33. *Perfluoroalkyl Derivatives of Sulphur. Part IV.* Perfluoroalkanesulphonic Acids.*

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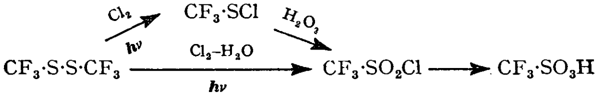
Electrolysis of methanesulphonyl fluoride or chloride in anhydrous hydrogen fluoride yields trifluoromethanesulphonyl fluoride almost quantitatively. The conversion of the last compound into $CF_3{\cdot}SO_2X$ ($X = NH_2$, NEt_2, OMe, and OEt) and $CF_3{\cdot}SO_3M$ ($M =$ K, Na, Ag, and $\frac{1}{2}$Ba) is described. The infrared spectra of compounds which contain $-SO_2-$ and $-SO_3^-$ groups are considered.

TRIFLUOROMETHANESULPHONIC ACID was first prepared by the route :

$$CS_2 \xrightarrow{IF_5} CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow[h\nu]{Hg} (CF_3{\cdot}S)_2Hg \xrightarrow{H_2O_2} CF_3{\cdot}SO_3H$$

and shown to be a very strong acid by conductivity measurements in aqueous and acetic acid solutions.[1] An alternative route from bistrifluoromethyl disulphide was described in Part II : [2]



$$CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow[h\nu]{Cl_2-H_2O} CF_3{\cdot}SO_2Cl \longrightarrow CF_3{\cdot}SO_3H$$

$$CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \xrightarrow[h\nu]{Cl_2} CF_3{\cdot}SCl \xrightarrow{H_2O_2} CF_3{\cdot}SO_2Cl$$

Although both these routes are potentially capable of extension to other perfluoroalkanesulphonic acids by use of disulphides prepared by the general reaction of perfluoroalkyl iodides with sulphur,[3] they suffer from the disadvantage that photochemical homolytic fission of the disulphide bond is slow. It was shown earlier[4] that perfluoroalkyl sulphur

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* Part III, *J.*, 1955, 3871.

[1] Haszeldine and Kidd, *J.*, 1954, 4228 (Part I); Haszeldine, *Angew. Chem.*, 1954, **66**, 693; Amer. Chem. Soc. Meetings, Chicago, 1953, and New York, 1954.

[2] Part II, Haszeldine and Kidd, *J.*, 1953, 2901.

[3] Haszeldine *et al.*, *J.*, 1952, 2198, 2549; 1953, 3219.

[4] Clifford, El-Shamy, Emeléus, and Haszeldine, *J.*, 1953, 2372.

compounds could be prepared by electrolysis of a solution of dimethyl sulphide or of carbon disulphide in anhydrous hydrogen fluoride, and a similar approach has now proved successful and given a convenient general route to perfluoroalkanesulphonic acids $CF_3\cdot[CF_2]_n\cdot SO_3H$. The present communication illustrates this for trifluoromethanesulphonic acid. It has been stated recently [5] that perfluoroalkanesulphonic acids have been prepared, but no details of technique, yield, or product have yet appeared.

Electrolysis of a solution of methanesulphonic acid in anhydrous hydrogen fluoride produces oxygen difluoride which, despite attempts to remove it in the absorption train, causes violent explosions which shatter parts of the apparatus. That production of oxygen difluoride is associated with the hydroxyl group of methanesulphonic acid, probably arising from water formed during fluorination of the acid, is shown by the fact that electrolysis of methanesulphonyl fluoride in anhydrous hydrogen fluoride proceeds smoothly and rapidly to give trifluoromethanesulphonyl fluoride in 96% yield. Methane sulphonyl fluoride was prepared for this purpose in high yield by reaction of the chloride with aqueous potassium hydrogen difluoride :

$$CH_3\cdot SO_3H \longrightarrow CH_3\cdot SO_2Cl \xrightarrow[\text{KHF}_2]{\text{Aq.}} CH_3\cdot SO_2F \xrightarrow[\text{in HF}]{\text{Electrol.}} CF_3\cdot SO_2F$$

Trifluoromethanesulphonyl fluoride (b. p. −21·7°) is swept out of the electrolysis cell by the hydrogen also produced, and the only by-products detected are fluoroform (1%) and carbon tetrafluoride.

The synthesis can be simplified still further by use of methanesulphonyl chloride rather than the fluoride, since electrolysis of this compound is also easily controlled and gives high yields of trifluoromethanesulphonyl fluoride; hydrogen chloride appears as additional product. The above reactions are of general application and make perfluoroalkanesulphonic acids available in quantity; subsequent communications will describe some of the properties of these extremely strong, surface-active acids.

The conductivity of methanesulphonyl chloride or fluoride in anhydrous hydrogen fluoride is doubtless due to formation of $CH_3\cdot\overset{+}{S}(:O)(OH)F$ and F^- ions. Electrolysis of the solution causes migration of the (solvated) fluoride ion to the anode where its discharge could be followed by one or both of two reactions. It could react with methanesulphonyl fluoride, adsorbed through the $-SO_2-$ group, on the surface of the anode. This does not mean that free fluorine atoms are necessarily produced, since a surface reaction could occur. Alternatively, discharge of fluoride could lead to formation of a higher fluoride of nickel containing ter- or quadri-valent nickel. If formed, this would undoubtedly be a powerful fluorinating agent which, like cobalt trifluoride, would replace hydrogen by fluorine in methanesulphonyl fluoride. The energy liberated during the last reaction would be dissipated efficiently in the liquid reaction medium and through the electrodes, and C–C, C–S, C–O, S–O, etc., fission, so prevalent in vapour-phase fluorination, could thus be substantially prevented.

Examination of the electrolysis cell after the preparation of trifluoromethanesulphonyl fluoride showed that a pale green friable solid had been deposited on the anodes, *i.e.*, on alternate electrodes. The cathodes remained bright and unattacked. The bottom of the cell also contained the pale green solid which had dropped from the anodes. The solid is mainly nickel difluoride, but is not analytically pure, and attempts to purify it failed; its formation on only the anodes supports the proposal of fluorination *via* nickel tri- or tetra-fluoride.

The relatively extensive breakdown caused when trifluoromethanesulphonic acid or moisture is present can be attributed to discharge of hydroxyl ions at the anodes, followed by formation of oxygen difluoride and oxidative attack on methanesulphonic acid or its fluoride present in solution or adsorbed on the anodes.

Trifluoromethanesulphonyl fluoride is hydrolysed by water only very slowly at room temperature, and only slowly by water at 100°. Methanesulphonyl fluoride is hydrolysed

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[5] Trott, Brice, Guenther, Severson, Coon, LaZerte, Nirschl, Danielson, Morin, and Pearlson, Amer. Chem. Soc. Meeting, New York, 1954.

much more rapidly (94% compared with 37% by water at 100° in 2 days.) Aqueous sodium or barium hydroxide causes complete hydrolysis within a few minutes to give the corresponding salts. Trifluoromethanesulphonic acid is stable to concentrated nitric acid at 150°.

Barium trifluoromethanesulphonate can easily be obtained pure and is a convenient starting point for the synthesis of other salts, since the barium can easily be removed as sulphate; potassium and silver trifluoromethanesulphonate were thus prepared. The melting points of the potassium, sodium, silver, and barium trifluoromethanesulphonate (230°, 248°, 356°, and >370°) should be compared with those of the corresponding methanesulphonates (>370°, 345°, 263°, and >360°).

Trifluoromethanesulphonyl fluoride is a convenient starting point for synthesis of derivatives of trifluoromethanesulphonic acid, *e.g.*, :

$$CF_3{\cdot}SO_2F \xrightarrow{R_2NH} CF_3{\cdot}SO_2{\cdot}NR_2 \quad (R = H \text{ or } Et)$$

Trifluoromethanesulphonamide, which sublimes *in vacuo*, is readily soluble in water. Its *NN*-diethyl derivative is a liquid which is only slightly soluble in water.

Trifluoromethanesulphonyl fluoride fails to react with ethanol at 100°. Excess of ethanolic sodium ethoxide converts it into sodium trifluoromethanesulphonate; ethyl ether is also formed, thus showing that ethyl trifluoromethanesulphonate reacts further :

$$CF_3{\cdot}SO_2F \xrightarrow{EtONa} CF_3{\cdot}SO_3Et \xrightarrow{EtONa} CF_3{\cdot}SO_3Na + Et_2O$$

The ethyl ester is best prepared by reaction of ethereal silver trifluoromethanesulphonate with ethyl iodide. The methyl ester was prepared by reaction of anhydrous silver trifluoromethanesulphonate with methyl iodide. The esters soon develop an acid reaction to litmus, although prolonged heating with water is necessary to achieve complete hydrolysis.

Infrared Spectra.—The spectra of compounds containing the $-SO_2-$, $-SO_3^-$, or $-SO_2-O-$ groups prepared during the present work are summarised and compared with other spectra in the Table.

The arguments in favour of the assignments of the symmetric (st.-s.) and asymmetric (st.-a.) stretching vibrations of the $-SO_2-$ group in sulphonyl halides have already been given.[2] In particular the 8·07 μ band was preferred for the st.-s. vibration in trifluoromethanesulphonyl chloride rather than that at 8·90 μ, since there is then a shift to shorter wavelength with increase in inductive effect of R in $R{\cdot}SO_2Cl$ along the series $R = CH_3$, CCl_3, or CF_3, as expected. A similar problem arises in the series $R{\cdot}SO_2F$, since trifluoromethanesulphonyl fluoride shows strong bands at 6·77 μ (st.-a.) and at 8·07 and 8·69 μ. Either of the last two bands could be assigned to the st.-s. vibration or to a C–F stretching vibration, and the fact that the 8·07 μ band is at precisely the same position as one in trifluoromethanesulphonyl chloride favours the assignment of this band in both compounds to the C–F vibration, with the 8·69 and 8·90 μ bands as st.-s. vibrations for $-SO_2F$ and $-SO_2Cl$ respectively, the shift to shorter wavelength being caused by the greater inductive effect of fluorine. A final decision cannot be made with the evidence currently available, but the 8·07 μ band in the trifluoromethanesulphonyl halides is given slight preference for the st.-s. vibration to maintain the sequence SO_2Cl_2 8·30, $CH_3{\cdot}SO_2Cl$ 8·07, $CF_3{\cdot}SO_2F$ 8·07, SO_2F_2 7·88 μ, and to maintain the difference in wavelength (1·0—1·4 μ) between the st.-a. and st.-s. wavelengths observed for all the other compounds which contain the $-SO_2-$ group.

Unsubstituted aliphatic sulphur compounds which contain the $-SO_2-$ group (*e.g.*, sulphonal) show the st.-a. and st.-s. vibrations at *ca.* 7·6 μ and 8·9 μ. Substitution of hydrogen by chlorine in the molecule causes a distinct shift to shorter wavelength. The aromatic sulphonyl fluorides show a further shift to shorter wavelength with absorption at *ca.* 7·10 and 8·25 μ. There is thus a shift to shorter wavelength of these vibrations in the series $R{\cdot}SO_2X$ with $X = C_{\text{aliph.}} > C_{\text{arom.}} > S > Cl > F$ and with R = Alkyl ~ Aryl > perchloroalkyl > perfluoroalkyl.

The st.-a. and the st.-s. vibrations of the nitro-group in *m*-nitrobenzenesulphonyl fluoride are clearly at 6·50 and 7·40 μ, regions which are free from strong bands in the

Compound *		C.S. no.	Asymmetric stretching μ	Symmetric stretching μ	Difference (st.-s.) — (st.-a.) μ
Acid halides and sulphones.					
SO_2F_2 [a]	(v)	—	6·66	7·88	1·22
$CF_3{\cdot}SO_2F$ [b]	(v)	283	6·77	8·07 or 8·69	1·30 or 1·92
$CF_3{\cdot}SO_2Cl$ [a]	(v)	—	6·95	8·07 or 8·90	1·12 or 1·95
SO_2Cl_2 [a]	(v)	—	6·96	8·30	1·34
$CH_3{\cdot}SO_2F$ [a]	(v)	284	6·90 6·97 }d	8·20	1·27
	(l)	285	7·20	8·30	1·10
$CCl_3{\cdot}SO_2Cl$ [a]	(v)	—	7·04	8·42	1·38
	(N)	—	7·12	8·45	1·33
$CH_3{\cdot}SO_2Cl$ [a, b]	(v)	286	7·15	8·42	1·27
	(l)	—	7·33	8·53	1·20
$Ph{\cdot}SO_2F$ [b]	(l)	287	7·10	8·27	1·17
$m\text{-}NO_2{\cdot}C_6H_4{\cdot}SO_2F$ [b]	(N)	288	7·07	8·26	1·19
$p\text{-}Cl{\cdot}C_6H_4{\cdot}SO_2F$ [b]	(N)	289	7·10	8·25	1·15
$(Et{\cdot}SO_2)_2CCl_2$ [b]	(N)	—	7·52	8·74	1·22
$(Et{\cdot}SO_2)_2CH_2$ [b]	(N)	—	7·55	8·90	1·35
$[(Et{\cdot}SO_2)_2CH]_2CH_2$ [b]	(N)	—	7·60	8·99	1·39
$(Et{\cdot}SO_2)_2CMe_2$ [b]	(N)	290	7·65	9·02 or 8·62	1·37 or 0·97
$(cyclo\text{-}C_6H_{11})_2SO_2$ [a]	(S)	—	7·62	8·85	1·23
Ph_2SO_2 [a]	(S)	—	7·48	8·59	1·11
Sulphonamides.					
$CF_3{\cdot}SO_2{\cdot}NH_2$ [b]	(N)	291	7·40	8·48	1·08
	(S)	—	7·07	8·72	1·65
$CF_3{\cdot}SO_2{\cdot}NEt_2$ [b]	(l)	292	7·23	8·45 (8·84)	1·22
	(S)	—	7·20	8·45 (8·84)	1·25
$CH_3{\cdot}SO_2{\cdot}NH_2$ [c]	(N)	—	7·49	8·55	1·06
	(S)	—	7·34	8·61	1·27
$Ph{\cdot}SO_2{\cdot}NH_2$ [c]	(N)	—	7·49	8·62	1·13
$CH_3{\cdot}SO_2{\cdot}NHMe$ [c]	(S)	—	7·50	8·62	1·12
Alkyl trifluoromethanesulphonates.					
$CF_3{\cdot}SO_2{\cdot}OMe$ [b]	(l)	293	7·08	8·30 or 8·74	1·22 or 1·66
	(v)	294	6·97	8·15 or 8·65	1·18 or 1·68
$CF_3{\cdot}SO_2{\cdot}OEt$ [b]	(l)	295	7·07	8·30 or 8·74	1·23 or 1·67
	(v)	296	6·97	8·17 or 8·65	1·20 or 1·68
Metal sulphonates.					
$CF_3{\cdot}SO_3Na$ [a]	(N)	137	7·82	9·60	1·78
$CF_3{\cdot}SO_3K$ [b]	(N)	297	7·95	9·70	1·75
$(CF_3{\cdot}SO_3)_2Ba$ [a, d]	(N)	139	7·92	9·62	1·70
$CF_3{\cdot}SO_3Ag$ [a]	(N)	138	7·90	9·75	1·85
$CH_3{\cdot}SO_3Na$ [a, e]	(N)	136	8·37	9·43	1·06
$CH_3{\cdot}SO_3K$ [b]	(N)	298	8·30	9·46	1·16
$(CH_3{\cdot}SO_3)_2Ba$ [b]	(N)	299	8·44	9·41	0·97
$CH_3{\cdot}SO_3Ag$ [b]	(N)	300	8·43	9·45 or 9·73	1·02 or 1·30
$[CH_2{\cdot}(SO_3Na)]_2$ [a]	(N)	—	8·45	9·60	1·15
$CH_2{:}CH{\cdot}SO_3Na$ [b]	(N)	—	8·45	9·55	1·10
$Et{\cdot}SO_3Na$ [f]		—	8·50	9·50	1·00
$Pr{\cdot}SO_3Na$ [f]		—	8·46	9·54	1·08
$Bu{\cdot}SO_3Na$ [f]		—	8·50	9·58	1·08
KSO_3F [b]		—	7·75	9·29	1·54

* v = vapour, l = liquid, N = Nujol mull, S = solution in CCl_4.

[a] Parts I and II, refs. 1 and 2. [b] Present work. [c] Baxter, Cymerman-Craig, and Willis, *J.*, 1955, 669. [d] The band at 7·85 μ reported in Parts I and II moves to 7·92 μ when the salt is recrystallised several times. [e] The band at 9·50 μ reported in Parts I and II moves to 9·43 μ when the salt is recrystallised. [f] Raman spectra : Houlton and Tartar, *J. Amer. Chem. Soc.*, 1938, **60**, 544.

spectrum of benzenesulphonyl fluoride. The C–H vibration in the arylsulphonyl fluorides appears at 6·88, 6·80, and 6·78 μ respectively for the two compounds shown in the Table.

The spectrum of solid trifluoromethanesulphonamide resembles that of methanesulphonamide. The $-SO_2-$ vibrations are well defined and lie at shorter wavelength for the fluoro-compound. The C–F stretching vibrations are at 8·11 and 8·69 μ. The N–H stretching vibrations are at 2·96 and 3·05 μ for solid trifluoromethanesulphonamide (cf. 2·99, 3·06, and 3·20 μ for $CH_3{\cdot}SO_2{\cdot}NH_2$ and 2·98 and 3·06 μ for $Ph{\cdot}SO_2{\cdot}NH_2$) and at 2·89, 2·99 μ for its solution in carbon tetrachloride (cf. 2·90 and 2·98 μ and 2·90 and 2·98 μ for similar solutions of $CH_3{\cdot}SO_2{\cdot}NH_2$ and $Ph{\cdot}SO_2{\cdot}NH_2$). The $-SO_2-$ vibrations for *NN*-diethyltrifluoromethanesulphonamide are scarcely changed at 7·20 and 8·45 or 8·84 μ for a solution in carbon tetrachloride compared with a spectrum of the liquid (see Table). Trifluoromethanesulphonamide is markedly associated in the solid, however, since the strong bands assigned to the $-SO_2-$ vibrations for the solid (7·40, 8·48 μ) shift to 7·07, 8·72 μ when the compound is dissolved in carbon tetrachloride. The last pair of bands must be assigned to the st.-a. and the st.-s. vibration of the unassociated amide. The st.-s. vibration for *NN*-diethyltrifluoromethanesulphonamide is thus probably at 8·84 rather than at 8·48 μ.

The st.-a. band in the alkyl trifluoromethanesulphonates is quite clear at *ca.* 7 μ, but more than one band could plausibly be assigned to the st.-s. vibration (see Table). Slight preference can be given to the band at lower wavelength in view of the assignments for trifluoromethanesulphonyl fluoride, but unambiguous distinction cannot yet be made. The liquid methyl ester shows a characteristic strong band at 12·45 and the ethyl ester one at 10·77 μ.

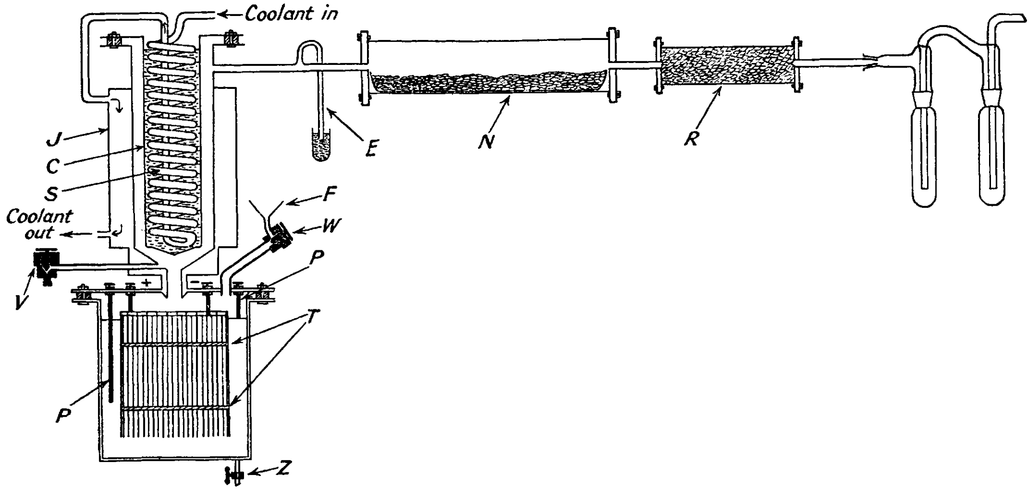
Further examples of metal sulphonates and trifluoromethanesulphonates enable a better comparison of infrared spectra to be made than was possible earlier.[1, 2] Metal alkanesulphonates absorb strongly at 8·4—8·6 μ (st.-a.) and 9·4—9·6 μ (st.-s.). Introduction of fluorine causes shift of the st.-a. vibration to shorter wavelength (7·8—7·95 μ) with hardly any change in the st.-s. vibration. The C–F stretching vibration in sodium, potassium, or silver trifluoromethanesulphonates lies near 8·5 μ.

The st.-a. and the st.-s. vibration of the $-SO_2-$ group in the $F{\cdot}SO_2{\cdot}O^-$ ion lie at 7·75 and 9·29 μ, and this fits well into the metal sulphonate series, since replacement of CF_3 in $CF_3{\cdot}SO_2{\cdot}O^-$ by the more electronegative fluorine would be expected to cause a shift to shorter wavelength.

EXPERIMENTAL

Apparatus.—The electrolytic cell is shown diagrammatically in the Figure, and is modelled on that described earlier,[4] with improvements resulting from prolonged operation of such cells. The cell body was a flanged nickel cylinder, 15 cm. long and 8 cm. in diameter, with silver-soldered joints, and with a small nickel valve (*Z*) for drainage. The 22 electrodes (each 12·7 × 6·3 × 0·17 cm.) served as alternate anodes and cathodes with a total surface area of *ca.* 3500 sq. cm. They were insulated from each other by Teflon spacers (*T*), and their leads, by which they were suspended from the nickel lid, were also insulated by Teflon bushings. A 3 mm. Teflon gasket clamped by 12 bolts rendered the flange leakproof. The two electrical probes (*P*) extended to two-thirds of the depth of the cell and to near the top of the electrode assembly respectively, and provided an easy method for determination of electrolyte level. In the centre of the lid was an exit tube leading to the efficient condenser (*C*), the cold finger of which was 16 cm. long,

Laboratory cell for electrochemical fluorination in anhydrous hydrogen fluoride.



4 cm. in diameter, and 5 mm. from the outer tube of the condenser. The efficiency of the condenser was greatly improved by a jacket (*J*) which cooled the outside of the outer tube of the condenser. Gas issuing from the cell had thus to pass up a 5 mm. annular tube cooled on both sides. The jacket (*J*) was welded to the outer tube of the condenser, and the aqueous glycol coolant was circulated rapidly at −5° by means of a powerful pump through the cooling spiral(*S*), then passed through *J*. The cold finger was filled with ethanol to provide contact between the cooling spiral and the inner wall of the condenser. The cell was filled with hydrogen fluoride (580 ml.) to the upper probe by means of the nickel valve *V*. The hydrogen fluoride was sufficiently anhydrous to render preliminary electrolysis unnecessary. Solute was added to the cell through a nickel valve (*W*) by means of the small nickel funnel (*F*).

A nickel tube led from the top of the condenser *via* a safety tube dipped in mercury (*E*) to a flanged copper cylindrical tube (*N*) (67 × 7 cm.) which contained a tray of sodium fluoride pellets (300 g.) to remove hydrogen fluoride swept through the condenser; the tube was heated to 60° to prevent possible condensation or adsorption of products. The cell gases then passed through a flanged cylindrical copper tube (*R*) (23 × 4 cm.) which contained 1 cm. squares of rubber sheet (100 g.) to absorb oxygen fluoride. The condensable products then collected in traps cooled at −78° and −183°, and the hydrogen and entrained carbon tetrafluoride were allowed to escape to atmosphere.

Methanesulphonyl Chloride.—A commercial sample was redistilled from phosphoric oxide (Found : S, 27·9. Calc. for CH_3O_2ClS : S, 27·7%).

Methanesulphonyl Fluoride.—Methanesulphonyl chloride (200 g.) was added with stirring to a suspension of potassium hydrogen difluoride (150 g.) in water (115 ml.) at 20°. After being stirred for 30 min. the mixture was steam-distilled, and the lower layer so obtained was separated, dried (Na_2SO_4), and distilled to give methanesulphonyl fluoride (144 g., 84%), b. p. 123—124° (Found : C, 12·7; H, 3·0. Calc. for CH_3O_2FS : C, 12·2; H, 3·1%). Davies and Dick [6] report b. p. 124·2° for a specimen prepared by prolonged reaction of methanesulphonyl chloride and zinc fluoride. The method used is based on that briefly reported in B.P. 628,796/1949.

Electrochemical Fluorination of Methanesulphonyl Fluoride.—In a typical experiment methanesulphonyl fluoride (30·0 g.) was added to anhydrous hydrogen fluoride (580 g.) in the cell to give a 5·2% solution by wt. Electrolysis was begun at 5 v and 6·4 amp., and during approx. 15 hr. the current fell steadily to 2·8 amp.; a voltage of 5 v was maintained during the electrolysis, and the average current was 5 amp. The current density was 0·0014 amp./sq. cm. Only a relatively small amount of hydrogen fluoride was swept from the cell and appeared in the absorption cylinder.

The product which passed through the traps cooled at −78° and −183° was mainly hydrogen, but infrared spectroscopic examination of the gas showed it to contain carbon tetrafluoride. The product which condensed at −78° was distilled; it was almost all *trifluoromethanesulphonyl fluoride* (42·5 g., 91%), b. p. −21·7° (Found: C, 8·0; S, 20·7%; *M*, 152. CO_2F_4S requires C, 7·9; S, 21·0%; *M*, 152), and for most purposes can be used without redistillation. The b. p. given above was calculated from the vapour-pressure curve determined for a redistilled sample over the temperature range −47° to −24° : $\log_{10} p$ (mm.) = 7·736 − 1221/T where T is in °K. The latent heat of vaporisation is 5590 cal./mole, and Trouton's constant is 22·2. Infrared spectroscopic examination before and after distillation showed that only minute amounts of impurities were present in the original material condensed at −78°.

Infrared spectroscopic examination of the material (3·2 g.; *M*, 128) which had condensed in the trap cooled at −183° showed that it was mainly trifluoromethanesulphonyl fluoride. This could be purified by distillation, or utilised by conversion into barium trifluoromethanesulphonate. Purification in this way showed that this crude material contained at least 66% of trifluoromethanesulphonyl fluoride; fluoroform (1% yield) was isolated as a minor product and was identified spectroscopically.

The total yield of trifluoromethanesulphonyl fluoride is thus 44·6 g., *i.e.*, 96%.

Electrochemical Fluorination of Methanesulphonyl Chloride.—The chloro-compound (25·0 g.), dissolved in 580 g. of anhydrous hydrogen fluoride (*i.e.*, 4·3% solution by wt.), was electrolysed under the conditions described above, for 19 hr. The initial current of 4·2 amp. fell to 2·2 amp. during this time, with the voltage maintained at 5 v.

The product which condensed in a trap cooled to −78° was distilled to give trifluoromethanesulphonyl fluoride (28·8 g., 87%), b. p. −21·7° (Found: *M*, 152). Infrared spectroscopy showed that it was identical with the compound described above, and in particular was free

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[6] Davies and Dick, *J.*, 1932, 483.

from trifluoromethanesulphonyl chloride. The small amount of impurity detected spectroscopically was the same as that obtained from methanesulphonyl fluoride.

Hydrolysis of Trifluoromethanesulphonyl Fluoride.—(a) *With water.* Trifluoromethanesulphonyl fluoride (0·994 g.) and water (5 ml.) were shaken vigorously in a sealed tube at 20° (48 hr.). Only 7% of the fluoride had then been hydrolysed, and spectroscopic examination of the volatile products revealed only starting material.

In a second experiment trifluoromethanesulphonyl fluoride (0·986 g.) and water (5 ml.), heated at 100° (48 hr.), gave unchanged starting material (63%) as gaseous product. The aqueous solution was neutralised with sodium carbonate and evaporated to dryness. The residue was extracted with dry acetone, and evaporation of the acetone solution, followed by crystallisation from acetone, gave sodium trifluoromethanesulphonate (0·370 g., 90% based on $CF_3{\cdot}SO_2F$ hydrolysed). The infrared spectrum of the salt was identical with that described in Part I.[1]

(b) *With sodium hydroxide.* Trifluoromethanesulphonyl fluoride (1·064 g.), sodium hydroxide (1 g.), and water (10 ml.) were shaken vigorously in a sealed tube at 20° (4 hr.). Quantitative hydrolysis occurred to give sodium trifluoromethanesulphonate (1·11 g., 92%), isolated by acetone extraction of the dried aqueous solution followed by recrystallisation from acetone.

(c) *With barium hydroxide.* Complete hydrolysis occurred when trifluoromethanesulphonyl fluoride (1·070 g.) was shaken with barium hydroxide octahydrate (4 g.) and water (50 ml.) at 20° (1 hr.). The aqueous solution was slightly acidified with dilute sulphuric acid to precipitate the excess of barium as sulphate, and the slight excess of sulphuric acid was removed by addition of an excess of solid barium carbonate. The solution was filtered, evaporated to dryness, then extracted with acetone to give barium trifluoromethanesulphonate (100%).

A portion (0·913 g.) of the product obtained in the trap at −183° during the electrochemical fluorination of methanesulphonyl fluoride, shaken with aqueous barium hydroxide (48 hr.), gave fluoroform (0·014 g., 1%) as the main residual volatile product, and barium trifluoromethanesulphonate (0·87 g., 66%), isolated as above, in the aqueous solution.

Hydrolysis of Methanesulphonyl Fluoride.—(a) *With water.* Methanesulphonyl fluoride (0·946 g.) and water (5 ml.), heated at 100° (48 hr.) under conditions similar to those used with trifluoromethanesulphonyl fluoride (above), gave unchanged methanesulphonyl fluoride (0·054 g., 6%) and methanesulphonic acid (94%).

(b) *With barium hydroxide.* Methanesulphonyl fluoride (1·080 g.), barium hydroxide octahydrate (4 g.), and water (50 ml.) were shaken at room temperature (1 hr.) under the conditions used for trifluoromethanesulphonyl fluoride (above). The fluoride was completely converted into barium methanesulphonate.

Derivatives of Trifluoromethanesulphonic Acid.—(a) *Salts.* The sodium salt, prepared as above, recrystallised from acetone and dried to constant weight *in vacuo* at 140°, had m. p. 248°. The barium salt, similarly treated, had m. p. >370°.

Barium trifluoromethanesulphonate (0·77 g.) was dissolved in water (5 ml.), and treated with dilute sulphuric acid. The filtered barium-free solution was then neutralised with potassium carbonate and evaporated to dryness, and the residual solid was extracted with acetone, evaporation of which gave *potassium trifluoromethanesulphonate* (0·56 g., 84%) (Found : K, 20·7. CO_3F_3SK requires K, 20·8%); recrystallised from acetone and dried at 140°/10^{-3} mm., it had m. p. 230°.

To a solution of barium trifluoromethanesulphonate (0·62 g.) in water (5 ml.) was added dilute sulphuric acid to precipitate the barium. The filtered solution was neutralised with silver carbonate, then evaporated to dryness; the residual silver trifluoromethanesulphonate (0·69 g., 95%), recrystallised from benzene–carbon tetrachloride or ether–carbon tetrachloride, had m. p. 356°.

The sodium, barium, and silver salts were spectroscopically identical with those described in Part I.[1]

(b) NN-*Diethyltrifluoromethanesulphonamide.* Trifluoromethanesulphonyl fluoride (3·0 g.) and anhydrous diethylamine (4·2 g.) reacted immediately, a solid being deposited; after being kept overnight in a sealed tube the products were treated with water (25 ml.) which caused separation of a lower layer. This and the ethereal extract of the aqueous layer were dried (Na_2SO_4) then distilled, to give NN-*diethyltrifluoromethanesulphonamide* (3·3 g., 83%), b. p. 55°/7 mm. (Found : C, 29·4; H, 5·2; N, 7·1. $C_5H_{10}O_2NF_3S$ requires C, 29·3; H, 4·9; N, 6·8%). The amide is soluble in the common organic solvents but not in water.

(c) *Trifluoromethanesulphonamide.* Anhydrous ammonia (0·88 g.) and trifluoromethanesulphonyl fluoride (3·10 g.) reacted immediately in a sealed tube, with deposition of solid.

Extraction with chloroform and evaporation of the extracts gave *trifluoromethanesulphonamide* (2·37 g., 78%), m. p. (after sublimation *in vacuo*) 119° (Found : C, 8·1; H, 1·3; N, 9·7. $CH_2O_2NF_3S$ requires C, 8·1; H, 1·3; N, 9·4%). The amide dissolves in water.

(d) *Ethyl trifluoromethanesulphonate.* Trifluoromethanesulphonyl fluoride (5·0 g.) and anhydrous ethanol (5 ml.) formed two layers and failed to react in a sealed tube at 100° during 24 hr.

Trifluoromethanesulphonyl fluoride (9·84 g.), sodium (3·0 g.), and anhydrous ethanol (50 ml.) reacted exothermically in a sealed tube at room temperature (1 hr.). Ethyl ether and excess of ethanol were the only volatile products obtained when the solution was evaporated. Extraction of the residual solid with acetone, followed by evaporation of the acetone, gave sodium trifluoromethanesulphonate (9·30 g., 84%).

Silver trifluoromethanesulphonate (10·0 g.) was suspended in anhydrous ether (50 ml.) and stirred whilst ethyl iodide (8·0 g.) was added. Immediate precipitation of silver iodide occurred and the reaction was completed by heating under reflux (30 min.). The ethereal solution was decanted from the silver iodide (100%), and distillation of the ethereal solution gave *ethyl trifluoromethanesulphonate* (5·1 g., 74%), b. p. 115° (Found : C, 19·9; H, 2·7. $C_3H_5O_3F_3S$ requires C, 20·2; H, 2·8%). The ester reacted only slowly with water or aqueous alkali but rapidly turned blue litmus red.

(e) *Methyl trifluoromethanesulphonate.* Silver trifluoromethanesulphonate (12·1 g.) was shaken whilst methyl iodide (6·3 g.) was added. When the vigorous reaction subsided, the volatile products were distilled *in vacuo* from the silver iodide produced, then redistilled to give *methyl trifluoromethanesulphonate* (4·4 g., 69%), b. p. 99° (Found : C, 14·8; H, 2·1. $C_2H_3O_3F_3S$ requires C, 14·6; H, 1·8%).

Stability of Trifluoromethanesulphonic Acid to Nitric Acid.—Sodium trifluoromethanesulphonate (0·84 g.), heated with concentrated nitric acid (5 ml.) in a sealed tube at 150° (48 hr.), liberated not even a trace of fluoride ion. Neutralisation with sodium carbonate followed by acetone extraction of the solid from the evaporated solution gave sodium trifluoromethanesulphonate (82%).

Salts of Methanesulphonic Acid.—Sodium, potassium, barium, and silver methanesulphonates were prepared from the acid by neutralisation with the corresponding carbonate. They were recrystallised from aqueous ethanol or aqueous acetone and dried to constant weight *in vacuo* at 140° (90° for the silver salt). Spectroscopic examination then showed them to be free from water. The following m. p.s were determined: $CH_3\cdot SO_3Na$ 345°, $CH_3\cdot SO_3K$ >360°, $(CH_3\cdot SO_3)_2Ba$ >360°, $CH_3\cdot SO_3Ag$ 263°.

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