500. *Fluorinated Sulphonic Acids. Part I. Perfluoro-methane-, -octane-, and -decane-sulphonic Acids and their Simple Derivatives.*

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Perfluoro-methane-, -*n*-octane-, and -*n*-decane-sulphonyl fluoride were prepared from alkanesulphonyl chlorides by electrochemical fluorination.[1, 2] Various derivatives of the fluorocarbonsulphonic acids were made. The long-chain acids were highly surface-active.

RECENT patents assigned to the Minnesota Mining and Manufacturing Company [1] on the preparation of perfluoroalkanesulphonyl fluorides prompt us to publish some of our preliminary, very similar, results. The present paper describes the preparation, by the well-known electrochemical procedure of Simons,[2] of perfluoro-methane-, -*n*-octane-, and -*n*-decane-sulphonyl fluoride from the corresponding alkanesulphonyl chloride (which was made from the alkyl bromide *via* the sodium alkanesulphonate). The acid fluorides were then converted into simple derivatives of the fluorocarbonsulphonic acids.

Trifluoromethanesulphonyl fluoride was obtained in 50—60% yield (cf. Gramstad and Haszeldine [3]). Yields of perfluoro-*n*-octane- and -*n*-decane-sulphonyl fluoride were lower (12—15%) and large amounts of sulphur-free material, probably perfluoro-*n*-octane and perfluoro-*n*-decane, were obtained, together with smaller amounts of shorter-chain fluorocarbons and some polymeric residue. It appeared that the chlorine atoms of the sulphonyl chlorides were displaced electrolytically, since no apparent reaction took place with anhydrous hydrofluoric acid alone but a chlorine-containing gas was obtained during the fluorination of methanesulphonyl chloride. The yields of the fluorocarbonsulphonyl fluorides could probably be increased by more detailed individual studies.

Various salts were prepared from these acid fluorides by treatment with the appropriate aqueous metal hydroxide. The sodium and potassium salts of the C_8 and C_{10} acids were almost insoluble in water. However, though salts of strong acids, they were rather more soluble in ethanol than in the more highly ionising solvent, water. They differed from the corresponding perfluorocarboxylates in their much greater thermal stabilities. They melted below 330°, and were stable for long periods at 300° but decomposed in air at 350° (over a period of days) with the formation of sulphate ion: perfluorocarboxylic salts, on the other hand, decompose rapidly at about 250° to give olefins.[4]

The free C_1 acid [5, 6] formed a hydrate sufficiently stable to be distilled from concentrated sulphuric acid. With phosphoric oxide the anhydrous acid gave the anhydride which decomposed partly after a few days, sulphur dioxide being evolved.

The C_8 and C_{10} acids were not isolated completely pure by distillation of mixtures of their salts with sulphuric acid because of their somewhat comparable volatilities. An aqueous solution of the C_{10} acid was prepared by treatment of a saturated solution of the sodium salt with an ion-exchange resin (Zeo-Karb 225). The free acid was converted, *in situ*, into its anilinium salt. An attempt to hydrolyse the C_8 sulphonyl fluoride with water at 160° for 60 hr. failed, no reaction taking place. Under milder conditions however, the C_1 fluoride was completely hydrolysed to the free acid. This difference in reactivity may have been due to the greater insolubility of the C_8 fluoride in water. These fluorosulphonic acids and their salts were very stable to acidic and to alkaline hydrolysis, and to strong oxidising agents. The perfluoro-*n*-octane- and -*n*-decane-sulphonic acids and

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[1] Brice and Trott, U.S.P. 2,732,398; B.P. 758,467.

[2] Simons, "Fluorine Chemistry," Academic Press Inc., New York, 1950, Vol. I, p. 414; 1954, Vol. II, p. 340.

[3] Gramstad and Haszeldine, *J.*, 1956, 173.

[4] Hals, Reid, and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4054.

[5] Haszeldine and Kidd, *J.*, 1954, 4228.

[6] *Idem*, *J.*, 1955, 2901.

their salts are very good surface-active agents, and aqueous solutions containing only small amounts foam readily.

Trifluoromethanesulphonanilide was prepared by the action of aniline on the anhydride or the acid chloride. This anilide and the analogous amide had remarkable acidic properties; because of the powerful negative inductive effect of the trifluoromethanesulphonyl group, and possibly the negative hyperconjugative effect of the trifluoromethyl group, they were stronger acids than carbonic acid, and on titration with alkali gave end-points between pH 8·5 and 9·5 (in 0·006N-solution).

The anilides of the C_8 and the C_{10} acid were prepared from the acid fluorides and anilinomagnesium iodide in ether. Orthodox methods failed; for example, no reactions took place between aniline alone or aniline in pyridine and the acid fluorides, owing partly perhaps to the immiscibility of the reactants. The C_{10} anilide was not hydrolysed appreciably by boiling 5N-sodium hydroxide or by boiling 6N-hydrochloric acid. This stability reflects the behaviour of hydrocarbonsulphonanilides; fluorocarboncarboxyanilides are easily hydrolysed.

With sodium borohydride the C_8 and the C_{10} acid fluoride were reduced to the sulphinic acids, which were isolated as their *S*-benzylthiuronium salts. This appears to provide a new method of preparation of sulphinic acids.

EXPERIMENTAL

Apparatus.—The electrolytic cell was similar to that described by Simons.[2] The cell body was cylindrical and made of heavy gauge nickel (9 in. long × $3\frac{3}{8}$ in. diam. × $\frac{3}{16}$ in. thick) with a flange. The lid ($5\frac{3}{4}$ in. diam. × $\frac{1}{4}$ in. thick) was sealed with a Neoprene gasket and had two openings (one to introduce hydrofluoric acid and the starting material, and the other which led to the reflux condenser). It also carried the electrode assembly, which consisted of a vertical pack of alternate cathodes and slightly smaller anodes all made of nickel plate and mounted on two Polythene rods. The whole assembly was circular in cross-section with a total anode area of 350 sq. in. The cathode lead was connected directly to the lid, and hence the cell body, which was thus itself part of the cathode; the anode lead was insulated from the lid with a "Fluon" washer. The capacity of the cell with this electrode assembly in place was about 1 l. The cell itself was seated in a bath containing 30% ethylene glycol solution which was cooled by a standard refrigerator unit using "Freon 12" as the working liquid. The refrigerator coils first cooled the reflux condenser [a straight copper tube (2 ft. × $\frac{1}{2}$ in. int. diam.) in a vessel containing 30% glycol solution] and then the cell cooling-bath. The effluent gases passed up the condenser, and then into two traps kept at $-78°$. During a fluorination, the condenser was kept at about $-12°$ and the cooling-bath at about $-3°$, but, even so, some hydrogen fluoride was invariably carried into the first receiver; this necessitated periodic additions of anhydrous hydrofluoric acid to the cell in order to keep up the liquid level (any large fall caused mild explosions).

Trifluoromethanesulphonyl fluoride was prepared essentially as described by others.[1, 3] Methanesulphonyl chloride (100 g.) was electrolysed for 14 hr. at 18 amp. and 4·5 v. The reaction could be run continuously since the product distilled from the cell as it was formed.

Hydrolysis of Trifluoromethanesulphonyl Fluoride.—(*a*) The acid fluoride (58·5 g.), hydrated barium hydroxide (200 g.), and ice (100 g.), all cooled in liquid air, were introduced into a cooled ($-78°$) autoclave which was then sealed and heated at 90° for 12 hr. After acidification with sulphuric acid, neutralisation with barium carbonate, and filtration, the solution was evaporated *in vacuo* and the residue extracted with hot acetone. Evaporation of the filtered extracts left barium trifluoromethanesulphonate (78 g.) (Found: Ba, 31·1. Calc. for $C_2O_6S_2F_6Ba$: Ba, 31·5%).

When cold aqueous *S*-benzylthiuronium chloride was added to a solution of the barium salt, there was precipitated *S-benzylthiuronium trifluoromethanesulphonate*, m. p. 138—139° (from water) (Found: C, 34·4; H, 3·4. $C_9H_{11}O_3N_2S_2F_3$ requires C, 34·2; H, 3·5%).

(*b*) The acid fluoride (*ca.* 17 g.) was heated with water (60 ml.) in a sealed tube at 140° until two liquid layers were no longer present (40 hr.). Neutralisation with barium carbonate and treatment as in (*a*) gave barium trifluoromethanesulphonate (21·5 g.).

Trifluoromethanesulphonic Acid Derivatives.—(*a*) On being kept, the acid [5] formed, very readily, a solid *monohydrate*, b. p. 120°/15 mm., m. p. *ca.* 45° (Found: equiv., 167. $CH_3O_4SF_3$ requires equiv., 168), which was white, crystalline, and very deliquescent, and could be distilled unchanged from concentrated sulphuric acid. It had infrared absorption peaks at 1037, 1180, and 1270 cm.$^{-1}$, in agreement with those found for the anhydrous acid.[5] The anhydrous and hydrated acids both gave, in the usual way (by precipitation from ethereal solutions), the same *anilinium salt*, m. p. 267—268° (from acetone–chloroform) (Found: C, 35·0; H, 3·2. $C_7H_8O_3NSF_3$ requires C, 34·6; H, 3·3%).

(*b*) The anhydrous acid (11·5 g.) and phosphoric oxide (11·5 g.) were mixed and kept at room temperature for 1 hr., and then the volatile products were distilled through a short Vigreux column to give trifluoromethanesulphonic anhydride (7·7 g.), b. p. 78—80° (Found: equiv., 286. Calc. for $C_2O_5S_2F_6$: equiv., 282). The compound was a mobile, hygroscopic liquid, readily hydrolysed by water, and had decomposed appreciably after being kept for a few days, with evolution of sulphur dioxide and formation of a brown, viscous, immiscible liquid. The anhydride was initially immiscible with aromatic hydrocarbons, ketones, and most carboxylic acids, but miscibility was gradually achieved in every case with the formation of dark-coloured tars.

(*c*) The anhydride (0·70 g.) was added to concentrated aqueous ammonia (30 ml.). After 12 hr. at 0° the solution was acidified and extracted with ether, and the extracts were dried ($MgSO_4$) and evaporated to leave a white residue which was sublimed at 100°/0·1 mm. to give trifluoromethanesulphonamide (0·25 g.), m. p. 117—118° (softens 112°) [cited value,[3] 119°] (Found: C, 8·0; H, 1·3%; equiv., 147. Calc. for $CH_2O_2NSF_3$: C, 8·05; H, 1·35%; equiv., 149). The equivalent weight was determined by electrometric titration of aqueous solutions (approx. 0·006N-amide against 0·05N-sodium hydroxide), the end-point lying between pH 8·5 and 9·5. An aqueous solution of the amide liberated carbon dioxide from saturated sodium hydrogen carbonate solution.

(*d*) A mixture of the acid chloride [5] (0·70 g.), aniline (1 ml.), pyridine (5 ml.), and dry ether (50 ml.) was kept at 13° for 20 hr. After being washed with dilute hydrochloric acid and water and dried ($MgSO_4$), this solution was evaporated to leave a residue which afforded trifluoromethanesulphonanilide (0·80 g.), m. p. 66—67° [from light petroleum (b. p. 40—60°)] (Found: C, 37·5; H, 2·7%; equiv., 225. Calc. for $C_7H_6O_2NSF_3$: C, 37·3; H, 2·7%; equiv., 225). The electrometric titration, done as before, showed an end-point between pH 8·5 and 9·5. The compound also liberated carbon dioxide from saturated sodium hydrogen carbonate solution.

(*e*) Treatment of the anhydride (1·0 g.) in ether with an excess of aniline gave an immediate precipitate of the anilinium salt which had m. p. 267—268°: the filtrate was treated as in (*d*) to give the anilide (0·52 g.), m. p. and mixed m. p. 66—67°.

Compounds mentioned previously [1] were the anhydride (b. p. 80·5°), the anilide (m. p. 65—66°), and the anilinium salt (m. p. 250—255°), no analyses being given.

n-*Octane- and* n-*Decane-sulphonyl Chloride*.—The parent alkyl bromide was treated [7] with concentrated aqueous sodium sulphite solution in an autoclave at 200°. The resulting sodium alkanesulphonate was filtered off, dried, and mixed at room temperature with an excess (2 mol.) of phosphorus pentachloride.[8] Heat was evolved, and after 2 hr. the liquid mixture was poured into ice-water, and the oil separated, washed, and dried. *n*-Octanesulphonyl chloride (yield 75—80%) had b. p. 90—91°/0·02 mm.; with concentrated aqueous ammonia it gave *n*-octanesulphonamide, m. p. 69—70° (from aqueous ethanol) (cited value,[9] 70—70·5°). n-*Decanesulphonyl chloride* (yield 75—80%) had m. p. 34° (from benzene) (Found: C, 49·7; H, 8·8. $C_{10}H_{21}O_2SCl$ requires C, 49·9; H, 8·8%). With aniline in pyridine it gave n-*decanesulphonanilide*, m. p. 51—52° (from aqueous ethanol) (Found: C, 64·4; H, 9·1. $C_{16}H_{27}O_2NS$ requires C, 64·6; H, 9·15%).

Preparation of Perfluoro-n-*octanesulphonyl Fluoride*.—In a typical experiment, *n*-octanesulphonyl chloride (205 g.) was fluorinated for 190 hr. at 14 amp. and 5·0 v. The cell was drained and the heavier layer was separated from the hydrofluoric acid, washed with water, and dried ($MgSO_4$). The product (223 g.) was fractionally distilled through a 1 ft. column packed with Dixon gauze spirals. Boiling commenced at 29° and small fractions were obtained at 57° and 82°; these sulphur-free fractions were probably perfluoro-*n*-hexane and perfluoro-*n*-heptane, respectively. A large fraction (41 g.), b. p. 103°, was probably perfluoro-*n*-octane.

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[7] Reed and Tartar, *J. Amer. Chem. Soc.*, 1935, **57**, 570.

[8] Carius, *Annalen*, 1860, **114**, 140.

[9] Kharasch and Mosher, *J. Org. Chem.*, 1952, **17**, 453.

Analytical gas chromatography on dinonyl phthalate–kieselguhr (1 : 2) at 80° with a rate of flow of nitrogen of 0·8 l./hr. showed that the combined sulphur-free distillates (64 g.) contained at least four compounds, probably the normal C_5, C_6, C_7, and C_8 fluorocarbons, the last being present in largest amount.

Continued fractionation gave perfluoro-*n*-octanesulphonyl fluoride (72 g.), b. p. 154°, n_D^{14} 1·3037 (Found : C, 19·2; F, 67·7. Calc. for $C_8O_2SF_{18}$: C, 19·1; F, 68·1%) (cited values [1] were b. p. 154·5° and n_D^{25} 1·2993 for this compound). The fractionation residue (33 g.) was a viscous, dark, fuming liquid, which was probably polymeric.

*Salts of Perfluoro-*n*-octanesulphonic Acid.*—The acid fluoride (5·0 g.) was treated with 10N-sodium hydroxide for 17 hr. at 15°, with occasional stirring. The precipitate was filtered off and recrystallised from ethanol to give *sodium perfluoro-*n*-octanesulphonate* (4·3 g.), m. p. 327—330° (Found: C, 18·1; F, 61·5. $C_8O_3SF_{17}Na$ requires C, 18·4; F, 61·9%). The potassium salt, prepared in the same way, had m. p. 277—280° (Found : C, 17·9; F, 60·1. Calc. for $C_8O_3SF_{17}K$: C, 17·85; F, 60·0%). Both these salts decomposed at 350° over a period of several days with the formation of sulphate ion. Saturated aqueous solutions formed very stable foams which could not be dispersed with either octyl alcohol or a Silicone anti-foaming preparation.

The S-*benzylthiuronium salt* was prepared from a hot aqueous solution of the sodium salt. Recrystallised from aqueous ethanol, it had m. p. 111—112° (Found : C, 28·7; H, 1·8; F, 48·0. $C_{16}H_{11}O_3N_2S_2F_{17}$ requires C, 28·8; H, 1·7; F, 48·5%).

*Preparation of Perfluoro-*n*-decanesulphonyl Fluoride.*—*n*-Decanesulphonyl chloride (160 g.) was electrolysed, as before, at 15 amp. and 5·2 v for 129 hr. Fractionation of the product (263 g.), initially at atmospheric pressure (for b. p.s < 135°) and finally at 27 mm., gave sulphur-free material (106 g.) which appeared to contain at least five components, probably the normal C_6, C_7, C_8, C_9, and C_{10} fluorocarbons, and then perfluoro-*n*-decanesulphonyl fluoride (48 g.), b. p. 90—91°/27 mm., which crystallised. After recrystallisation from ether–ethanol the pure *fluoride* had m. p. 57—59° (Found : C, 19·8; F, 69·2. $C_{10}O_2SF_{22}$ requires C, 19·9; F, 69·4%). The fractionation residue (47 g.) was a dark viscous tar.

*Salts of Perfluoro-*n*-decanesulphonic Acid.*—The *sodium salt*, m. p. 322—325° (Found : C, 19·0; F, 63·7. $C_{10}O_3SF_{21}Na$ requires C, 19·3; F, 64·1%), the *potassium salt*, m. p. 280—287° (Found: C, 18·8; F, 62·0. $C_{10}O_3SF_{21}K$ requires C, 18·8; F, 62·5%), and the S-*benzylthiuronium salt*, m. p. 134—135° (Found : C, 28·2; H, 1·4. $C_{18}H_{11}O_3N_2S_2F_{21}$ requires C, 28·2; H, 1·4%), were prepared as described above. The sodium and potassium salts were almost insoluble in cold ethanol (*ca.* 0·6%), and even less soluble in cold water (*ca.* 0·2%), as were the C_8 salts. They were also excellent foaming agents, and had thermal stabilities similar to those of the C_8 salts.

A solution of the sodium salt (2·0 g.) in water (4 l.) was passed down a column of ion-exchange resin (Zeo-Karb 225). The aqueous effluent was concentrated to 50 ml., aniline (5 ml.) was added, and the precipitate was filtered off and recrystallised from aqueous ethanol to give *anilinium perfluoro-*n*-decanesulphonate* (1·6 g.), m. p. 213—216° (decomp.) (Found : C, 28·1; H, 1·0; F, 57·3. $C_{16}H_8O_3NSF_{21}$ requires C, 27·7; H, 1·2; F, 57·55%).

Preparation of C_8 *and* C_{10} *Anilides.*—The C_8 acid fluoride (5·0 g.) was added to a solution of anilinomagnesium iodide [made from ethyl iodide (3·5 ml.), magnesium (1·0 g.), and aniline (4 ml.) in ether (100 ml.)] and the mixture was refluxed for 1 hr. Dilute sulphuric acid was added and the ether layer was separated, dried ($MgSO_4$), and evaporated. Recrystallisation of the residue from benzene afforded *perfluoro-*n*-octanesulphonanilide* (2·9 g.), m. p. 101—102° (Found : C, 29·5; H, 1·3; F, 56·2. $C_{14}H_6O_2NSF_{17}$ requires C, 29·2; H, 1·05; F, 56·15%).

In the same way the C_{10} acid fluoride (2·0 g.) afforded the corresponding *anilide* (1·3 g.), m. p. 117—118° [from light petroleum (b. p. 60—80°)] (Found : C, 28·3; H, 1·0; F, 59·6. $C_{16}H_6O_2NSF_{21}$ requires C, 28·5; H, 0·9; F, 59·1%). After being refluxed for 6 hr. with 5N-sodium hydroxide (100 ml.) this compound (0·20 g.) was recovered, by acidification of the solution and extraction with ether, in almost quantitative yield (0·19 g.). With boiling 6N-hydrochloric acid the compound slowly distilled from the solution in the steam and was deposited unchanged in the condenser.

Preparation of Sulphinic Acids.—To a stirred solution of the C_8 acid fluoride (1·0 g.) in ether (75 ml.), a solution of sodium borohydride (0·50 g.) in ethanol (75 ml.) was added dropwise. A vigorous reaction took place with the evolution of gaseous products. After 15 hr. at 16°, acetone (5 ml.) was added to destroy the excess of sodium borohydride. After a further 2 hr.

at room temperature, the solution was concentrated *in vacuo* at 15° to 25 ml. Water (25 ml.) was added, followed by sufficient 2N-hydrochloric acid to bring the pH to 7. A saturated aqueous solution of *S*-benzylthiuronium chloride was added and the resulting precipitate was filtered off and recrystallised twice from aqueous ethanol to give S-*benzylthiuronium perfluoro*-n-*octanesulphinate* (0·9 g.), m. p. 129—130° (Found: C, 29·9; H, 1·4; F, 50·2. $C_{16}H_{11}O_2N_2S_2F_{17}$ requires C, 29·55; H, 1·7; F, 49·7%).

In the same way the C_{10} acid fluoride (1·0 g.) gave S-*benzylthiuronium perfluoro*-n-*decanesulphinate* (1·1 g.), m. p. 140—141°, depressed to 119—123° on admixture with the corresponding sulphonic acid derivative (Found: C, 28·9; H, 1·6; F, 54·0. $C_{18}H_{11}O_2N_2S_2F_{21}$ requires C, 28·8; H, 1·5; F, 53·2%).

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