529. *Perfluoroalkyl Derivatives of Sulphur. Part V.**
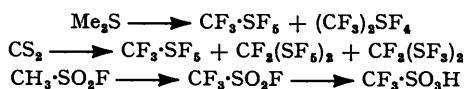*αα-Difluoro-α-(trifluorothio)acetic Acid.*

By R. N. Haszeldine and F. Nyman.

Electrolysis of a solution of thioglycollic (mercaptoacetic) acid in anhydrous hydrogen fluoride yields the acid $SF_3 \cdot CF_2 \cdot CO_2H$. Salts and derivatives of this acid are described and their infrared spectra are reported. Reaction of the salt $SF_5 \cdot CF_2 \cdot CO_2Ag$ with chlorine yields the compound $CF_2Cl \cdot SF_5$. Electrochemical fluorination of methyl iodide fails to give iodocompounds such as CF_3I, IF_5, or $CF_3 \cdot IF_4$.

EARLIER studies [1] showed that electrochemical fluorination by a technique originally developed by Simons and his colleagues [2] provides an excellent route to perfluoroalkyl derivatives of sulphur ; *e.g.* :

$$Me_2S \longrightarrow CF_3 \cdot SF_5 + (CF_3)_2SF_4$$
$$CS_2 \longrightarrow CF_3 \cdot SF_5 + CF_2(SF_5)_2 + CF_2(SF_3)_2$$
$$CH_3 \cdot SO_2F \longrightarrow CF_3 \cdot SO_2F \longrightarrow CF_3 \cdot SO_3H$$

It is evident that the sulphur atom in suitable starting compounds can be oxidised during electrochemical fluorination to its quadri- or sexa-valent state without complete degradation by C–S cleavage. The possibility thus arose of preparing compounds which are (*a*) partly inorganic, since they may be regarded as related to sulphur tetra- or hexafluoride, and (*b*) partly organic, since they may be regarded as derivatives of acetic acid. Such compounds, *e.g.*, αα-difluoro-α-(pentafluorothio)acetic acid (I) or αα-difluoro-α-(tri-

(I) $SF_5 \cdot CF_2 \cdot CO_2H$ $\qquad\qquad$ $SF_3 \cdot CF_2 \cdot CO_2H$ (II)

fluorothio)acetic acid (II) would open up a new branch of sulphur chemistry, since the carboxyl group in perfluoroalkanecarboxylic acids is capable of a wide variety of reactions.[3]

The present communication reports a study of the electrochemical fluorination of thioglycollic (mercaptoacetic) acid. Extensive breakdown occurs, some of which is doubtless caused by the fluorine oxide produced from the water liberated from the carboxyl group (*e.g.*, $R \cdot CO_2H + HF \longleftarrow R \cdot COF + H_2O$), and this necessitates use of equipment on a larger scale than described earlier.[1] Preparation of the acid fluoride of thioglycollic acid, which would be the ideal starting material, is precluded by the thiol group. The products from the electrolysis of thioglycollic acid in anhydrous hydrogen fluoride are thus complex, but from them can be isolated αα-difluoro-α-(trifluorothio)acetic acid (II) as a colourless fuming acid (b. p. 132·5°) which is stable in dry apparatus. This acid is related to sulphur tetrafluoride, and it is probable that the acid (I), which is analogously related to sulphur hexafluoride, is also produced, although attempts to obtain it analytically pure failed.

The infrared spectrum of the liquid acid (II) shows the acid-carbonyl absorption at 5·60 μ, bonded OH at 3·15 μ (cf. $CF_3 \cdot CO_2H$, 5·60, 3·18 μ), the C–F stretching vibrations at 8·20, 8·47, and 8·80 μ, and the S–F stretching vibration as a powerful doublet at 11·40, 11·65 μ. The infrared spectrum of the vapour shows the carbonyl absorption as a doublet at 5·46 (non-bonded carbonyl) and 5·60 μ (cf. $CF_3 \cdot CO_2H$, 5·46, 5·56 μ) and the free OH vibration is at 2·80 μ (cf. $CF_3 \cdot CO_2H$, 2·80 μ) ; the S–F vibration shifts to 11·17 μ.

αα-Difluoro-α-(trifluorothio)acetic acid is readily soluble in water and the solution can be titrated with aqueous sodium hydroxide without attack on the SF_3 group. The sodium salt, prepared in this way, shows carbonyl absorption at 5·89 μ, C–F absorption centred on 8·46 μ, and the S–F vibration at 11·63 μ. It decomposes slowly in aqueous or alkaline

* Part IV, *J.*, 1956, 173.

[1] (*a*) Clifford, El-Shamy, Eméleus, and Haszeldine, *J.*, 1953, 2372 ; (*b*) Gramstad and Haszeldine, *J.*, 1956, 173.
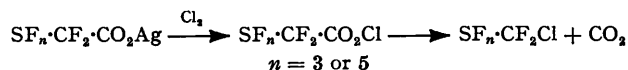
[2] Brice, Dresdner, Francis, Harland, Hogg, Pearlson, Simons, and Wilson, *Trans. Electrochem. Soc.*, 1949, **95**, 47.

[3] See, *e.g.*, Haszeldine, *Ann. Reports*, 1954, **51**, 279.

solution. The silver salt, prepared by reaction of the acid with silver carbonate, also decomposes in aqueous solution, but is stable when dry. Its infrared spectrum shows carbonyl absorption at 6·15 μ, C–F absorption centred on 8·43 μ, and S–F absorption at 11·55 μ. The *S*-benzylthiuronium salt of the acid was readily prepared, but attempts to recrystallise it failed. The aniline salt could not be obtained pure. The instability of derivatives of αα-difluoro-α-(trifluorothio)acetic acid can be attributed to the hydrolysis of the SF₃ group on prolonged contact with basic media.

Trifluoroacetic acid was also isolated from the liquid reaction products from the electro-chemical fluorination of thioglycollic acid, as was a fraction believed to be αα-difluoro-α-(pentafluorothio)acetyl fluoride, $SF_5 \cdot CF_2 \cdot COF$. The last compound had b. p. 22°, and showed acyl fluoride absorption in the infrared at 5·27 μ, C–F absorption at 8·12 μ, and S–F absorption at 11·12 μ, but was contaminated by small amounts of a by-product which was insoluble in aqueous base and could not be separated from the acyl fluoride.

The reaction of chlorine with the mixed anhydrous silver salts of acids (I) and (II) was briefly investigated to determine whether decarboxylation with simultaneous chlorination occurred, to give chlorodifluoromethyl sulphur tri- and penta-fluoride by a reaction analogous to that described earlier for silver salts of polyfluoroalkanecarboxylic acids : [4]

$$SF_n \cdot CF_2 \cdot CO_2Ag \xrightarrow{Cl_2} SF_n \cdot CF_2 \cdot CO_2Cl \longrightarrow SF_n \cdot CF_2Cl + CO_2$$
$$n = 3 \text{ or } 5$$

Silver αα-difluoro-α-(trifluorothio)acetate reacted immediately with chlorine, but underwent complete breakdown to carbon dioxide, carbonyl fluoride, thionyl fluoride, and, by attack on the reaction vessel, silicon tetrafluoride. By contrast, the silver αα-difluoro-α-(penta-fluorothio)acetate present in the mixture yielded chlorodifluoromethylsulphur penta-fluoride as a colourless gas (b. p. 16·5°) which was stable to dilute aqueous alkali; its infra-red spectrum showed the absence of $>CO$ or $>CH$ groups and revealed the C–F stretching absorptions at 8·04, 8·36, and 8·74 μ and the S–F stretching vibration at 11·15 μ. The b. p. increment is as expected for replacement of fluorine in trifluoromethyl sulphur penta-fluoride (b. p. –22°) by chlorine.

Examination of the gaseous products produced by the electrochemical fluorination of thioglycollic acid revealed the following approximate composition : SF₆ 30%, CHF₃ 25%, SO₂F₂ + SOF₂ 20%, COF₂ 8%, C₂F₆ 7%, CF₃·SF₅ 5%, CF₃·COF 2%, and CO₂ 2%. Carbon tetrafluoride was a major product produced by breakdown. The compounds $SF_3 \cdot CF_2 \cdot CO_2H$, $SF_5 \cdot CF_2 \cdot CO_2H$, $CF_3 \cdot CO_2H$, and $SF_5 \cdot CF_2 \cdot COF$ present in the products of higher b. p. have been mentioned above. The following conclusions can thus be drawn : (*a*) The fluorination of thioglycollic acid can occur to the state where sulphur is in the quadri- or sexa-valent state without complete breakdown of the molecule. (*b*) αα-Difluoro-α-(trifluorothio)-acetic acid is produced either by reaction of an intermediate such as $SF_3 \cdot CF_2 \cdot COF$ with water produced during the electrolysis, or by fluorination of the $-CH_2 \cdot SH$ group without attack on the carboxyl group. (*c*) The CH₂ group of thioglycollic acid is fluorinated before attack, or completion of the attack, on the thiol group, since products such as $SF_5 \cdot CH_2 \cdot CO_2H$, $SF_3 \cdot CHF \cdot CO_2H$, or $SF_5 \cdot CH_2 \cdot COF$ were not detected. (*d*) Partially fluorin-ated products containing more than one hydrogen atom, *e.g.*, $SH \cdot CF_2 \cdot CO_2H$, $SF \cdot CH_2 \cdot COF$, are not obtained. (*e*) C–S fission occurs with fluorination of the resultant fragments, to give SF₆ and $CF_3 \cdot COF$ or $CF_3 \cdot CO_2H$. (*f*) C–C fission occurs with fluorination of the resultant fragments to give $CF_3 \cdot SF_5$ and COF₂. (*g*) C–C and C–S fission occur to give SF₆, CF₄, CHF₃, COF₂, CO₂. (*h*) Compounds containing an S–S bond, *e.g.*, S₂F₁₀, are not obtained, but combination of CF₃ radicals produced during the electrolysis can occur to give C₂F₆. (*i*) Fluoroform is an important breakdown product. The isolation of fluoro-form, though not of other compounds containing one or more hydrogen atoms, can be attributed to its volatility and decreased solubility in hydrogen fluoride or to its failure to be adsorbed on the anodes. As long as the partially fluorinated organic compound contains two or more hydrogen atoms it is apparently soluble in hydrogen fluoride and/or adsorbed

⁴ Haszeldine, *Nature*, 1950, **166**, 192; *J.*, 1951, 584; 1952, 4259; Wenne and Finnegan, *J. Amer. Chem. Soc.*, 1950, **72**, 3806; Haszeldine and Sharpe, *J.*, 1952, 993.

on the anodes, and is hence fluorinated further. The products obtained thus tend to be perfluorinated.   (*j*) An induction period was noted during the early stages of the electrolysis of thioglycollic acid, during which free fluorine, as distinct from fluorine oxide, was produced at a voltage less than that normally required to give fluorine by electrolysis.   In addition to the ideas outlined earlier,[1b] namely, fluorination by adsorption of the organic compound on the anode followed by fluorination by a higher fluoride of nickel, one must thus also consider the possibility that fluorine atoms or molecular fluorine is involved either as direct fluorinating agent, or, more probably, as a means of producing the higher fluoride of nickel.   The induction period might be attributed to the time necessary to build up a suitable concentration of nickel polyfluoride.   It is noteworthy that only the anodes are attacked during the fluorination, to give ultimately nickel difluoride as a friable powder which drops off the anodes and collects at the bottom of the cell.

The electrochemical fluorination of methyl iodide was also investigated to determine whether compounds such as CF_3I or $CF_3 \cdot IF_4$ would be obtained.   Methyl iodide does not conduct when dissolved in hydrogen fluoride, and lithium fluoride was added to provide a conducting solution.   The products were CF_4 (main product), CHF_3 16%, CH_2F_2 1%, CH_3F 1%, and solid iodine.   It is evident that :   (*a*) The weak C–I bond in methyl iodide is broken before the C–H bond.   (*b*) Perfluorination occurs, probably because CH_3F and CH_2F_2 are soluble in hydrogen fluoride and adsorbed on the anodes.   (*c*) Solid iodine, substantially insoluble in hydrogen fluoride, is produced and its fluorination to iodine fluorides such as IF_5 does not occur.

EXPERIMENTAL

Apparatus.—The electrolytic cell was considerably larger than that described earlier.[1b]   The cell body was a flanged closed steel cylinder, 28 cm. long and 21 cm. in diameter, with silver-soldered and welded joints.   The cell was filled with anhydrous hydrogen fluoride (7 kg.) by means of a nickel valve and was drained by use of a similar valve in the base.   Solute was added to the cell through a nickel valve by means of a small nickel funnel.   The 36 electrodes were each 25·6 cm. long and 0·05 cm. thick, and varied in width from 8·7 to 18·0 cm. so as to get the maximum surface area in the volume available.   The electrodes were alternate anodes and cathodes with a total surface area of *ca.* 24,500 sq. cm., and were insulated from each other by Teflon spacers.   The electrodes were suspended from the cell lid by their electrical leads which were also insulated by Teflon bushings.   A Teflon gasket 1·0 cm. wide and 0·6 cm. thick clamped by 12 bolts rendered the flange leakproof.   Two electrical probes, used to determine the electrolyte level, extended to near the top of the electrode pack and to two-thirds of the depth of the cell respectively.   The efficiency and capacity of the condenser is of particular importance and the multiple concentric vertical tube condenser used initially was later discarded, since, although it was extremely efficient as a condenser, attack of hydrogen fluoride on the numerous brazed joints soon led to leaks of coolant into the cell.   The spiral condenser finally used proved to be satisfactory; it was made of steel tubing of 2·2 cm. internal diameter and was approximately 25 cm. in diameter, with 6 spirals in its height of 80 cm.   The cooling jacket welded to the bottom of the condenser contained aqueous glycol as coolant, circulated rapidly at −5° to −12° by means of a powerful pump.

The exit gases from the cell passed from the top of the condenser, *via* a safety tube dipping into mercury, to two flanged copper tubes (each 65 cm. by 5·5 cm.) containing sodium fluoride pellets (500 g.), then to a similar tube packed loosely with 1 cm. squares of rubber sheet to absorb fluorine oxide.   The condensable products were collected in traps cooled at −78° and −183°, and hydrogen and carbon tetrafluoride escaped to the atmosphere.   In the experiments described below, none of the products was obtained as a lower layer in the cell; the stream of hydrogen was sufficient to carry even liquids with b. p. >130° through the condenser and into the cooled trap.

Methyl iodide and thioglycollic acid were commercial samples dried and distilled before use. The hydrogen fluoride was sufficiently anhydrous to render preliminary electrolysis unnecessary.

Electrochemical Fluorination of Methyl Iodide.—To the electrochemical apparatus containing anhydrous hydrogen fluoride (7 kg.) and lithium fluoride (10 g.) (to provide conductivity) was added methyl iodide (25 g.), and electrolysis was started at 50 amp. and 4·6 v (current density 0·004 amp./cm.²).   Further quantities of methyl iodide (30 g.) were added after every

100 amp. hr. (175 g. total), and anhydrous hydrogen fluoride was added periodically to maintain the electrolyte level constant. Current was passed at an average of 50 amp. for 14·5 hr. A representative sample of the gas which passed through traps cooled at $-183°$ was examined spectroscopically and found to contain carbon tetrafluoride. Distillation *in vacuo* of the material which had condensed in the cooled traps (33·7 g.) gave unchanged methyl iodide (2·9 g.), b. p. 42·5°, n_D^{17} 1·528 (Found : M, 142. Calc. for CH_3I : M, 142), carbon tetrafluoride (16·5 g., 16% based on methyl iodide), fluoroform (13·3 g., 16% based on methyl iodide), and small amounts (*ca.* 1%) of methyl fluoride and methylene fluoride. Distillation *in vacuo* did not give quantitative separation of the last compounds, and a combination of infrared spectroscopy and molecular-weight determinations on a series of fractions was used to determine the yields. The carbon tetrafluoride isolated as above represents only a small portion of the carbon tetrafluoride formed during the reaction, since most of it is swept through the cooled traps by the stream of hydrogen.

The bottom of the cell was found to be covered with solid iodine when it was opened at the end of the experiment.

Electrochemical Fluorination of Thioglycollic Acid.—In a typical experiment the apparatus was charged with anhydrous hydrogen fluoride (7 kg. ; water content $<0·2\%$) and thioglycollic acid (200 g.), and electrolysis was begun at 10 amp. and 4·2 v (current density 0·0008 amp./cm.²). After 780 amp. hr. a further 100 g. of thioglycollic acid were added and electrolysis was continued for a further 320 amp. hr. At this stage the amperage and voltage were increased to 14 amp. and 4·4 v respectively (current density 0·0011 amp./cm.²) and electrolysis was continued for 630 amp. hr. A further 200 g. of thioglycollic acid were added (500 g. total) and the electrolysis was completed at 14 amp. and 4·4 v (1040 amp. hr.). A total of 2770 amp. hr. was thus required. The electrolyte level was maintained constant during the experiment by periodic addition of anhydrous hydrogen fluoride.

The reaction products which had condensed in traps cooled to $-78°$ and $-183°$ were divided into three arbitrary fractions A (110 g.), B (25 g.), and C (750 g.) by distillation at 10^{-3} mm., and condensing the material in traps cooled to $-64°$, $-96°$, and $-183°$ respectively. These fractions were examined separately as described below.

When the cell was examined at the end of the experiment, a layer of dark brown solid (*ca.* 200 g.) was found on the bottom, and a yellowish deposit was noted on the anodes, but not on the cathodes. The solid did not contain any ether-soluble material, and analysis of its solution in concentrated hydrochloric acid showed it to consist of ferric fluoride (80%) and nickel fluoride (20%).

αα-*Difluoro-α-(trifluorothio)acetic Acid* (*Fraction A*).—Fraction A, b. p. $>20°$, was distilled from phosphoric anhydride (0·2 g.) and a few small pellets of sodium fluoride through a short column packed with glass helices. Hydrofluoric acid liberated during the distillation etched the apparatus and made redistillation of the fractions necessary to remove fluorosilicates. The major constituents finally isolated were trifluoroacetic acid (43·0 g., 7% based on thioglycollic acid), b. p. 72°, identified by means of its infrared spectrum, and αα-*difluoro-α-(trifluorothio)acetic acid* (30·2 g., 3% based on thioglycollic acid), b. p. 132·5° (Found : C, 12·9 ; H, 1·0 ; F, 51·8 ; S, 17·6% ; equiv., 184·9. $C_2HO_2F_5S$ requires C, 13·0 ; H, 0·5 ; F, 51·6 ; S, 17·4% ; equiv., 184·0). The αα-difluoro-α-(trifluorothio)acetic acid was analysed for fluorine and sulphur by fusion with sodium at 600° for 2 hr. in a Pyrex tube. The resultant sodium fluoride was determined as fluorosilicic acid by titration with thorium nitrate solution. The sodium sulphide was converted into sulphate by treatment with an excess of 30% hydrogen peroxide, and, after removal of the residual hydrogen peroxide, sulphate was determined gravimetrically as barium sulphate.

Fraction B.—Attempts to purify this material by fractionation *in vacuo* failed. It was therefore distilled through a 12″ Podbielniak Heli-Grid column with reflux condenser at $-60°$ and a reflux ratio of 30 : 1. The material boiled over the range 11—26°, and the major fraction, b. p. 21·5—22·5°, was impure αα-difluoro-α-(pentafluorothio)acetyl fluoride (Found : C, 11·7 ; H, 0% ; M, 226. Calc. for C_2OF_8S : C, 10·7 ; H, 0% ; M, 224) contaminated by material which was resistant to concentrated aqueous sodium hydroxide. Further purification by distillation could not be effected on the scale used.

Fraction C.—Preliminary attempts at purification by distillation *in vacuo* showed that the material was a complex mixture. It was therefore split into arbitrary fractions by distillation and each fraction was analysed by infrared spectroscopy ; the average molecular weight of the fraction was also determined and used in the analysis. The results so obtained were combined with those from partial hydrolysis of the fraction with 20% aqueous sodium hydroxide ; this

treatment removed trifluoroacetyl fluoride, carbonyl fluoride, carbon dioxide, sulphuryl fluoride, and sulphonyl fluoride. The alkaline solution was neutralised with sulphuric acid, then evaporated to dryness, and the residual solid was extracted with anhydrous ethanol; evaporation of the ethanol gave spectroscopically pure sodium trifluoroacetate. The average composition of fraction C determined in this way was: CHF_3 25; C_2F_6 7; $CF_3 \cdot COF$ 2; COF_2 8; CO_2 2; SF_6 30; SO_2F_2 plus SOF_2 20; $CF_3 \cdot SF_5$ 5%. No great accuracy is claimed for these figures in view of the complexity of the mixture; the figures for $CF_3 \cdot COF$, CHF_3, C_2F_6, and $CF_3 \cdot SF_5$ are the most accurate.

Induction Period during Electrochemical Fluorination.—Evolution of product of b. p. $> -80°$ from the electrolysis cell does not begin immediately electrolysis is started. There is an induction period of up to 100—200 amp. hr. (at <4.5 v) during which a gas containing free fluorine is evolved.

Derivatives of αα-Difluoro-α-(trifluorothio)acetic Acid.—The acid (0·52 g.) was dissolved in water (5 ml.) and treated with freshly precipitated silver carbonate in slight excess. The mixture was centrifuged to remove the excess of silver carbonate, and the solution was immediately freeze-dried in the dark. The solid so obtained was extracted with anhydrous ether, and the extract was filtered, then evaporated to dryness, to give the white *silver salt* (0·8 g., 98%) (Found: C, 8·7; H, 0; Ag, 36·7. $C_2O_2F_5SAg$ requires C, 8·3; H, 0; Ag, 37·1%). The salt was dried *in vacuo* over phosphoric anhydride before analysis until infrared spectroscopy showed the absence of water; a weighed sample was then dissolved in water, and the solution was treated with concentrated nitric acid, then hydrochloric acid to precipitate silver chloride.

αα-Difluoro-α-(trifluorothio)acetic acid (1·0 g.) was dissolved in water, then immediately exactly neutralised (pH meter) with 0·1N-sodium hydroxide. Freeze-drying of the solution gave the white *sodium salt* which was dried *in vacuo* over phosphoric anhydride before analysis (Found: Na, 11·2. $C_2O_2F_5SNa$ requires Na, 11·2%). Sodium was determined as sodium sulphate after decomposition of the salt with concentrated sulphuric acid followed by repeated evaporation to dryness with further quantities of sulphuric acid.

The acid (0·10 g., 0·54 mmole) in water (2 ml.), mixed with S-benzylthiuronium chloride (0·11 g., 0·54 mmole) in water (2 ml.), gave a white precipitate which was immediately filtered off, washed with water, and dried *in vacuo* over phosphoric anhydride. Fluoride ion was not liberated during the reaction. Attempts to recrystallise the S-*benzylthiuronium salt* (0·132 g., 70%) (Found: N, 7·7. $C_{10}H_{11}O_2N_2F_5S_2$ requires N, 8·0%), m. p. approx. 112° (decomp.), prepared in this way were unsuccessful, since evolution of a gas and liberation of fluoride ion accompanied extensive decomposition. The infrared spectrum shows the CO_2^- band at 6·00 μ, C–F absorption at 8·40 and 8·47 μ, and S–F absorption at 11·50 μ.

Attempts to prepare the aniline salt from an ethereal solution of αα-difluoro-α-(trifluorothio)-acetic acid gave a white solid which was not analytically pure and which could not be recrystallised without decomposition from any of the several solvent systems examined. The crude solid showed CO_2^- absorption at 5·97 μ, C–F absorption at 8·35, 8·51 μ, and S–F absorption at 11·50 or 11·75 μ.

Chlorodifluoromethylsulphur Pentafluoride [Chlorodifluoro(pentafluorothio)methane].—A mixture (5·24 g.) of silver αα-difluoro-α-(trifluorothio)acetate and silver αα-difluoro-α-(pentafluorothio)acetate was thoroughly dried *in vacuo* (7 days), then sealed in a 50 ml. Pyrex tube with dry chlorine (1·007 g.). Reaction occurred when the tube was allowed to warm to −23° and was apparently complete within a few minutes. The gaseous products were removed after 24 hr. at room temperature and fractionated *in vacuo* to give carbon dioxide, silicon tetrafluoride, thionyl fluoride, carbonyl fluoride (all identified by means of their infrared spectra), and a fraction (0·937 g.) (Found: M, 204) which spectroscopic examination showed to be contaminated by silicon tetrafluoride. The last fraction was shaken with water in a sealed tube (24 hr.), then with 5% aqueous sodium hydroxide (15 min.), and refractionated, to give *chlorodifluoromethylsulphur pentafluoride* (0·512 g.), b. p. 16·5° (Found: C, 6·8; Cl, 17·2%; M, 212·5. $CClF_7S$ requires C, 5·7; Cl, 16·7%; M, 212·5. Cf. calc. for $CClF_5S$: C, 6·9; Cl, 20·3%; M, 174·5). Reliance should be placed on the chlorine analysis and molecular-weight determination, since analysis of these oxygen-free derivatives of sulphur hexafluoride for carbon has proved difficult.

Infrared Spectra.—These were determined on a Perkin-Elmer Model 21 with sodium chloride optics.

$SF_3 \cdot CF_2 \cdot CO_2H$ (liquid): 3·15 (s broad), 3·7, 3·9 (w side bands), 5·60 (s sharp), 6·93 (m), 7·40 (m), 8·20 (vs), 8·47 (vs), 8·80 (vs), 11·40, 11·65 (vs doublet), 14·40, 14·73 (w doublet). Here and below, s = strong, w = weak, vs = very strong, m = medium strength.

$SF_3 \cdot CF_2 \cdot CO_2H$ (vapour) : 2·80 (w sharp), 5·46, 5·60 (s sharp doublet), 7·41 (w), 8·05 (vs), 8·45 (m), 8·83 (s broad), 9·55 (w), 11·17 (vs), 11·54 (m).

$SF_5 \cdot CF_2 \cdot COF$ (vapour) : 5·27 (s sharp), 7·79 (m), 7·93 (s), 8·12 (vs), 8·50 (w), 8·60 (w), 8·82 (vs), 9·10 (w), 9·98 (m), 10·66 (m), 11·12 (vs), 11·54 (vs), 13·05 (w), 14·73 (m).

$SF_5 \cdot CF_2Cl$ (vapour) : 7·44 (w), 8·04 (vs), 8·36 (vs), 8·74 (vs), 9·47 (w), 10·30 (vs), 11·15 (vs), 11·97 (vs), 13·33 (w), 14·43, 14·53 (w doublet).

$SF_3 \cdot CF_2 \cdot CO_2Na$ (Nujol mull) : 5·89 (s sharp), 6·87 (w), 7·15 (w), 7·55 (w), 8·1 (s), 8·46 (vs), 8·95 (m), 9·25 (m), 11·63 (vs broad), 12·30 (m), 13·75 (s).

$SF_3 \cdot CF_2 \cdot CO_2Ag$ (Nujol mull) : 6·15 (s sharp), 7·07 (w), 8·10 (m), 8·43 (vs), 8·93 (m), 9·30 (m), 10·53, (w), 11·55 (vs broad), 12·25 (m), 13·83 (s), 14·63 (w).