

Perfluoroalkyl Derivatives of Sulphur. Part III. Some Reactions of Trifluoromethanethiol, and Spectroscopic Properties of the >C:S Group.*

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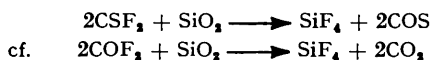
Trifluoromethanethiol is converted by anhydrous ammonia into trifluoromethyl fluorodithioformate and bistrifluoromethyl trithiocarbonate with intermediate formation of thiocarbonyl fluoride. Attempts to prepare the last compound are described. Its chloro-analogue yields dichlorodifluoromethane when treated with antimony trifluorodichloride, and carbonyl sulphide when hydrolysed. Other syntheses of trifluoromethyl fluorodithioformate and bistrifluoromethyl trithiocarbonate are given. Aqueous hydrolysis of trifluoromethanethiol yields thiocarbonyl fluoride and thence carbonyl sulphide. The hydrolysis of heptafluoropropanethiol, synthesised from bis(heptafluoropropyl) disulphide *via* bis(heptafluoropropylthio)mercury, is more complex, and is considered in connection with the hydrolysis of the disulphide.

The infrared spectra of compounds containing the >C:S group are considered and assignments are made for this group in various environments.

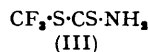
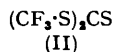
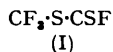
A CONVENIENT synthesis of trifluoromethanethiol from carbon disulphide was described earlier (*J.*, 1953, 3219), where it was shown that the thiol is stable *in vacuo* but decomposed by dilute aqueous sodium hydroxide with complete liberation of fluorine as fluoride and formation of carbonate and sulphide; no sulphur was formed. Further studies on the breakdown of trifluoromethanethiol under various conditions are now reported.

In ionising solvents or in presence of an acceptor for hydrogen fluoride, decomposition of trifluoromethanethiol occurs as follows: $\text{CF}_3\cdot\text{SH} \longrightarrow \text{CSF}_2 + \text{HF}$, and the thiocarbonyl fluoride often shows further reactions. Analytically pure thiocarbonyl fluoride has not been isolated, but its formation can be inferred from a series of related experiments.

Anhydrous ammonia reacts with trifluoromethanethiol to give, as volatile products, carbonyl sulphide, silicon tetrafluoride, and small amounts of a compound believed to be thiocarbonyl fluoride. The formation of carbonyl sulphide and silicon tetrafluoride, and the further etching of glass vessels when the mixture containing the probable thiocarbonyl fluoride is kept, together with a decrease in concentration of the last compound, show that it reacts with glass

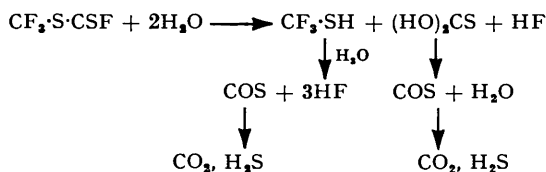


The major products from the reaction with ammonia are a yellow liquid (b. p. 43°) of formula $\text{C}_2\text{S}_2\text{F}_4$, a red liquid (b. p. 110°) of formula $\text{C}_3\text{S}_3\text{F}_6$, and small amounts of a yellow solid, together with ammonium fluoride. The yellow liquid is trifluoromethyl fluorodithioformate (I) and the red liquid is bistrifluoromethyl trithiocarbonate (II). The yellow solid is possibly (III), produced by reaction of (I) with ammonia.



Photochemical reaction of (I) with chlorine yields chlorotrifluoromethane, thus showing the presence of a CF_3 group, and the formation of a small amount of trifluoromethanethiol by reaction with water indicates a CF_3S group. Hydrolysis is slow at room temperature but rapid and complete at 75°. The aqueous solution then contains most of the fluoride

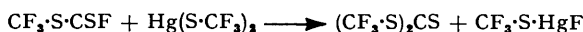
and 13% of the sulphide, and carbonyl sulphide, carbon dioxide, and a small amount of trifluoromethanethiol are volatile products :



Bistrifluoromethyl trithiocarbonate (II) similarly yields carbonyl sulphide when treated with water [(II) \longrightarrow $2\text{CF}_3\cdot\text{SH} + (\text{HO})_2\text{CS} \longrightarrow$ etc.]. The trithiocarbonate was synthesised by two routes :

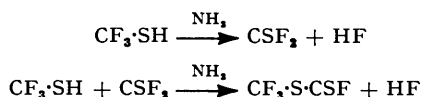


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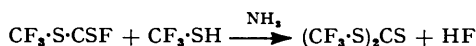


These provide proof of structure and establish the relationship between (I) and (II).

Trifluoromethyl fluorodithioformate is clearly formed *via* intermediate formation of thiocarbonyl fluoride :

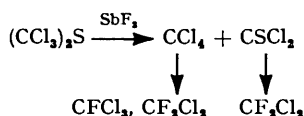


and bistrifluoromethyl trithiocarbonate by the further reaction

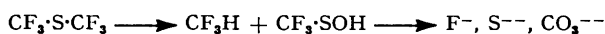


Ammonia is essential to these reactions by acting as acceptor for hydrogen fluoride, since trifluoromethanethiol fails to yield bistrifluoromethyl trithiocarbonate when heated with thiocarbonyl chloride, or when treated with trifluoromethyl fluorodithioformate alone or in sulphur dioxide solution.

Attempts were made to synthesise thiocarbonyl fluoride, since, although Ruff is reported to have prepared this compound, it was shown (*J.*, 1953, 3219) that the compound obtained was actually thionyl fluoride. Reaction of thiocarbonyl chloride with zinc fluoride or antimony trifluoride failed to yield thiocarbonyl fluoride. At higher temperatures dichlorodifluoromethane was formed by replacement of sulphur by fluorine ($\text{CSCl}_2 \longrightarrow \text{CF}_2\text{Cl}_2$), and by decomposition of thiocarbonyl chloride ($2\text{CSCl}_2 \longrightarrow \text{CS}_2 + \text{CCl}_4$) followed by replacement of chlorine by fluorine in the carbon tetrachloride so produced. These reactions also explain the formation of trichlorofluoromethane and dichlorodifluoromethane during unsuccessful attempts to prepare bistrifluoromethyl sulphide from its chloro-analogue (Truce, Birum, and McBee, *J. Amer. Chem. Soc.*, 1952, **74**, 3594) :



Bistrichloromethyl sulphide is thermally unstable (Feichtinger and Moos, *Ber.*, 1948, **81**, 371) in sharp contrast to bistrifluoromethyl sulphide (*J.*, 1952, 2198). The chloro-compound differs also in its ready and complete breakdown to chloride, sulphide, and carbonate in presence of aqueous base, whereas bistrifluoromethyl sulphide is stable (*J.*, 1952, 2198); the fluoro-compound is cleaved by alcoholic potassium hydroxide at higher temperatures, however, to give a mixture of fluoroform, fluoride, sulphide, and carbonate :

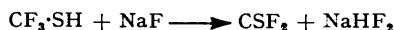


Pyrolysis of bis(trifluoromethylthio)mercury also gave material containing thiocarbonyl fluoride :

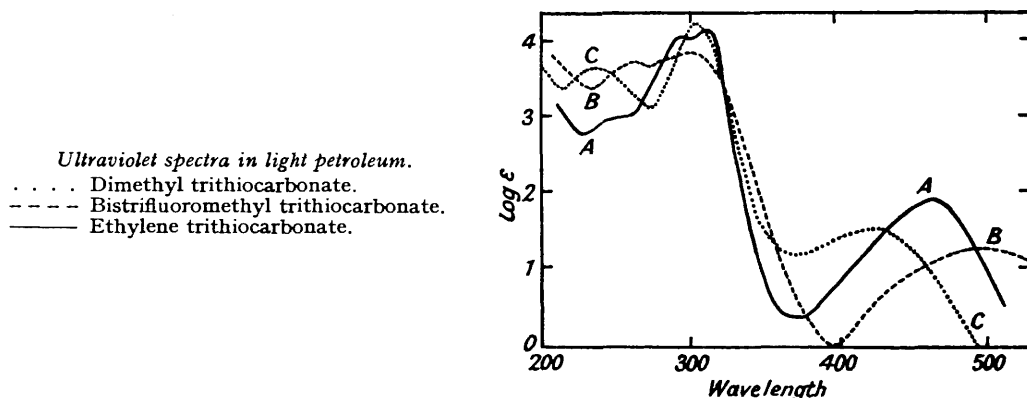


but attack of the last compound on the glass vessel again prevented its isolation pure. Pyrolysis of bistrifluoromethyl disulphide yielded carbon disulphide, carbon tetrafluoride, and bistrifluoromethyl sulphide, but only small amounts of thiocarbonyl fluoride.

The reaction of trifluoromethanethiol with anhydrous sodium fluoride gave a relatively high concentration of the compound believed to be thiocarbonyl fluoride:



but carbonyl sulphide and silicon tetrafluoride formation again prevented complete identification. Trifluoromethyl fluorodithioformate (I) was also formed by reaction of the thiocarbonyl fluoride with trifluoromethanethiol, and sodium fluoride acts like ammonia in this respect, though less efficiently.



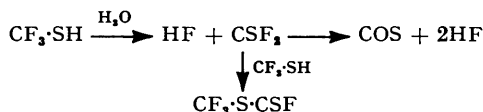
The general similarity of the ultraviolet spectra of bistrifluoromethyl, dimethyl, and ethylene trithiocarbonates is brought out by the diagram better than by the precise values given in the annexed Table, which includes data for diethyl trithiocarbonate and trifluoromethyl fluorodithioformate.

Compound	Solvent	λ_{\max}	ϵ_{\max}	λ_{\min}	ϵ_{\min}
$\text{CF}_3\text{-S-CSF}$	Light petroleum	393	22	343	9
		269	7400	240	6150
	Vapour	393	16	330.5	2.48
		330	2.54	328.5	2.44
		327	2.58	325.5	2.48
		324	2.65	322.5	2.60
		322.5	2.80	322	2.73
$(\text{CF}_3\text{-S})_2\text{CS}$	Light petroleum	263	4100	235	660
		496	16	396	1
		299	6400	267	4300
	Vapour	259	4900	230	2250
		293	4150	282	3790
		277	3900	262	3120
		254	3790	251	3780
$(\text{CH}_3\text{-S})_2\text{CS}^1$	<i>cyclo</i> Hexane	248	3800	247	3780
		246	3790	226	1900
		430	28	—	—
		302	16,900	—	—
$(\text{C}_2\text{H}_5\text{-S})_2\text{CS}^1$,,	238	3780	—	—
		432	36	—	—
		305	19,400	—	—
$\begin{array}{l} \text{CH}_3\text{-S} \\ \\ \text{CH}_2\text{-S} \end{array} \text{CS}^2$	Light petroleum	238	4000	—	—
		460	69	298	10,300
		311	12,500	227	335
		292	10,600	—	—

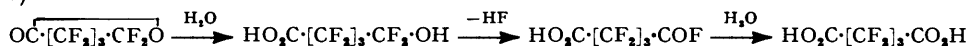
¹ Challenger, Mason, Holdsworth, and Emmett, *J.*, 1953, 292. ² Challenger *et al.* report maxima at 458, 311.5, and 293 $m\mu$ (ϵ 72, 14,780, and 12,640 respectively) for a solution in *cyclo*hexane.

The results of the aqueous hydrolysis of trifluoromethanethiol can now be interpreted. Reaction with a large excess of water at 0° produces a small amount of a yellow liquid shown

to be trifluoromethyl fluorodithioformate (I). This slowly disappears when kept in contact with water, and the aqueous solution then contains all the fluorine as fluoride, and carbonyl sulphide is the major volatile product. Since carbonyl sulphide is slowly hydrolysed to carbon dioxide and hydrogen sulphide, small amounts of these compounds are also formed. The formation of carbonyl sulphide and trifluoromethyl fluorodithioformate is again evidence for intermediate formation of thiocarbonyl fluoride :



The instability of perfluoroalkanethiols in aqueous media is in agreement with the similar instability noted for primary perfluoro-alcohols when such compounds are plausible intermediates in certain reactions, *e.g.*, the hydrolysis of perfluoro-lactones (Hauptschein, Stokes, and Grosse, *J. Amer. Chem. Soc.*, 1952, **74**, 1974; Haszeldine, *Nature*, 1951, **168**, 1028) :

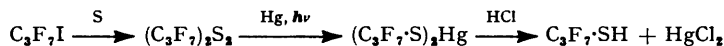


Attempts were made to produce thiocarbonyl fluoride by reaction of trifluoromethanethiol with less water than that required to cause complete hydrolysis to carbonyl sulphide. The formation of thiocarbonyl fluoride was again very probable, but its reaction with glass, and hydrolysis to give carbonyl sulphide, rendered its purification impossible.

According to the above, thiocarbonyl fluoride should yield carbonyl sulphide when hydrolysed by water. Although reaction of thiocarbonyl chloride with ethanol is reported to give carbonyl sulphide (Klason, *Ber.*, 1887, **20**, 2384), its aqueous hydrolysis is said to give only carbon dioxide and hydrogen sulphide (Bergreen, *Ber.*, 1888, **21**, 337), not carbonyl sulphide. Böhme (*ibid.*, 1941, **74**, B, 248) studied the rate of hydrolysis of thiocarbonyl chloride with water at room temperature, but did not report any gaseous products. Re-examination has now shown that thiocarbonyl chloride reacts only slowly with water at room temperature, but that carbonyl sulphide, together with its hydrolysis products carbon dioxide and hydrogen sulphide, is formed at 100°; this is completely in accord with the reactions postulated for thiocarbonyl fluoride.

Thiocarbonyl fluoride could probably be prepared in high yield by pyrolysis of trifluoromethanethiol in a platinum tube. At low temperatures and in absence of moisture it will probably be stable to glass, like carbonyl fluoride.

Studies on the hydrolysis of heptafluoro-*n*-propanethiol were made in attempt to throw further light on the proposed mechanism for perfluoroalkanethiol hydrolysis. The thiol was prepared by a method analogous to that used for trifluoromethanethiol :



The preparation of the disulphide by the general method outlined earlier (*Nature*, 1950, **166**, 225; *J.*, 1952, 2198) offered no difficulty, but formation of the mercurial was more troublesome. At an optimum reaction temperature of 75° a crystalline solid appears within a few minutes of exposure to ultraviolet light, but reaction is then inhibited, and prolonged irradiation only decomposes the yellow solid. Bis(heptafluoro-*n*-propylthio)mercury was isolated as a thick oil, and when treated with anhydrous hydrogen chloride gave heptafluoro-*n*-propanethiol, b. p. 23·7°; the overall yield from the disulphide was low. The infrared spectrum of the thiol shows a sharp band at 3·82 μ assigned to the S-H stretching vibration (cf. trifluoromethanethiol 3·84 μ).

The following reaction scheme was expected for the aqueous hydrolysis of heptafluoro-*n*-propanethiol :



with possibly further reaction of the thio-acid to give pentafluoropropionic acid. Two atoms of fluorine should thus be liberated as fluoride, with a negligible amount of

trithiocarbonates. The following argument leads to a fairly certain assignment for the C:S vibration in such compounds, however.

Dialkyl carbonates, $(RO)_2CO$, absorb strongly at *ca.* 5.70μ and this is assigned to the C:O stretching vibration in such compounds (unpublished results). The C:O stretching vibration in carbonyl chloride is at 5.45μ (doublet at $5.43, 5.47 \mu$), so that the groups RO and Cl have much the same effect on the C:O vibration, with the more powerful inductive effect of the chlorine atom causing a shift to shorter wavelength. To a first approximation, therefore, the C:S stretching vibration in thiocarbonyl chloride should lie at longer wavelength than the C:O vibration in carbonyl chloride, and should be not far removed from the C:S vibration in a trithiocarbonate $(RS)_2CS$. The infrared spectrum of thiocarbonyl chloride (C.S. No. 277) * shows a powerful band at 8.80μ which is assigned to the C:S stretching vibration. The doublet at $12.33, 12.60 \mu$ is assigned to the C-Cl stretching vibrations; that at $5.44, 5.47 \mu$ cannot be the C:S stretching vibration, since it is at the same position as the C:O vibration in carbonyl chloride. It is noteworthy that similar doublets occur in the spectra of carbon disulphide ($4.57, 4.60 \mu$) and carbonyl sulphide (C.S. No. 278; $4.84, 4.87 \mu$). The strong doublet in the spectrum of carbonyl sulphide at $11.55, 11.80 \mu$ is presumably the 11.64μ band noted by the earlier workers, and their band at 9.52μ is similarly resolved into a doublet at $9.47, 9.65 \mu$.

The infrared spectrum of ethylene trithiocarbonate (C.S. No. 279) shows a very powerful band at 9.27μ and this is assigned to the C:S stretching vibration. It is at the expected position relative to thiocarbonyl chloride. Introduction of fluorine into the molecule, as with bistrifluoromethyl trithiocarbonate, should cause a shift of the C:S vibration to shorter wavelength just as the C:O, NO_2 , or SO_2 stretching vibrations are shifted to shorter wavelength by the increased inductive effect on replacement of alkyl by perfluoroalkyl (Haszeldine, *Nature*, 1951, **163**, 1028; *J.*, 1953, 2525; Haszeldine and Kidd, Part II, *loc. cit.*). The infrared spectrum of bistrifluoromethyl trithiocarbonate (C.S. No. 280) is simple, with a strong doublet at $8.36, 8.45 \mu$ and a strong band at 9.09μ . The 9.09μ absorption is assigned to the C:S vibration, and the $8.36, 8.45 \mu$ doublet to the C-F stretching vibrations which usually appear in this region; it should be noted that there are no bands of even medium intensity between 2 and 8μ , so the C:S vibration cannot appear in this region. Finally, trifluoromethyl fluorodithioformate shows a spectrum (C.S. No. 281) with powerful absorption at $8.10, 8.45$, and 8.89μ . Replacement of a CF_3 group in bistrifluoromethyl trithiocarbonate by a fluorine atom should cause a shift of the C:S vibration to shorter wavelength, and the 8.89μ band is therefore assigned to this vibration, and the 8.10 and 8.45μ bands to the C-F stretching vibrations.

The position of the C:S vibration for other compounds can now be predicted, as shown in the annexed Table.

Compound	R = alkyl	R = perfluoroalkyl	Compound	R = alkyl	R = perfluoroalkyl
$(RO)_2C:S$	8.95—9.30	8.75—9.10	$RS \cdot CSF$	8.9—9.3	8.85—9.05
$(RS)_2C:S$	9.25—9.50	9.05—9.20	$RS \cdot CSCl$	9.1—9.4	9.1—9.3
$R_2C:S$	9.3—9.7	9.1—9.5			

EXPERIMENTAL

See earlier papers for preparation of starting materials and techniques used.

Reaction of Trifluoromethanethiol with Ammonia.—In a typical experiment, trifluoromethanethiol (0.9465 g., 0.00937 mole) and anhydrous ammonia (0.1605 g., 0.00944 mole) in a 30-ml. sealed tube were allowed to warm from -80° to room temperature. During this time a red compound was formed and a white solid was deposited. Fractionation of the volatile products by bulb-to-bulb distillation *in vacuo* gave (i) a small volatile fraction (0.0804 g.; *M*, 72), (ii) *trifluoromethyl fluorodithioformate* (0.3076 g., 40%), a yellow liquid, b. p. $42.9^\circ/762$ mm. (isoteniscope) (Found: F, 45.9; S, 39.2%; *M*, 164. $C_2F_4S_2$ requires F, 46.3; S, 39.0%; *M*, 164), and (iii) *bistrifluoromethyl trithiocarbonate* (0.2045 g., 10%), a red liquid, b. p. 110° (micro) (Found: F, 45.7; S, 38.3%; *M*, 248. $C_3F_6S_3$ requires F, 46.3; S, 39.0%; *M*, 246). The first

* Spectra thus marked have been deposited with the Society. Photocopies may be obtained, price 3s. 0d. each, on application to the General Secretary, quoting the C.S. No.

fraction was treated with anhydrous hydrogen chloride to remove any ammonia, then refractionated; infrared spectroscopic examination showed it to contain trifluoromethanethiol, carbonyl sulphide, silicon tetrafluoride, and probably thiocarbonyl fluoride.

The solid produced in the reaction was extracted with water to remove ammonium fluoride, leaving a yellow solid containing fluorine and nitrogen.

Reaction of Trifluoromethyl Fluorodithioformate with Chlorine.—Chlorine (0.274 g.) and the thioformate (0.1029 g.) in a silica tube were exposed to ultraviolet light (2 weeks). A yellow crystalline solid formed in the early stages slowly disappeared as irradiation continued. Distillation gave chlorotrifluoromethane (0.0351 g., 53%) (*M*, 105), identified spectroscopically, unchanged chlorine (0.192 g., 70%), and a mixture (0.131 g.) of unchanged trifluoromethyl fluorodithioformate and sulphur chlorides.

Synthesis of Bistrifluoromethyl Trithiocarbonate.—(a) *From trifluoromethyl fluorodithioformate.* The dithioformate (0.1638 g.) and bis(trifluoromethylthio)mercury (0.493 g.) underwent no reaction at room temperature in a sealed tube. After 24 hours' heating at 70° a red liquid had formed and appreciable etching was apparent. Distillation gave bistrifluoromethyl trithiocarbonate (0.0852 g., 34%) (Found: *M*, 244. Calc. for $C_3F_6S_3$: *M*, 246), identified spectroscopically, and two smaller unidentified fractions. Ether extraction of the solid reaction products gave unchanged mercurial (0.256 g., 52%), m. p. 36°.

(b) *From thiocarbonyl chloride.* Bis(trifluoromethylthio)mercury (0.8775 g.) and thiocarbonyl chloride (0.1819 g.) in a 30-ml. sealed tube reacted only when heated at 50° (24 hr.) to give bistrifluoromethyl trithiocarbonate (0.2362 g., 61% based on thiocarbonyl chloride) (Found: *M*, 245), identified spectroscopically, and unchanged thiocarbonyl chloride. The colourless, needle-like crystals also produced during the reaction were extracted with ether to give trifluoromethylthiomeric chloride (0.7107 g., 97%), m. p. 124–126° (Found: Cl, 11.6. Calc. for $CClF_3SHg$: Cl, 10.5%), slightly contaminated by mercuric chloride from which it could not be separated by differential solvent extraction. The mercurichloride has the typical pungent odour associated with perfluoroalkylmercury compounds.

(c) *Attempted syntheses.* Trifluoromethanethiol (0.0982 g.) and trifluoromethyl fluorodithioformate (0.1080 g.) were unchanged after being kept at 20° (2 days). Addition of liquid sulphur dioxide to act as ionising solvent failed to cause reaction after 3 days.

Thiocarbonyl chloride (0.1268 g.) and trifluoromethanethiol (0.2863 g.) showed no signs of reaction in a 10-ml. sealed tube at 20°, but after 4 days' heating at 75° considerable etching and a faint red coloration could be detected. Distillation gave only unchanged thiocarbonyl chloride (0.1075 g.) and breakdown products, and not more than a small amount of bistrifluoromethyl trithiocarbonate.

Hydrolysis of Trifluoromethyl Fluorodithioformate.—The dithioformate (0.0884 g.) slowly reacted with water (2.5 ml.) in a 10-ml. sealed tube; after 12 hours' heating at 75° no yellow liquid remained. Distillation gave a volatile product shown by infrared spectroscopic examination to contain mainly carbonyl sulphide with small amounts of carbon dioxide and trifluoromethanethiol. The gaseous product was completely decomposed by 15% aqueous sodium hydroxide, and the fluoride and sulphide so formed were estimated (Found: F^- , 2.5; S^{--} , 86% based on trifluoromethyl fluorodithioformate). The fluoride and sulphide in the aqueous solution from the original hydrolysis were also estimated (Found: F^- , 98; S^{--} , 13%).

Hydrolysis of Bistrifluoromethyl Trithiocarbonate.—The thiocarbonate (0.0825 g.) and water (2 ml.) showed no reaction in a 10-ml. sealed tube, but reacted completely at 80° (18 hr.). The volatile product was shown by infrared spectroscopic examination to be mainly carbonyl sulphide; it was completely absorbed by 15% aqueous sodium hydroxide (Found: F^- , 2; S^{--} , 74%). The aqueous solution from the hydrolysis contained F^- , 96; and S^{--} , 23%.

Hydrolysis of Thiocarbonyl Chloride.—The chloro-compound (0.2320 g.) and water (4 ml.) in a 30-ml. Pyrex tube underwent little reaction at 25° (12 hr.), but at 100° (1 hr.) almost complete reaction occurred to give unchanged thiocarbonyl chloride (0.0341 g., 14%) (Found: *M*, 113. Calc. for $CSCl_2$: *M*, 115) and slightly impure carbonyl sulphide (0.112 g.), identified by means of its infrared spectrum. Analysis of the gaseous reaction products other than thiocarbonyl chloride gave S^{--} , 81; Cl^- , 2%, based on the thiocarbonyl chloride taken. Analysis of the aqueous solution showed it to contain S^{--} , 3; Cl^- , 84%, based on the thiocarbonyl chloride taken; with allowance for that recovered unchanged (14%), the weight balance for chloride is 100%, and for sulphide 98%.

Carbonyl sulphide (Found: *M*, 60. Calc. for COS: *M*, 60) was prepared as reference compound from ammonium thiocarbamate (Stock and Kuss, *Ber.*, 1917, 50, 159). The vapour pressures at various temperatures agreed with those reported by Stock and Kuss.

Attempted Preparation of Thiocarbonyl Fluoride from Thiocarbonyl Chloride.—Thiocarbonyl chloride, b. p. 74.2—74.4° (Found : M , 115. Calc. for CCl_2S : M , 115) was dried over phosphoric anhydride. (a) Anhydrous zinc fluoride (10 g.) and thiocarbonyl chloride (3.0 g.), heated at 130° (12 hr.) in a 100-ml. autoclave in absence of air, underwent no reaction.

(b) Freshly-sublimed antimony trifluoride and thiocarbonyl chloride failed to react when heated at 90° (12 hr.) in an autoclave.

(c) Antimony trifluoride (35 g.) and chlorine (2.6 g.) were heated in an autoclave to form the quinquivalent salt. Thiocarbonyl chloride (3.6 g.) was then added, and the mixture heated at 230° (4 hr.) to give dichlorodifluoromethane (1.12 g., 30%), b. p. -29.9° (Found : M , 121. Calc. for CCl_2F_2 : M , 121), identified by means of its infrared spectrum, and a mixture (0.190 g.) containing dichlorodifluoromethane and chlorotrifluoromethane. Similar products were formed at lower temperatures.

Pyrolysis of Bis(trifluoromethylthio)mercury.—The mercurial (0.976 g.), heated at 220° (48 hr.) in a silica tube, gave volatile products containing carbonyl sulphide, a small amount of bistrifluoromethyl sulphide, carbon dioxide, silicon tetrafluoride, and a material believed to be thiocarbonyl fluoride.

Pyrolysis of Bistrifluoromethyl Disulphide.—Small amounts of thiocarbonyl fluoride were produced when bistrifluoromethyl disulphide was heated at 320° (24 hr.) in a steel autoclave. The main products were (a) carbon disulphide, b. p. 45° (Found : M , 77. Calc. for CS_2 : M , 76), (b) a mixture of unchanged bistrifluoromethyl disulphide and carbon disulphide, (c) carbon tetrafluoride (Found : M , 88. Calc. for CF_4 : M , 88), and (d) bistrifluoromethyl sulphide (Found : M , 169. Calc. for $\text{C}_2\text{F}_6\text{S}$: M , 170). The products were identified spectroscopically.

Hydrolysis of Trifluoromethanethiol.—(a) *With an excess of water.* The thiol (0.131 g.) was sealed with water (2 ml.) in a 10-ml. Pyrex tube, and allowed to warm to room temperature. As soon as the ice was melted fumes were evolved and a small amount of a yellow immiscible liquid was formed; the yellow liquid disappeared after 12 hr. The aqueous solution was made alkaline and the fluoride and sulphide present were determined (Found : F^- , 98% of total fluorine; S^{--} , 7% of total sulphur). The volatile reaction products (0.079 g.) of the aqueous hydrolysis were carbonyl sulphide and a very small amount of unchanged trifluoromethanethiol as shown by an infrared spectrum of the mixture. The mixture was completely decomposed by 15% aqueous sodium hydroxide (Found : F^- , 1% of total fluorine; S^{--} , 90% of total sulphur).

In another experiment trifluoromethanethiol (0.141 g.) and water (2.5 ml.) were allowed to react as above to give the yellow liquid which was then transferred to a vacuum apparatus for the manipulation of gases. After purification the yellow liquid (0.032 g.) was shown by molecular-weight determination (Found : M , 164) and infrared spectroscopic examination to be trifluoromethyl fluorodithiocarbonate.

(b) *With small amounts of water.* The thiol (0.1017 g., 0.00099 mole) and water (0.0122 g., 0.00068 mole) were kept in a 30-ml. Pyrex tube at room temperature (12 hr.) to give unchanged trifluoromethanethiol, small amounts of carbonyl sulphide, silicon tetrafluoride, and a substance believed to be thiocarbonyl fluoride. The products were identified by means of their infrared spectra. The amount of the material believed to be thiocarbonyl fluoride decreased, and finally disappeared, when it was treated with successive small quantities of water, and carbonyl sulphide and silicon tetrafluoride were produced and identified spectroscopically. Similar decomposition was detected in subsequent experiments when the thiocarbonyl fluoride fraction was heated in a glass vessel. Attempts to purify thiocarbonyl fluoride failed.

Reaction of Trifluoromethanethiol with Sodium Fluoride.—Anhydrous sodium fluoride (0.490 g.) in a 30-ml. Pyrex tube was heated *in vacuo* to remove last traces of moisture before addition of trifluoromethanethiol (0.1061 g.). After 2 days at room temperature, distillation gave trifluoromethyl fluorodithioformate (0.0151 g.) (Found : M , 160. Calc. for $\text{C}_2\text{S}_2\text{F}_4$: M , 164), identified by means of its infrared spectrum, and a more volatile fraction (0.0470 g.) shown by infrared spectroscopic examination to contain trifluoromethanethiol, carbonyl sulphide, silicon tetrafluoride, and a comparatively large amount of thiocarbonyl fluoride.

A similar reaction at 55° (6 hr.) failed to yield thiocarbonyl fluoride, and the amounts of carbonyl sulphide and silicon tetrafluoride had increased, thus revealing the thermal instability of thiocarbonyl fluoride.

Reaction of Bistrifluoromethyl Sulphide with Alcoholic Potassium Hydroxide.—The sulphide was recovered unchanged after treatment with an excess of 10% alcoholic potassium hydroxide at 70—75° for 24 hr. Bistrifluoromethyl sulphide (0.2189 g.) and 20% alcoholic potassium hydroxide (10 ml.), heated at 100° (48 hr.), gave unchanged bistrifluoromethyl sulphide (5%) and fluoroform (25%) (Found : M , 70. Calc. for CHF_3 : M , 70), identified by means of their

infrared spectra. The alcoholic solution was diluted with water and the fluoride in it (0.0880 g., 60%) was determined by distillation to give fluorosilicic acid and titration with thorium nitrate in the usual way.

Bis(heptafluoro-n-propyl) Disulphide.—Heptafluoroiodopropane was prepared in 86% yield by reaction of silver heptafluorobutyrate (150 g., 0.467 mole) and dry iodine (240 g., 0.945 mole) as described earlier (*J.*, 1951, 584; 1952, 4259).

Little reaction occurred between heptafluoroiodopropane and sulphur in a steel autoclave at temperatures up to 350°; at 400° there was 50% reaction, and at 450° no heptafluoroiodopropane remained unchanged. In a typical experiment, sulphur (60 g.) and heptafluoroiodopropane (86 g.) were heated (14 hr.) at 450° in a 300-ml. stainless-steel autoclave to give bis(heptafluoro-*n*-propyl) disulphide (21 g., 36%), b. p. 122°, and several fractions containing impure disulphide and small amounts of monosulphide and polysulphides. Hauptschein and Grosse (*J. Amer. Chem. Soc.*, 1951, 73, 5461) used this general method as developed for trifluoroiodomethane and reported b. p. 122° for the disulphide.

Bis(heptafluoropropyl) disulphide has the following ultraviolet spectrum: λ_{\max} , 244, ϵ 875, λ_{\min} , 218, ϵ 385 in ethanol, and λ_{\max} , 242, ϵ 860, λ_{\min} , 218, ϵ 370 in light petroleum; this shows the expected shift to longer wavelength relative to bistrifluoromethyl disulphide (*J.*, 1952, 2549) (λ_{\max} , 236, ϵ 390 in light petroleum) on change of a CF_3 to a heavier C_3F_7 group. The infrared spectrum of bis(heptafluoropropyl) disulphide (C.S. No. 282) shows the typical carbon-sulphur stretching vibrations.

Heptafluoropropanethiol.—Reaction of bis(heptafluoropropyl) disulphide with mercury in a silica tube in ultraviolet light at room temperature was slow and any mercurials formed were decomposed to mercuric sulphide. A vigorously-shaken 30-ml. silica tube containing bis(heptafluoropropyl) disulphide (2.0 g.) and mercury (15 g.) was heated at 80° by means of an open framework heater designed so that ultraviolet light from a Hanovia S-250 arc could enter the tube. After 2 days' irradiation a black solid had been formed. The liquid and volatile products were removed by pumping to leave a viscous black mass in the tube which was extracted with ether; subsequent evaporation of the ether yielded a pale yellow viscous liquid with a very pungent odour. This is bis(heptafluoropropylthio)mercury.

A series of similar reactions at temperatures between 40° and 100° showed that the optimum temperature was 70–80°; above this temperature excessive decomposition occurred, and below it only small amounts of the mercurial were obtained. A large excess of mercury (80 moles per mole of disulphide) was also necessary. Formation of a yellow crystalline compound could be observed within a few minutes of exposure to light at 75°, but the reaction slowed rapidly and an irradiation time of 2 days was found convenient. Repeated experiments were thus necessary to obtain an appreciable quantity of the mercurial. The yield was *ca.* 10%.

Bis(heptafluoropropylthio)mercury (1.0 g.) was treated with anhydrous hydrogen chloride (0.2 g.) in a 30-ml. sealed tube to give (24 hr.) mercuric chloride and *heptafluoropropanethiol* (0.301 g.), b. p. 23.7°/759 mm. (isotenoscope) (Found: F, 65.0; S, 15.5%; *M*, 202. $\text{C}_3\text{HF}_7\text{S}$ requires F, 65.8; S, 15.8%; *M*, 202).

Hydrolysis of Heptafluoropropanethiol.—(a) *With water.* The thiol (0.0720 g.) and water (2 ml.) showed but little reaction at 20° (3 days), but after 3 days at 55° and 12 hr. at 75° most of the thiol had disappeared. The temperature was raised to 100° (24 hr.), and only a small amount of yellow immiscible liquid remained. There were no volatile products. The aqueous solution was extracted with ether to remove any organic matter, then analysed for fluoride in the usual way. The fluoride was equivalent to 2.07 fluorine atoms per molecule of heptafluoropropanethiol taken; the sulphide was negligible.

In a second experiment heptafluoropropanethiol (0.0653 g.) and water (2 ml.) were heated at 100° (36 hr.). The fluoride liberated was equivalent to 2.3 fluorine atoms per molecule of the thiol, and negligible sulphide was formed.

(b) *With aqueous sodium hydroxide.* The thiol (0.1001 g.) was condensed into a tube containing 10% aqueous sodium hydroxide (2.5 ml.), and the tube was then sealed. As the aqueous solution began to melt the suspension of the thiol turned deep yellow then slowly disappeared (14 hr.) to give a deep red aqueous solution. There were no volatile products, and the aqueous solution contained fluoride equivalent to 2.8 fluorine atoms and sulphide equivalent to 0.84 sulphur atom per molecule of heptafluoropropanethiol.

A second experiment with the thiol (0.1209 g.) and 10% aqueous sodium hydroxide (4 ml.) at 75° (6 hr.) gave fluoride equivalent to 3.0 fluorine atoms and sulphide equivalent to 1.0 sulphur atom per molecule of thiol. A third experiment, at 130–140° (20 hr.), gave fluoride equivalent to 2.93 fluorine atoms.

Reaction of Bisheptafluoropropyl Disulphide with Aqueous Sodium Hydroxide.—The disulphide (0.2338 g.) and 20% aqueous sodium hydroxide (6 ml.) in a 30-ml. sealed tube reacted slowly at room temperature to give an orange aqueous layer. Only a small amount of immiscible liquid remained after 8 hr. at 85°, and the solution was deep red; there were no volatile products. The aqueous solution was extracted with ether then analysed for fluoride and sulphide (Found : F⁻ equivalent to 4.3 fluorine atoms, S⁻ equivalent to 1.0 sulphur atom per molecule of disulphide). A second experiment at 85° (4 days) gave F⁻ equivalent to 5.04 fluorine atoms, S⁻ equivalent to 1.6 sulphur atoms.

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