were collected in a trap at −197°, care being taken to prevent any of the mercury derivative from subliming into the same trap. From the volatile products, *silyl trifluoromethyl sulphide*, involatile at −118°, was obtained (610 mg.) (Found: M, 132; SiH, 2·27; S, 24·05; F, 43·3%. CH_3F_3SSi requires M, 132; SiH, 2·29; S, 24·25; F, 43·2%). The remainder was volatile at −132° (450 mg.) (Found: M, 67. Calc. for SiH_3F: M, 50. Calc. for SCF_2: M, 82); its infrared spectrum showed that a considerable amount of silyl fluoride was present; [3] bands were also observed at 1375s (type A), 1310w (type A), 1210s (? type B), 1188s (type B), 788m (type A), 624w (type C), and 526m (type A). The branch separations in bands of the same contour-type were roughly equal. By repeated distillation at −150° a fraction with $M = 79$ was obtained whose infrared spectrum showed the presence of little silyl fluoride, though the bands listed above were more intense. The

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[9] Filipovitch and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.

[10] MacDiarmid, (*a*) *Quart. Rev.*, 1956, **10**, 208; (*b*) Ph.D. Thesis, Cambridge, 1955.

[11] Ebsworth and Emeléus, *J.*, 1958, 2150.

[12] Emeléus and Miller, *J.*, 1939, 819.

fraction volatile at −150° had *M* 56. On this basis the other component of the mixture was identified as thiocarbonyl fluoride whose infrared spectrum has not previously been reported. The observed infrared frequencies are assigned as follows: 1375, ν_2 (C=S stretching); 1310, 788 + 526; 1210, ?788 + ν_5 (CF_2 rocking, which would then be at 422 but was not observed); 1188, ν_4 [CF stretching (a)]; 788, ν_1 [CF stretching(s)]; 624, ν_6 (out-of-plane bending); 526 cm.$^{-1}$, ν_3 (in-plane CF_2 bending). The frequencies of carbonyl fluoride are:[13] ν_1, 965; ν_2, 1942; ν_3, 626; ν_4, 1249; ν_5, 584; ν_6, 774 cm.$^{-1}$. In each case ν_1 and ν_2 may interact. The proton resonance spectrum of the mixture dissolved in cyclohexane consisted of a doublet centred at −3·35 p.p.m. (C_6H_{12} = 0) and with separation of 45·8 c./sec. (observed for SiH_3F:[4] −3·34, 45·9). Satellite doublets, assigned to ^{29}SiH, were also observed. The fluorine resonance spectrum consisted of a quartet, with multiplet splitting of 45·9 c./sec., at 217 ± 3 p.p.m. relative to trichlorofluoromethane as solvent and internal standard (observed for Et_3SiF, 176 p.p.m.)[9] together with a single line at −40·5 ± 3 p.p.m. Thiocarbonyl fluoride would be expected to give a single resonance line, but the probable field value is uncertain. The ^{19}F resonance of the CF group in $(CF_3)_2N{\cdot}COF$ was observed at −81·0 p.p.m. relative to trifluoroacetic acid as (presumably) external standard;[14] the latter at infinite dilution in trichlorofluoromethane gave a resonance at 76·5 p.p.m. (CCl_3F = 0),[9] so the CF resonance in $(CF_3)_2N{\cdot}COF$ might be expected at ∼−5 p.p.m. in dilute solution in trichlorofluoromethane (CCl_3F = 0). This suggests that the single line at −40·5 p.p.m. can reasonably be assigned to thiocarbonyl fluoride.

Unchanged bis(trifluoromethylthio)mercury (6·8 g.) was recovered; the yield of silyl trifluoromethyl sulphide, based on the amount of silyl iodide taken, was about 60%. The maximum yield obtained was ∼90%.

Stability. Decomposition was so rapid in a vacuum-line contaminated with mercuric iodide and bis(trifluoromethylthio)mercury that a steady vapour pressure could not be obtained at −46°, but in clean glass apparatus pure samples of the compound were usually stable at room temperature even in the liquid phase for up to 18 hr. The decomposition products were identical with those obtained in the preparation.

Physical properties. These were determined on samples that had been repeatedly distilled at −96° and collected at −118°. The compound melts at −127° ± 0·5° and boils at 13·6° ± 0·2°; between −20° and the b. p. the vapour pressure is related to the temperature by the expression: $\log_{10} p$ (mm.) = $-1339/T + 6{\cdot}548_2$, and over the same range the latent heat of vaporisation is 6150 ± 50 cal./mol. Trouton's constant is 21·4.

The infrared spectrum was recorded at frequencies between 4000 and 400 cm.$^{-1}$ with a Perkin–Elmer model 21 double-beam spectrometer fitted with sodium chloride or potassium bromide prisms. The observed frequencies are set out in Table 1, with vibrational assignments and the corresponding values for disilyl sulphide[6] and trifluoromethanesulphenyl chloride.[7]

The nuclear resonance spectra were recorded with a Varian Associates V-4300B high-resolution nuclear-magnetic resonance spectrometer with flux stabiliser, using the sample-spinning technique, and operating at 40 Mc./sec. The samples were contained in Pyrex tubing of 5 mm. outside diameter. The pure liquids were used for measuring coupling constants and the chemical shift values were obtained from dilute solutions with internal standards; the values are summarised in Table 2, with analogous values for disilyl sulphide.[4]

Reactions. (i) The compound neither reacted with, nor was decomposed by, mercuric sulphide at −78°, mercuric iodide at room temperature, or methyl iodide at room temperature; with boron trifluoride, no sign of reaction was observed between −196° and room temperature. In each case the volatile material taken was recovered unchanged.

(ii) Hydrogen iodide (40 mg.) and silyl trifluoromethyl sulphide (41 mg.) at −78° (18 hr.) gave trifluoromethanethiol (35 mg.) (Found: *M*, 103. Calc. for CHF_3S: *M*, 101) and silyl iodide (44·5 mg.) (Found: *M*, 153; v. p. at −15°, 5·65 cm. Calc. for SiH_3I: *M*, 158; v. p.[15] 5·8 cm.). The infrared spectra confirmed this identification.

(iii) Silyl trifluoromethyl sulphide (64 mg.) and mercuric chloride (155 mg.) at −78° (18 hr.) gave silyl chloride (31 mg.) (Found: *M*, 66; v. p. at −46°, 34·8 cm. Calc. for SiH_3Cl: *M*, 67; v. p.,[16] 36·4 cm.). From the solid residue trifluoromethylthiomercuric chloride was obtained

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[13] Nielson, Burke, Woltz, and Jones, *J. Chem. Phys.*, 1952, **20**, 596.

[14] Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

[15] Emeléus, Maddock, and Reid, *J.*, 1941, 353.

[16] Stock and Somieski, *Ber.*, 1919, **52**, 695.

by sublimation (m. p., found, 125°; lit.,[17] 120—130°); its identity was confirmed spectroscopically. The amount of silyl chloride recovered corresponds to 95% reaction according to the reaction: $SiH_3{\cdot}S{\cdot}CF_3 + HgCl_2 \longrightarrow SiH_3Cl + CF_3{\cdot}S{\cdot}HgCl$.

TABLE 1. *Silyl trifluoromethyl sulphide.*

Frequency (cm.$^{-1}$)	Assignment	Analogy
3150w	940 + 2210	3095 in $(SiH_3)_2S$
2210vs	SiH stretch	2180 in $(SiH_3)_2S$
1885w	1124 + 756	1885 in $CF_3{\cdot}SCl$
1304w	756 + 550	1305 in $CF_3{\cdot}SCl$
1260w	756 + 510	
1235w	2 × 625	1278 in $(SiH_3)_2S$
1164 1147 } vs	CF stretch (a)	1189 in $CF_3{\cdot}SCl$
1124vs	CF stretch (s)	1133 in $CF_3{\cdot}SCl$
940s, sh	SiH_3 def.	956 in $(SiH_3)_2S$
910 906 } vs 762	SiH_3 def.	907 in $(SiH_3)_2S$
756 751 } m	CF_3 def. (CS stretch)	764 in $CF_3{\cdot}SCl$
635m, sh	SiH_3 rock	?675 in $(SiH_3)_2S$
625m, C *	SiH_3 rock (out-of-plane)	635 in $(SiH_3)_2S$
555 545 } mw	CF_3 def.	570 in $CF_3{\cdot}SCl$
514 507 } m	SiS stretch	517 in $(SiH_3)_2S$
449 444 } mw 438	SC stretch (CF_3 def.)	468 in $CF_3{\cdot}SCl$

* C = type C-contour.

TABLE 2.

Compound	(*a*) τ(H) (p.p.m. ± 0·02)	(*b*) $\phi(F)$ (p.p.m. ± 0·02) (CCl_3F = 0)	J (^{29}SiH) (c./sec.)	(*c*) J (^{19}FH) (c./sec.)
$SiH_3{\cdot}S{\cdot}CF_3$	−5·58	31·15	234 ± 1	1·75 ± 0·10
$(SiH_3)_2S$	−5·64	—	226 ± 2	—

(*a*) Measured in ~5% solutions in cyclohexane as internal standard and solvent.
(*b*) No significant change in chemical shift values was observed between the pure liquid containing a drop of internal standard and ~5% solutions in the standard as solvent.
(*c*) Mean from ^{19}F and H resonances.

(iv) Silyl trifluoromethyl sulphide and mercuric bromide at −78° (18 hr.) gave a mixture of products including a small amount of silyl bromide. At room temperature the sulphide (57 mg.) and mercuric bromide (200 mg.) gave, after 0·5 hr., 49 mg. of a mixture of volatile products from which no pure component could be isolated. The infrared spectrum suggested that the material contained thiocarbonyl fluoride, silyl bromide, silyl fluoride, and unchanged sulphide. The mixture was hydrolysed and the bromide content estimated gravimetrically (Found: AgBr, 25 mg.), since silyl bromide could not be separated from silyl trifluoromethyl sulphide by distillation (b. p.[18] 1·9°). If all the bromine in the mixture was present as silyl bromide, about 30% of the sulphide had reacted according to an equation such as that given above. The involatile solid residue was shown spectroscopically to contain trifluoromethylthio-groups.

(v) Silyl trifluoromethyl sulphide (65 mg.) and bis(trifluoromethylthio)mercury (150 mg.) at room temperature (2 hr.) gave unchanged silyl trifluoromethyl sulphide (46 mg.) (Found: *M*, 131; v. p. at −46°, 4·40 cm. Calc. for $C_2H_3F_3S$: *M*, 132; v. p., 4·30 cm.) with a more volatile material (22 mg.) (*M*, 87) that was shown spectroscopically to contain silyl fluoride (*M*, 50), thiocarbonyl fluoride (*M*, 82), and trifluoromethanethiol (*M*, 102). The solid blackened during the reaction, and there appeared to be a little free mercury present when the tube was opened.

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[17] Pugh, M.Sc. Thesis, Cambridge, 1959.

[18] Stock and Somieski, *Ber.*, 1917, **50**, 1739.

(vi) Silver chloride (300 mg.) and the sulphide (77 mg.) at −78° (18 hr.) gave a mixture in which no silyl chloride could be detected, and the solid did not contain trifluoromethylthio-groups. After 18 hr. at room temperature no unchanged sulphide was recovered; the volatile products included silyl fluoride, silyl chloride, a small amount of thiocarbonyl fluoride, and ~3 mg. of a red liquid whose infrared spectrum indicated that it was a mixture of $(CF_3{\cdot}S)_2CS$ and $CF_3{\cdot}S{\cdot}CSF$, common decomposition products of trifluoromethylthio-compounds [19] that are probably derived from polymerisation of thiocarbonyl fluoride. On hydrolysis, the chloride content of the volatile products was estimated gravimetrically (Found: AgCl, 27 mg.); if all the chloride was present as silyl chloride, this corresponds to about 35% reaction according to the equation: $SiH_3{\cdot}S{\cdot}CF_3 + AgCl = SiH_3Cl + AgS{\cdot}CF_3$. The solid residue was shown spectroscopically to contain trifluoromethylthio-groups.

(vii) Silyl trifluoromethyl sulphide and silver cyanide did not react at −78° (18 hr.), and the starting material was recovered unchanged. At room temperature, the solid became first brown and then (after a few minutes) black. A complex mixture of volatile products was recovered, whose infrared spectrum indicated the presence of silyl fluoride, some thiocarbonyl fluoride, and a very small amount of silyl cyanide, with a red liquid identified spectroscopically as $(CF_3{\cdot}S)_2CS$.[19] The black solid residue was shown spectroscopically to contain trifluoromethylthio-groups. Silyl trifluoromethyl sulphide (102 mg.) was passed twice over solid silver cyanide; the solid became brown, but no silyl cyanide was detected among the volatile products, which consisted of unchanged sulphide and a mixture of silyl fluoride, thiocarbonyl fluoride, and trifluoromethanethiol. No trifluoromethylthio-groups were detected in the solid residue.

(viii) Silyl trifluoromethyl sulphide (84 mg.) immediately gave a white solid when mixed with trimethylamine (158 mg.) at −78°. Trimethylamine (81 mg.) was recovered (Found: *M*, 60; v. p. at 0°, 67·45 cm. Calc. for C_3H_9N: *M*, 59; v. p.[20] at 0°, 68·5 cm.); its identity was confirmed spectroscopically. The other volatile substance recovered was a white solid (Found: *M*, 55·5; v. p. at room temperature, 7 cm.) whose infrared spectrum was very similar to that expected for an equimolar mixture of trimethylamine and silyl fluoride (Calc.; *M*, 54·5). The solid was identified as the equimolar silyl fluoride–trimethylamine adduct. On each distillation a little involatile solid was left behind, suggesting that, as in analogous cases,[11] the dissociation is accompanied by irreversible decomposition; accordingly, no analysis was attempted. The other solid product, involatile at room temperature, was brown. When the tube in which it was contained was filled with dry nitrogen, the colour of the solid deepened considerably, and the infrared spectrum of the darkened sample gave no absorption at characteristic Si–H, C–H, or C–F frequencies.

The overall combining ratio, trimethylamine : silyl trifluoromethyl sulphide, was 1 : 1·97.

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UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.

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[19] Haszeldine and Kidd, *J.*, 1955, 3871.

[20] Aston, Sagenkahn, Szasz, Moessen, and Zuhr, *J. Amer. Chem. Soc.*, 1944, **66**, 1171.