512. *Perfluoroalkyl Derivatives of Sulphur. Part VI.** *Perfluoroalkanesulphonic Acids* $CF_3{\cdot}[CF_2]_n{\cdot}SO_3H$ (n = 1—7).†

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Electrolysis of solutions of alkanesulphonyl chlorides $CH_3{\cdot}[CH_2]_n{\cdot}SO_2Cl$ (n = 1—7) in anhydrous hydrogen fluoride gives the perfluoroalkanesulphonyl fluorides $CF_3{\cdot}[CF_2]_n{\cdot}SO_2F$ in 25—80% yield; the fluorides are readily converted into the corresponding sulphonic acids $CF_3{\cdot}[CF_2]_n{\cdot}SO_3H$. Certain of the by-products from the electrolysis of *n*-octanesulphonyl chloride have been identified.

Salts and other derivatives of the acids have been prepared, and a survey has been made of the chemical and physical properties of these compounds.

A GENERAL method for the preparation of the acid fluorides of perfluoroalkanesulphonic acids by electrolysis of the corresponding alkanesulphonyl chloride or fluoride was described in Part IV[1] and exemplified by trifluoromethanesulphonic acid. Preparation of the homologues containing 2—8 carbon atoms is now recorded. Since this work was completed a patent[2] has dealt with related studies (cf. the Experimental part below).

Electrochemical fluorination of an alkanesulphonyl chloride gives smoothly the perfluoroalkanesulphonyl fluoride, which can be converted into the corresponding acid:

$$CH_3{\cdot}[CH_2]_n{\cdot}SO_2Cl \longrightarrow CF_3{\cdot}[CF_2]_n{\cdot}SO_2F \longrightarrow CF_3{\cdot}[CF_2]_n{\cdot}SO_3K \longrightarrow CF_3{\cdot}[CF_2]_n{\cdot}SO_3H$$

The yield of trifluoromethanesulphonyl fluoride by this procedure was 87%[1] and, as expected, the yield decreases steadily as the chain length is increased (79% for perfluoroethane- to 25% for perfluoro-octane-sulphonyl fluoride). The breakdown products from the electrochemical fluorination of *n*-octanesulphonyl chloride contained $CF_3{\cdot}[CF_2]_{0-6}{\cdot}SO_2F$, C_8F_{18}, C_4F_{10}, C_3F_8, C_2F_6, SO_2F_2, SF_6, and $CF_3{\cdot}[CF_2]_{2-5}{\cdot}CO_2H$, formed mainly by carbon–sulphur fission to give perfluoro-octane, which is a major product, and then by carbon–carbon fission: the low yield of perfluoroalkanesulphonic acids containing 1—7 carbon atoms shows, however, that carbon–carbon fission can occur without carbon–sulphur fission. The presence of small amounts of perfluoroalkanecarboxylic acids indicates that electrochemical oxidation (*e.g.*, by oxygen, oxygen difluoride, or sulphuryl fluoride) of the fluorocarbon chain occurs, to give perfluoroacyl fluorides, $CF_3{\cdot}[CF_2]_n{\cdot}COF$, which are subsequently hydrolysed by moist air on removal from the electrolysis cell. Material of b. p. much greater than that of perfluoro-octanesulphonyl fluoride was also noted; it was

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* Part V, *J.*, 1956, 2684.

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[1] Gramstad and Haszeldine, *J.*, 1956, 173; cf. Haszeldine and Kidd, *J.*, 1954, 4228; 1955, 2901.

[2] Brice and Trott, U.S.P. 2,732,398; *Chem. Abs.*, 1956, 13982.

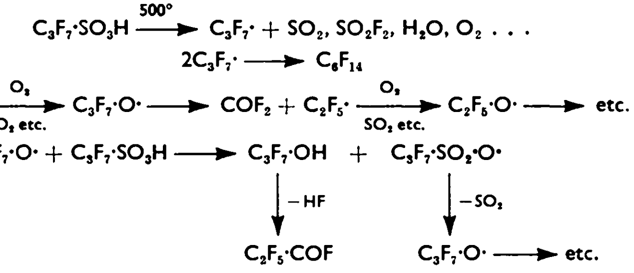
free from hydrogen and in view of the b. p. it must contain more than 8 carbon atoms. Free-radical formation and combination on the anode surface thus seems probable, *e.g.*,

$$C_8F_{17}{\cdot} \longrightarrow C_{16}F_{34}; \quad {\cdot}C_8F_{16}{\cdot}SO_2F \longrightarrow (C_8F_{16})_2(SO_2F)_2$$

The perfluoroalkanesulphonyl fluorides are quite volatile (*e.g.*, $C_2F_5{\cdot}SO_2F$, b. p. 8°; $C_8F_{17}{\cdot}SO_2F$, b. p. 155°) and have the typical odour of a fluorocarbon. They are hydrolysed only very slowly by water, the more slowly with increase in the length of the chain, doubtless because of decreased solubility; thus perfluoro-octanesulphonyl fluoride is only slightly attacked by water at 180° after several days. Direct reaction of the sulphonyl fluoride with ammonia, piperidine, or aniline yields the corresponding amides $C_8F_{17}{\cdot}SO_2Z$ (*e.g.*, $Z = NH_2$, piperidino, or NHPh).

Aqueous potassium hydroxide, like aqueous barium hydroxide,[1] hydrolyses a perfluoroalkanesulphonyl fluoride rapidly and quantitatively to the sulphonate. Alkali-metal perfluoroalkanesulphonates containing 1—4 carbon atoms are appreciably soluble in water; those containing 4—8 carbon atoms show decreasing water-solubility, ultimately less than 2% at 25°, and are surface-active. The salts have high melting points (often >300°), and when anhydrous are stable for prolonged periods at 400°; liberation of fluoride becomes important only above 420°. Formation of fluoride could be detected when potassium perfluoro-octanesulphonate was heated with aqueous potassium hydroxide at 270°, but the salt was stable to water alone at 300°.

The perfluoroalkanesulphonic acids are liberated from their salts by 100% sulphuric acid; they are relatively volatile (*e.g.*, $C_2F_5{\cdot}SO_3H$, b. p. 178°; $C_8F_{17}{\cdot}SO_3H$, b. p. 258—260°), hygroscopic (yielding initially solid monohydrates) oils or waxy solids. Their solubility in water and polar solvents decreases with increase in chain length; with this is associated an increase in their marked surface-activity. The anhydrous acids are stable at 400° in absence of air, but liberate fluoride at this temperature when moisture is present; an aqueous solution of a perfluoroalkanesulphonic acid is stable at 280°. Concentrated nitric acid fails to liberate fluoride at 160°. Pyrolysis of perfluoropropanesulphonic acid at 500° gives perfluorohexane, pentafluoropropionyl fluoride, and products of complete breakdown; the C–S bond is again the point of weakness, and degradation of the C_3F_7 radical *via* the alkoxy-radical[3] is indicated:



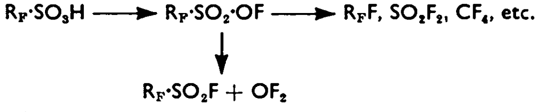
$$C_3F_7{\cdot}SO_3H \xrightarrow{500^\circ} C_3F_7{\cdot} + SO_2,\ SO_2F_2,\ H_2O,\ O_2 \ldots$$

$$2C_3F_7{\cdot} \longrightarrow C_6F_{14}$$

$$C_3F_7{\cdot} \xrightarrow[SO_2\text{ etc.}]{O_2} C_3F_7{\cdot}O{\cdot} \longrightarrow COF_2 + C_2F_5{\cdot} \xrightarrow[SO_2\text{ etc.}]{O_2} C_2F_5{\cdot}O{\cdot} \longrightarrow \text{etc.}$$

$$\begin{tikzcd} C_3F_7{\cdot}O{\cdot} + C_3F_7{\cdot}SO_3H \arrow[r] & C_3F_7{\cdot}OH \arrow[d, "-HF"] & + & C_3F_7{\cdot}SO_2{\cdot}O{\cdot} \arrow[d, "-SO_2"] & \\ & C_2F_5{\cdot}COF & & C_3F_7{\cdot}O{\cdot} \arrow[r] & \text{etc.} \end{tikzcd}$$

Electrolysis of a solution of a perfluoroalkanesulphonic acid in anhydrous hydrogen fluoride caused explosions, and only a moderate yield of the perfluoroalkanesulphonyl fluoride was obtained. This is in accord with the difficulty experienced earlier[1] with alkanesulphonic acids, and suggests that water is liberated $[2R_F{\cdot}SO_3H \rightleftharpoons (R_F{\cdot}SO_2)_2O + H_2O]$, ultimately yielding oxygen difluoride, or that an explosive hypofluorite is formed as intermediate:



$$\begin{tikzcd} R_F{\cdot}SO_3H \arrow[r] & R_F{\cdot}SO_2{\cdot}OF \arrow[r] \arrow[d] & R_FF,\ SO_2F_2,\ CF_4,\ \text{etc.} \\ & R_F{\cdot}SO_2F + OF_2 & \end{tikzcd}$$

Perfluoroalkanesulphonic acids are very strong acids, which readily yield organic or inorganic salts by conventional methods. Derivatives of the acids [*e.g.*, $C_8F_{17}{\cdot}SO_2Cl$,

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[3] Francis and Haszeldine, *J.*, 1955, 2151; Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

$(C_8F_{17}{\cdot}SO_2)_2O]$ have been obtained by standard techniques or by application of the methods described earlier.[1] Apart from the expected increase in surface-activity, the longer-chain perfluoroalkanesulphonic acids closely resemble trifluoromethanesulphonic acid, the properties of which will be described in more detail in Part VII.

EXPERIMENTAL

Electrochemical Fluorination Apparatus.—The apparatus and techniques used were similar to those described earlier.[1] Fresh anhydrous hydrogen fluoride, sodium fluoride pellets, and squares of rubber sheet were used for each experiment, and a short preliminary electrolysis was sufficient to remove traces of water.

Preparation of the Sulphonic Acids $CF_3{\cdot}[CF_2]_{1-7}{\cdot}SO_3H$ *by Electrochemical Fluorination of the Compounds* $CH_3{\cdot}[CH_2]_{1-7}{\cdot}SO_2Cl$.—The electrolysis cell contained 700 g. of anhydrous hydrogen fluoride. A 5% solution of the alkanesulphonyl chloride (35 g.) in hydrogen fluoride was electrolysed at a constant 5·0 v until the current (average approx. 6—6·5 amp.) fell to less than 2 amp., then the electrolysis was assumed to be complete (20—40 hr.). The product, collected in traps cooled by liquid oxygen and/or drained from the cell, was given a preliminary distillation to isolate a crude perfluoroalkanesulphonyl fluoride fraction which was then redistilled carefully; all other product were discarded. The b. p.s of the pure *perfluoroalkanesulphonyl fluorides* are shown in Table 1. Somewhat higher yields (5—10%) are obtained by electrolysis of the alkanesulphonyl fluorides, but on a laboratory scale this scarcely merits the extra step in the procedure.

TABLE 1.

Compound	Yield (%)	B. p.	n_D^{25}	Found C (%)	Found M	Required C (%)	Required M
$C_2F_5{\cdot}SO_2F$	79	8°	—	11·8	202	11·9	202
$C_3F_7{\cdot}SO_2F$	68	36	—	14·2	250	14·3	252
$C_4F_9{\cdot}SO_2F$	58	64	1·281	15·9	301	15·9	302
$C_5F_{11}{\cdot}SO_2F$	45	90	1·288	17·0	349	17·1	352
$C_6F_{13}{\cdot}SO_2F$	36	114	1·292	17·7	398	17·9	402
$C_7F_{15}{\cdot}SO_2F$	31	135	1·297	18·4	446, 447	18·6	452
$C_8F_{17}{\cdot}SO_2F$	25	155	1·302	See below		—	—

These fluorides were hydrolysed quantitatively by a 20% excess of 10% aqueous potassium hydroxide in a sealed tube at 20° in 15 hr. The potassium salts of the C_2—C_4 acids were isolated by the extraction procedure described earlier; the potassium salts of the C_5—C_8 acids are moderately to sparingly soluble in water and were separated by filtration. Yields were >90%. Thus, in a typical experiment, perfluoro-octanesulphonyl fluoride (3·8 g.) was shaken vigorously at room temperature in a sealed tube with an excess of 10% aqueous potassium hydroxide for 15 hr. Filtration of the white solid produced, and careful washing with cold water and drying *in vacuo* for 48 hr., gave *potassium perfluoro-octanesulphonate* (93%) (Found: C, 17·7; S, 6·0; K, 7·2. $C_8O_3F_{17}SK$ requires C, 17·9; S, 5·9; K, 7·3%), m. p. 285°. Similarly prepared were the *sodium salt* (96%) (Found: C, 18·3; Na, 4·3. $C_8O_3F_{17}SNa$ requires C, 18·4; Na, 4·4%), m. p. 331—332°, the *barium salt* (92%) (Found: Ba, 12·0. $C_{16}O_6F_{34}S_2Ba$ requires Ba, 12·1%), m. p. >330°, and the *silver salt* (91%) (Found: Ag, 17·6. $C_8O_3F_{17}SAg$ requires Ag, 17·8%).

Potassium (Found: K, 16·1. $C_2O_3F_5SK$ requires K, 16·4%), sodium (Found: Na, 10·4. Calc. for $C_2O_3F_5SNa$: Na, 10·3%), *barium* (Found: Ba, 25·1. $C_4O_6F_{10}S_2Ba$ requires Ba, 25·6%), and silver (Found: Ag, 34·9. Calc. for $C_2O_3F_5SAg$: Ag, 35·2%) *perfluoroethanesulphonate* had m. p. 310°, 395°, >350°, and 287° respectively; they are appreciably soluble in ethanol, acetone, and water.

The perfluoroalkanesulphonic acids were prepared from their anhydrous potassium or barium salts by distillation from 100% sulphuric acid as described in Part IV.[1] Isolation of the more volatile acids was relatively easy, but more trouble was experienced with the higher acids, and careful fractionation was necessary to remove traces of sulphuric acid. The b. p.s of the *perfluoroalkanesulphonic acids* are given in Table 2.

Properties of the Perfluoroalkanesulphonic Acids.—The C_2—C_6 perfluoroalkanesulphonic acids, like trifluoromethanesulphonic acid, are colourless oils which fume in moist air and form solid *monohydrates*, *e.g.*, $C_2F_5{\cdot}SO_3H,H_2O$ (Found: equiv., 218), $C_3F_7{\cdot}SO_3H,H_2O$ (Found: equiv. 266), $C_5F_{11}{\cdot}SO_3H,H_2O$ (Found: equiv., 369) (equiv. required 218, 268, and 368 respectively).

The hydrates are reconverted into the parent sulphonic acids by distillation from sulphuric acid. Perfluoro-heptane- and -octane-sulphonic acid are solids with the typical waxy appearance of long-chain fluorocarbons and perfluoroalkanecarboxylic acids. The C_2 and C_3 acids are miscible with water in all proportions and are readily soluble in ethanol, ether, or acetone; there is immediate chemical reaction with ethanol and a slower reaction, with tar formation, with the last two solvents. The acids are only slightly soluble in benzene and carbon tetrachloride. The C_4, C_5, and C_6 acid show decreased solubility in water, ethanol, etc., and are substantially insoluble in carbon tetrachloride and benzene. The C_7 and C_8 acid have only moderate solubility in water and are markedly surface-active in that solvent.

TABLE 2.

Compound	Yield * (%)	B. p./mm.†	Found C (%)	Found Equiv.	Required C (%)	Required Equiv.
$C_2F_5{\cdot}SO_3H$	90	178°/760 87°/25	11·8	199	12·0	200
$C_3F_7{\cdot}SO_3H$	86	196°/760	14·5	248	14·4	250
$C_4F_9{\cdot}SO_3H$	88	210—212°/760 105°/22	16·1	299	16·0	300
$C_5F_{11}{\cdot}SO_3H$	83	224—226°/760 97°/4	16·9	350	17·1	350
$C_6F_{13}{\cdot}SO_3H$	80	238—239°/760 110°/5	17·8	398	18·0	400
$C_7F_{15}{\cdot}SO_3H$	77	247—249°/760 122°/5	18·6	446	18·7	450
$C_8F_{17}{\cdot}SO_3H$	70	258—260°/760 145°/10	19·2	499	19·2	500

* Yield from perfluoroalkanesulphonyl fluoride. † B. p.'s at atmospheric pressure are open to error, since partial conversion into perfluoroalkanesulphonic anhydrides occurs at these high temperatures.

The anhydrous acids can be heated to 400° in absence of air without appreciable breakdown. Moisture and air decrease the decomposition temperature of the acids. Thus, anhydrous perfluoro-octanesulphonic acid (2·7 g.), heated to 400° for 3 hr., liberated only a trace of fluoride, but a mixture of the acid (1·0 g.) and water (5·0 g.), heated at the same temperature for 3 hr., liberated 17% of the theoretical amount of fluoride; the aqueous solution of the acid was not decomposed at 280° in 20 hr. A mixture of perfluoro-octanesulphonic acid (1·0 g.) and concentrated nitric acid (5·0 ml.) failed to react or liberate fluoride at 160° during 12 hr.; the surface tension of nitric or sulphuric acid is reduced appreciably by the presence of the sulphonic acid. Pyrolysis of anhydrous perfluoropropanesulphonic acid (2·3 g.) in a platinum tube at 500° during 1 hr. gave perfluorohexane (19%), pentafluoropropionyl fluoride (23%), sulphur dioxide, carbonyl fluoride, and sulphuryl fluoride identified spectroscopically, and hydrogen fluoride and unchanged perfluoropropanesulphonic acid (29%).

Electrochemical fluorination of perfluoroethanesulphonic acid (4·7 g.) in anhydrous hydrogen fluoride (700 g.) at 5 v and 5·9 amp. gave perfluoroethanesulphonyl fluoride (56%), hexafluoroethane, carbon tetrafluoride, and sulphuryl fluoride; several explosions occurred during the electrolysis.

The perfluoroalkanesulphonic acids readily form salts by direct neutralisation. The sodium and potassium salts of the C_1, C_2, and C_3 acid are readily soluble in water, and solubility decreases steadily with increase in chain length: $C_5F_{11}{\cdot}SO_3K$, $C_5F_{11}{\cdot}SO_3Na$, $C_6F_{13}{\cdot}SO_3K$, and $C_6F_{13}{\cdot}SO_3Na$ give approximately 3—4%, 3%, 2%, and 1—2% solutions in water at 25°. Further increase in chain length lowers the solubility even further. The surface-active effect of the alkali-metal perfluoro-octanesulphonates is readily detectable even at these low concentrations in water.

Potassium perfluoro-octanesulphonate (0·9 g.), heated to 300° for 8 hr. with water (5 ml.), failed to liberate fluoride. A parallel reaction with 10% aqueous potassium hydroxide (5 ml.) showed that <2% of fluoride was liberated at 200° after 8 hr., and 8% at 270° after 8 hr.

Anhydrous potassium perfluoro-octanesulphonate (1·1 g.) was unaffected at 400° *in vacuo* for 5 hr.; liberation of fluoride was detected after a similar reaction at 430°. Anhydrous silver perfluoro-octanesulphonate (0·9 g.) became light brown at 400° *in vacuo* in the dark during 3 hr., but no volatile products were detected and only a weak fluoride test was given on treatment of the solid with water. In general the potassium sodium, lithium, or barium salts of the perfluoroalkanesulphonic acids can be heated to 350—400° without decomposition, and fluoride liberation occurs only above 420°.

Electrochemical Fluorination of n-*Octanesulphonyl Chloride.*—This reaction was investigated more fully. *n*-Octanesulphonyl chloride (30·5 g.) was added to the electrolysis cell to give a 5% solution by weight in hydrogen fluoride (580 g.). Electrolysis was started at 5·0 v and 3·8 amp., and the potential was maintained at 5·0 v throughout. The average current was 6·4 amp. After 44 hr. the current fell to 1·2 amp. and the electrolysis was complete. The product (excluding carbon tetrafluoride and hydrogen chloride) was examined in two portions: *A*, material (28·5 g.) of higher b. p. which collected as a lower layer and was drained from the cell by means of valve *Z*;[2] *B*, more volatile products (28 g.) which were swept from the cell by the hydrogen evolved and collected in traps at −78° and −183°.

Distillation of *A* gave fractions: (i) perfluoro-octane (5·7 g.), b. p. 103—110°, identified by means of its b. p. (103°)[4] and comparison of its infrared spectrum with that of a reference sample made by reaction of *n*-octane with cobalt trifluoride.[4] A small amount (*ca.* 0·3 g.) of perfluorohexanesulphonyl fluoride, b. p. 113°, contaminated the perfluoro-octane but was readily detected by means of the strong asymmetric and symmetric $-SO_2F$ stretching vibrations in the infrared spectrum. (ii) Perfluoro-octanesulphonyl fluoride (17·8 g., 25%) (Found: C, 19·1%; H, 0; *M*, 500, 496. Calc. for $C_8F_{18}O_2S$: C, 19·1%; H, 0; *M*, 502), b. p. 155°, n_D^{20} 1·302. (iii) Polymeric material (3·1 g.), b. p. 100—120°/14 mm. Infrared spectroscopy showed that carbon–hydrogen bonds were absent, and that chains of CF_2 groups were present; SO_2F groups were also present. (iv) A residue (0·9 g.) which solidified.

Distillation of *B in vacuo* gave a series of arbitrary fractions. Infrared spectroscopy, molecular-weight determination, and the b. p. range revealed the presence of (i) $CF_3{\cdot}[CF_2]_{4-6}{\cdot}SO_2F$ (2·2 g.), b. p. 80—98° and 105—140°, (ii) $CF_3{\cdot}[CF_2]_{1-3}{\cdot}SO_2F$ (2·1 g.), b. p. 0—80°, (iii) $CF_3{\cdot}SO_2F$ (0·7 g.), b. p. *ca.* −20°, (iv) perfluoroalkanecarboxylic acids $CF_3{\cdot}[CF_2]_{2-5}{\cdot}CO_2H$ (0·3 g.), originally mixed with fractions (i) and (ii), but easily detected by means of the infrared carbonyl stretching vibration and separated from the sulphonyl fluorides by their preferential solubility in ice-water (5 g.) (neutralisation of the aqueous extract with aqueous sodium hydroxide and freeze-drying of the solution gave the mixed sodium salts $CF_3{\cdot}[CF_2]_{2-5}{\cdot}CO_2Na$ identified by means of their infrared spectra), (v) perfluoro-octane (7·4 g.), b. p. 98—105°, identified by means of its infrared spectrum, (vi) perfluoro-butane (0·7 g.), -propane (0·7 g.), and -ethane (1·0 g.), as a mixture analysed spectroscopically, (vii) sulphuryl fluoride (4·0 g.), (viii) sulphur hexafluoride (1·3 g.), and (ix) unidentified material (5·9 g.), probably containing other fluorocarbons. Hydrogen chloride was removed from fractions (vi)—(ix) by washing with water before distillation.

Fractions *B*(i) and (ii) were examined further. Gas–liquid chromatography (5 mg. samples on to a 10′ column, 1/4″ int. diam., packed with 40—80 mesh Celite containing 30% of dinonyl phthalate; nitrogen flow 2 l./hr.; 20°) showed qualitatively that *B*(i) contained three components in approximately equal amounts. A 5 mg. portion of *B*(i) was then added to the column, and the three fractions were collected separately in traps cooled by liquid oxygen; this was repeated five times. The fractions were then identified by their b. p.s (isoteniscope) and molecular weights. *B*(ii) was similarly treated and shown to contain three components in approximately equal amounts. The results are shown in Table 3. The b. p.s and molecular weights should be compared with those of the analysed perfluoroalkanesulphonyl fluorides (Table 1).

TABLE 3.

Fraction	Wt. (g.)	$CF_3{\cdot}[CF_2]_n{\cdot}SO_2F$ *n*	B. p.	*M*	Fraction	Wt. (g.)	$CF_3{\cdot}[CF_2]_n{\cdot}SO_2F$ *n*	B. p.	*M*
B(i)	0·7	4	90°	345	*B*(ii)	0·7	1	8°	202
B(i)	0·7	5	115	399	*B*(ii)	0·7	2	35	244
B(i)	0·7	6	136	448	*B*(ii)	0·7	3	65	297

The above procedure thus shows that approximate yields of products from the electrochemical fluorination of octanesulphonyl chloride are $C_8F_{17}{\cdot}SO_2F$ (25%); $CF_3{\cdot}[CF_2]_{0-6}{\cdot}SO_2F$ (approx. 1·5% each; 9% total); $CF_3{\cdot}[CF_2]_{2-5}{\cdot}CO_2H$ (1%); C_8F_{18} (21%); C_4F_{10} (1%); C_3F_8

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[4] Haszeldine and Smith, *J.*, 1950, 2619, 2787, 3617; 1951, 603.

(1%); C_2F_6 (1·5%); SO_2F_2 (23%); SF_6 (6%). Carbon tetrafluoride and unidentified material account for most of the missing product.

Derivatives of Perfluoro-octanesulphonic Acid.—The inorganic salts have been described above. The S-*benzylthiuronium salt* (Found: C, 28·5; H, 1·9. $C_{16}H_{11}O_3N_2F_{17}S_2$ requires C, 28·8; H, 1·7%) has m. p. 112—113° (from aqueous ethanol).

(a) *Amides.* Perfluoro-octanesulphonyl fluoride (1·3 g.), an excess of anhydrous ammonia, and anhydrous ether (1 ml.) were allowed to warm from −40° to room temperature overnight. Anhydrous ether (15 ml.) was added to the white solid produced to dissolve the amide; the ammonium fluoride was filtered off, and the extraction was repeated with the solid obtained by evaporation of the filtrate to dryness *in vacuo*. The crude amide, m. p. 149—150°, was recrystallised three times from chloroform, to give perfluoro-octanesulphonamide (85%) (Found: C, 19·1; H, 0·5; N, 2·8. Calc. for $C_8H_2O_2NSF_{17}$: C, 19·2; H, 0·4; N, 2·8%), m. p. 152°. The amide has an acid reaction in aqueous solution and liberates carbon dioxide from concentrated aqueous sodium hydrogen carbonate.

Reaction of perfluoro-octanesulphonyl fluoride (1·0 g.) with a 10% excess of piperidine at 100° for 4 hr., followed by ether-extraction, etc., gave the *piperidide* (78%) (Found: C, 27·2; H, 1·8; N, 2·5. $C_{13}H_{10}O_2NSF_{17}$ requires C, 27·5; H, 1·7; N, 2·5%), m. p. 77° (from chloroform).

The *anilide* (Found: C, 29·1; H, 1·1; N, 2·5. $C_{14}H_6O_2NSF_{17}$ requires C, 29·2; H, 1·0; N, 2·4%), m. p. 102° (from benzene), was similarly prepared in 70% yield by reaction of perfluoro-octanesulphonyl fluoride (1·3 g.) with aniline at 100° for 8 hr.

(b) *Perfluoro-octanesulphonyl chloride.* The sulphonic acid (4·1 g.) and a three-fold excess of phosphorus pentachloride were heated *in vacuo* at 120° for 4 hr., then heated with a free flame to distil out the crude sulphonyl chloride, b. p. 180—210°. This was redistilled *in vacuo* then again at atmospheric pressure, to give *perfluoro-octanesulphonyl chloride* (78%) (Found: C, 18·4. $C_8O_2SClF_{17}$ requires C, 18·5%), b. p. 194—195°, n_D^{20} 1·324. When treated with anhydrous ammonia and ether it yields perfluoro-octanesulphonamide identical with the material described above. The anilide (see above) is more readily prepared by use of the sulphonyl chloride than by use of the sulphonyl fluoride.

(c) *Perfluoro-octanesulphonic anhydride.* Perfluoro-octanesulphonic acid (5·3 g.) was mixed with a six-fold excess of phosphoric oxide, kept at 100° for 4 hr., then heated *in vacuo* with a free flame to distil out the crude anhydride, b. p. 100—120°/*ca.* 10^{-3} mm.; cautious even heating must be applied to prevent extensive charring and frothing. Redistillation *in vacuo* and again at 760 mm. gave *perfluoro-octanesulphonic anhydride* (63%) (Found: C, 19·4%; equiv., 978, 979. $C_{16}O_5F_{34}S_2$ requires C, 19·5%; equiv., 982), b. p. 269—270°.

(d) *Perfluoro-octanesulphonyl fluoride.* The acid fluoride (1·8 g.), heated with water (3 ml.) at 180° in a sealed tube for 3 days, underwent 10% hydrolysis. In a parallel experiment with 50% aqueous dioxan as solvent, extensive reaction of the perfluoro-octanesulphonyl fluoride occurred, but this was accompanied by attack on the dioxan to give tarry products.

Since this work was completed some of the compounds described above have been reported by Brice and Trott,[2] in some instances without analytical data. In general, however, there is satifactory agreement with our results: $C_2F_5{\cdot}SO_2F$, b. p. 7·5°; $C_2F_5{\cdot}SO_3H$, b. p. 175°; $C_2F_5{\cdot}SO_3M$ (M = Na, Ag); $C_5F_{11}{\cdot}SO_2F$, b. p. 89—91°; $C_5F_{11}{\cdot}SO_3K$; $C_6F_{13}{\cdot}SO_2F$, b. p. 114—115°; $C_6F_{13}{\cdot}SO_3H$, b. p. 95/3·5 mm.; $C_8F_{17}{\cdot}SO_2F$, b. p. 154·5°/744 mm.; $C_8F_{17}{\cdot}SO_3K$; $(C_8F_{17}{\cdot}SO_2)_2O$, b. p. 260—275°; $C_8F_{17}{\cdot}SO_2Cl$, b. p. 194°; $C_8F_{17}{\cdot}SO_2{\cdot}NH_2$, m. p. 151—152°.

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