

483. *Organometallic and Organometalloidal Fluorine Compounds. Part VIII.* The Electrochemical Fluorination of Dimethyl Sulphide and Carbon Disulphide.*

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Electrochemical fluorination of dimethyl sulphide in anhydrous hydrogen fluoride yields the compounds $\text{CF}_3\cdot\text{SF}_5$ and $(\text{CF}_3)_2\text{SF}_4$. Carbon disulphide similarly gives the compounds $\text{CF}_3\cdot\text{SF}_5$, $\text{CF}_2(\text{SF}_5)_2$, and $\text{CF}_2(\text{SF}_3)_2$. Attempts to fluorinate the corresponding selenium compounds were unsuccessful.

THE process for the electrochemical fluorination of organic compounds developed by Brice, Dresner, Francis, Harland, Hogg, Pearson, Simons, and Wilson (*Trans. Electrochem. Soc.*, 1949, **95**, 47) has been widely applied to the preparation of fully fluorinated compounds: it has not, as yet, been examined as a method for converting organometallic or organometalloidal compounds into their fluorocarbon analogues, and this paper records the beginning of investigations in this direction.

Two sulphur compounds, dimethyl sulphide and carbon disulphide, were chosen, since bistrifluoromethyl sulphide, a possible reaction product from dimethyl sulphide, has been characterised earlier (Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198), and the reaction of carbon disulphide with cobalt trifluoride has been found by Silvey and Cady (*J. Amer. Chem. Soc.*, 1950, **72**, 3624) to yield trifluoromethylsulphur pentafluoride. The experiments described below have been made mainly to develop and test a convenient laboratory cell for electrolysis in hydrogen fluoride, and no attempt has been made to examine the effect of the concentration of solute, temperature, applied voltage, current density, etc., on the yield. The experiments with dimethyl sulphide have demonstrated the possibility of converting the $\text{S}\cdot\text{CH}_3$ group into $\text{S}\cdot\text{CF}_3$ directly, even though extensive cleavage occurs and carbon tetrafluoride and sulphur hexafluoride are major products. The less volatile products, $\text{CF}_3\cdot\text{SF}_5$ and $(\text{CF}_3)_2\text{SF}_4$, constituted 20 and 2% respectively of the gas liberated from the cell, and the former was shown to be identical with the compound obtained by Silvey and Cady (*loc. cit.*). Bistrifluoromethylsulphur tetrafluoride has a vapour pressure in the temperature range -40° to $+20^\circ$ expressed by the equation $\log_{10} p(\text{mm.}) = 7.027 - 1217.6/T$, whence the boiling point is 20.5° , the latent heat of vaporisation is 5.57 kcal./mole, and Trouton's constant is 19.0.

There is as yet no full understanding of the electrode processes involved in electrolysis in anhydrous hydrogen fluoride. It is to be noted, however, that the electrolysis products contained sulphur in its highest valency state. Careful examination was made for bistrifluoromethyl sulphide, but this was not a reaction product. Conversion of the sulphur into the hexavalent state must occur at an early stage in the electrolysis [*e.g.*, by formation of $(\text{CH}_3)_2\text{SF}_4$, $(\text{CHF}_2)_2\text{SF}_4$, etc.] to give compounds which remain soluble in hydrogen fluoride and then undergo complete replacement of hydrogen by fluorine. Replacement of hydrogen by fluorine initially would give bistrifluoromethyl sulphide which, like perfluorodimethyl ether, is insoluble in hydrogen fluoride and would be collected as a reaction product. Carbon-sulphur bond fission thus probably occurs in the later stages of the electrolysis.

Carbon disulphide yielded trifluoromethylsulphur pentafluoride, in agreement with the recent work of Silvey and Cady (*ibid.*, 1952, **74**, 5792), but in addition small yields of the new compounds $\text{CF}_2(\text{SF}_5)_2$ and $\text{CF}_2(\text{SF}_3)_2$ were isolated. Secondary reactions also occurred, since free sulphur was deposited in the cell. The vapour pressure of difluoromethylenebis(sulphur pentafluoride) is expressed by the equation $\log_{10} p(\text{mm.}) = 7.423 - 1516.1/T$ between 23° and 36° , whence the boiling point is 60.5° , the latent heat of vaporisation is 6.93 kcal./mole, and Trouton's constant is 20.8. The compound is immiscible with carbon disulphide at low temperature and only partly miscible at room temperature. It is immiscible with ethanol at room temperature and completely miscible with trifluoromethyl sulphur pentafluoride. Like sulphur hexafluoride and trifluoro-

* Part VII, Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

methylsulphur pentafluoride, difluoromethylenebis(sulphur pentafluoride) is inert to sodium ethoxide solution at 100°. Only small amounts of difluoromethylenebis(sulphur trifluoride) (b. p. 35°) were isolated, and it is again apparent that electrochemical fluorination, like reaction with elementary fluorine, yields compounds with sulphur in its highest valency state.

Preliminary experiments with dimethyl selenide and carbon diselenide showed that extensive decomposition occurred on electrolysis; selenium was deposited on the electrodes and then, with carbon diselenide, no current could be passed.

The ultra-violet spectra of the compounds $\text{CF}_3\cdot\text{SF}_5$ and $\text{CF}_2(\text{SF}_5)_2$ are tabulated and their infra-red spectra are reported in the Experimental section.

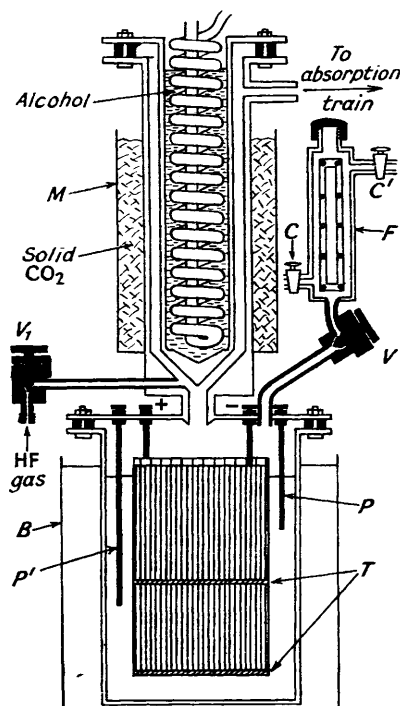
Ultra-violet spectra.

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| $\text{CF}_3\cdot\text{SF}_5$ | λ_{max} 228, ϵ , 5.6; λ_{min} 225.5, ϵ , 2.8. |
| $\text{CF}_2(\text{SF}_5)_2$ | General absorption: ϵ_{240} 2, ϵ_{230} 2.5, ϵ_{220} 2.9, ϵ_{210} 8.5. |

EXPERIMENTAL

Apparatus.—The electrolytic cell employed is shown diagrammatically in the Figure. It is based on that described by Simons ("Fluorine Chemistry," Vol. I, Academic Press Inc., p. 417), but several improvements and modifications make it suitable for laboratory research as distinct from use in an industrial process.

The body of the cell was a flanged nickel cylinder, 15 cm. long and 8 cm. in diameter, closed at the bottom by a silver-soldered nickel disc. The electrode assembly consisted of 26 nickel sheets (each 12.7 × 6.3 × 0.08 cm. thick) as alternate anodes and cathodes. The electrodes were insulated from each other by Teflon spacers (*T*), and were suspended from the nickel lid of the cell by their leads, which were also insulated by Teflon bushings. The lid was secured to the flange of the cell body by 12 bolts and was rendered leakproof by a 0.3-cm. Teflon gasket. In addition to the main electrode system the lid carried two insulated electrical probes (*P*, *P'*), which extended to $\frac{1}{3}$ and $\frac{2}{3}$ of the depth of the cell respectively, and were used to determine the electrolyte level. A cylindrical chamber (*F*) of 65-ml. capacity, fitted with a polychlorotrifluoroethylene window, was silver-soldered to the lid and fitted with inlet and exit valves (*C*, *C'*) by means of which it could be flushed with dry nitrogen. This chamber was used for the gradual addition of solute through the nickel needle valve (*V*) (packed with Teflon). In the centre of the lid was an exit tube leading to a condenser, the cold finger of which was 16 cm. long, 4 cm. in diameter, and 0.7 cm. from the outer tube of the condenser. The cold finger was filled with alcohol and cooled to -10° by a coil through which brine was circulated. An outer vessel *M* was filled with solid carbon dioxide when the cell was being filled with hydrogen fluoride (500 ml. of liquid) though valve *V*₁. The hydrogen fluoride used was sufficiently anhydrous to render a preliminary electrolysis unnecessary. The cell was cooled externally to 0° during electrolysis by immersion in the cooling bath *B*.



Laboratory cell for electrochemical fluorination in anhydrous hydrogen fluoride.

Solutions of dimethyl sulphide and selenide were sufficiently conducting, but, in experiments with carbon disulphide and diselenide, 1–2 g. of sodium fluoride or barium fluoride were added to increase the conductivity. The average operating conditions were 3.5–5 amp. at 5 v, with a current density *ca.* 0.0025 amp./sq. cm.

A nickel tube led from the top of the condenser to the absorption train, all joints in the metal parts of which were silver soldered. The first tube in the train was of brass (60 × 5 cm.) and

was filled with sodium fluoride pellets to remove hydrogen fluoride from the exit gases. The second tube (of glass) was inserted to remove fluorine monoxide which might arise from traces of moisture entering the electrolyte during operation. Initially this tube was filled with cobalt carbonate, but in later experiments a packing consisting of lengths of small-bore rubber tubing was preferred since contamination of the products by carbon dioxide was thereby avoided. In the experiments with carbon disulphide a further tube packed with piperazine was inserted to remove traces of carbon disulphide vapour. The volatile reaction products were then condensed from the hydrogen stream (the cathode gas) by three traps cooled in liquid air and protected by a phosphoric oxide guard tube; these products were transferred to a vacuum system for purification.

Electrochemical Fluorination of Dimethyl Sulphide.—The cell was charged with redistilled dimethyl sulphide (16.9 g.) and hydrogen fluoride (500 ml.), further additions of which were made from time to time to maintain the electrolyte level. Electrolysis was started with a current of 6.5 amp., which fell to 3.5 amp. during the experiment. After 15 hr. a rapid decrease in current was apparent, indicating the completion of the electrolysis. The reaction products were washed with 10% aqueous sodium hydroxide, dried (P_2O_5), and fractionated to give carbon tetrafluoride and sulphur hexafluoride, identified by molecular-weight and infra-red spectroscopic measurements; these compounds were 58 and 17%, respectively, of the total gaseous products. Two less volatile products were isolated: The first was trifluoromethylsulphur pentafluoride (30.5 g.; 20% of total product), b. p. -20° (Found: F, 77.0; S, 16.3%; M , 196. Calc. for CF_3S : F, 77.5; S, 16.4%; M , 196); Silvey and Cady's vapour-pressure measurements were confirmed. The second was *bistrifluoromethylsulphur tetrafluoride* (3.5 g.; ca. 2% of total product), b. p. 20.5° (Found: F, 77.3; S, 13.0%; M , 243. $C_2F_{10}S$ requires F, 77.3; S, 13.0%; M , 246); the products from several experiments were combined for the final purification, but the low Trouton constant may indicate a slight impurity.

Trifluoromethylsulphur pentafluoride was recovered unchanged after 60 hr. at 100° in 20% aqueous or alcoholic potassium hydroxide.

For analysis, the sulphur compounds were fused with sodium at 600° ; fluoride was determined by thorium nitrate, and sulphide by use of standard iodine and sodium thiosulphate.

Electrochemical Fluorination of Carbon Disulphide.—Electrolysis of carbon disulphide (55 g.; added in 5-ml. portions during 35 hr.) for 45 hr. by the procedure described above gave trifluoromethylsulphur pentafluoride as the major product (> 90% yield), and a small amount of sulphur hexafluoride. Small amounts of a less volatile material were also isolated, and were combined with similar material from two further experiments on the same scale as the above: distillation gave *difluoromethylenebis(sulphur pentafluoride)* (0.5%), b. p. 60.5° (Found: F, 75.1; S, 21.7%; M , 303. $CF_{12}S_2$ requires F, 75.0; S, 21.1%; M , 304), and *difluoromethylenebis(sulphur trifluoride)* (0.5%), b. p. 35° (micro) (Found: M , 229. Calc. for $C_2F_8S_2$: M , 228); the latter was not isolated in sufficient yield for full characterisation.

Electrochemical Fluorination of Dimethyl Selenide and Carbon Diselenide.—Extensive decomposition occurred during these experiments, and no selenium compounds were collected in the traps cooled in liquid air. Small amounts of methyl fluoride (Found: M , 37. Calc. for CH_3F : M , 34) were isolated from dimethyl selenide. The cell contained a black residue which contained nickel and selenium after the dimethyl selenide experiment, and anodic decomposition during electrolysis is indicated. Decomposition is not caused by solvolysis by hydrogen fluoride, since unchanged dimethyl selenide was recovered at the end of the experiment. On electrolysis of carbon diselenide solution the cell resistance increased rapidly until no current could be passed; reversal of the polarity of the cell did not increase the conductivity, and the electrodes were found to be coated with red selenium.

Ultra-violet and Infra-red Spectra.—The ultra-violet spectra were recorded on a Unicam Spectrophotometer. Silica cells were used, and the extinction coefficient, ϵ , was given by $\epsilon = 760 \times 22.4 \times DT/273 lp$, where D = optical density, T = temperature ($^\circ K$), l = cell length (cm.), and p = pressure (mm.).

Infra-red spectra were taken by a Perkin-Elmer Model 21 Double Beam Instrument with sodium chloride optics; the results were:

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| $CF_3 \cdot SF_5$ | 3.36, 3.50(vw doublet), 4.03(w), 4.15(m), 4.68(w), 4.88(w), 4.98(w), 5.40(w), 5.66(w), 6.13(w), 6.29(m), 6.60(m), 6.80(w), 7.24(w), 7.45(m), 7.70(s), 7.97(vs), 8.20(s), 8.57(vs), 9.35(w), 9.92(w), 11.10(vs), 11.26, 11.32(m doublet), 13.15, 13.24, 13.35(vs triplet), 14.40, 14.50(vs doublet). |
| $(CF_3)_2SF_4$... | 4.16(m), 6.70(m), 6.87(m), 7.50(m), 7.70(s), 7.94(vs), 8.64(s), 9.29(m), 10.15(m), 11.08(s), 11.67(s), 12.21(m), 13.24—13.45(s), 14.44—14.57(s). |

$\text{CF}_2(\text{SF}_5)_2$... 4.17(w), 6.33(m), 6.45(m), 6.60(m), 8.12(vs), 8.47(vs), 8.82(s), 9.05(m), 10.1(m), 10.83(vs),
11.33(vs), 12.5(vs), 13.6(w), 14.5(s).

m = medium, s = strong, vs = very strong, w = weak.

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