Perfluoroalkyl Derivatives of Sulphur. Part I. Trifluoromethanesulphonic Acid.*

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Oxidation of bis(trifluoromethylthio)mercury yields trifluoromethanesulphonic acid, isolated by treatment of its barium salt with sulphuric acid. Trifluoromethanesulphonic acid is relatively volatile, and is a strong acid as shown by conductivity measurements; it liberates hydrogen chloride from sodium chloride. Silver trifluoromethanesulphonate is soluble in benzene, like other silver salts of strong acids. Characteristic infra-red absorption bands have been assigned to the $CF_3\cdot SO_3^-$ group.

EARLIER studies * have shown that bistrifluoromethyl disulphide can be prepared in good yield by interaction of trifluoroiodomethane and sulphur or, more conveniently, of iodine pentafluoride and carbon disulphide and that it yields bis(trifluoromethylthio)mercury and thence trifluoromethanethiol and trifluoromethanesulphenyl chloride. The present paper concerns trifluoromethanesulphonic acid.

Few of the methods of preparation of alkane- or arene-sulphonic acids can be applied to the synthesis of perfluoroalkanesulphonic acids : *e.g.*, the Strecker synthesis ($RX + Na_2SO_3 \longrightarrow R\cdot SO_3Na + NaX$) fails since trifluoroiodomethane does not undergo nucleophilic substitution under mild conditions; bistrifluoromethyl disulphide is inert to concentrated nitric acid up to 115° (cf. alkyl disulphides); fluorohydrocarbons are either inert to fuming sulphuric acid or liberate fluoride at higher temperatures. Only one polyfluoro-sulphonic acid had been described before this work began—tetrafluoroethanesulphonic acid, prepared (Coffman, Raasch, Rigby, Barrick, and Hanford, *J. Org. Chem.*, 1949, **14**, 747) by the addition of sodium hydrogen sulphite to tetrafluoroethylene under pressure. Trifluoromethanesulphonic acid, described below, is the first perfluoro-sulphonic acid, and the method used can be applied to higher members of the series.

Trifluoromethanesulphonic acid was prepared by the oxidation of bis(trifluoromethylthio)mercury by aqueous hydrogen peroxide. It was isolated as its acetone-soluble barium salt which, when anhydrous, was treated with concentrated sulphuric acid to liberate trifluoromethanesulphonic acid. The acid is a mobile liquid which boils at a considerably lower temperature (162°) than does methanesulphonic acid (165°/8·5 mm.) [cf. $CF_3\cdot NO_2$ and $CH_3\cdot NO_2$ (*J.*, 1953, 2075), etc.]. Trifluoromethanesulphonic acid is thermally extremely stable; it shows a marked resistance to decomposition by aqueous base, thus resembling bistrifluoromethyl sulphide, and differing from most other trifluoromethyl derivatives of sulphur which liberate fluoride quantitatively (*e.g.*, $CF_3\cdot S_2\cdot CF_3$, $CF_3\cdot S_3\cdot CF_3$, $CF_3\cdot SH$, $CF_3\cdot SCl$). The resistance of trifluoromethyl oxy-acids to hydrolytic attack appears to be at a maximum when the hetero-atom displays its maximum valency; thus, trifluoromethylphosphonic acid also resists basic hydrolysis, whereas most other trifluoromethyl derivatives of phosphorus liberate fluoroform quantitatively (Bennett, Emeléus, and Haszeldine, *J.*, 1954, 3598).

Sodium and silver trifluoromethanesulphonate are very soluble in water and ethanol, and the silver salt is also soluble in benzene, in which the sodium and barium salts are insoluble. The solubility in benzene is very probably caused by the ability of the Ag^+ ion to form addition compounds with suitable donor molecules [cf. silver perchlorate (Rundle and Goring, *J. Amer. Chem. Soc.*, 1950, **72**, 5337) and silver trifluoroacetate (Swarts, *Bull. Sci. Acad. roy. Belg.*, 1922, **8**, 343)].

A study of the infra-red spectra of the derivatives of trifluoromethanesulphonic acid, combined with earlier studies on the Raman spectra of sodium alkanesulphonates, enables two strong bands to be assigned as characteristic of the $CF_3\cdot SO_3^-$ group (Table 1). The asymmetric and symmetric stretching vibrations lie at 8·4—8·6 and 9·4—9·6 μ for alkanesulphonic acids and their salts. Introduction of fluorine causes hardly any change in the

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* For previous, related papers see *J.*, 1952, 2198, 2549; 1953, 3219.

symmetric vibration but the asymmetric vibration is shifted appreciably to shorter wavelength (*ca.* 7·9 μ). A similar effect was noted for the asymmetric stretching vibration of the nitro-groups in polyfluoro-nitro-compounds (Haszeldine, *J.*, 1953, 2525). The assignment of the asymmetric vibrations for the trifluoromethanesulphonates is less certain than that of the symmetric vibrations, since the very powerful C–F stretching vibrations appear in the 8—9-μ region. The strong band in the 8—9-μ region, shown in parentheses in Table 1, which is in the same position as for the asymmetric vibration in alkanesulphonates, is assigned to a C–F rather than to a $-SO_2-$ vibration; if it were assigned to a $-SO_2-$ vibration, the strong band at 7·9μ, which is outside the C–F region, could not then be assigned. Furthermore, the above assignments are independently supported by spectroscopic studies on other compounds containing the $CF_3{\cdot}SO_2$ group to be described later.

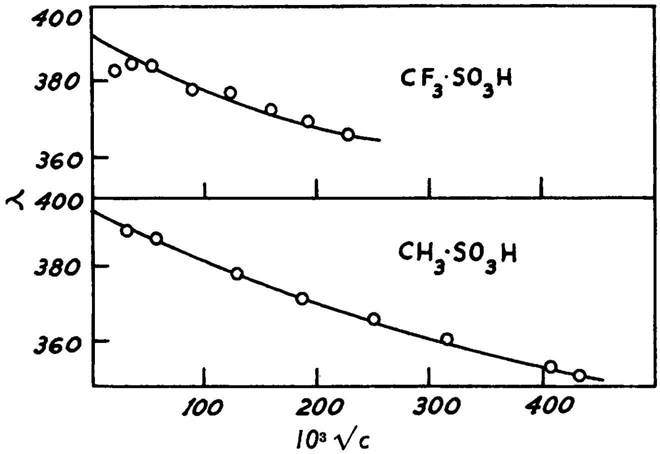
TABLE 1. *Bands characteristic of* $R{\cdot}SO_3^-$.

Compound	C.S. No.*	Asymmetric stretching	Symmetric stretching	Compound	C.S. No.*	Asymmetric stretching	Symmetric stretching
$CF_3{\cdot}SO_3H$ [1]	—	7·85 (8·5)	*ca.* 9·7	$(CF_3{\cdot}SO_3)_2Ba$ [1] ...	139	7·85 (8·45)	9·62
$CH_3{\cdot}SO_3H$ [1] ...	135	8·4	9·44	$Et{\cdot}SO_3Na$ [2] ...	—	8·50	9·50
$CH_3{\cdot}SO_3Na$ [1] ...	136	8·37	9·50	$Pr{\cdot}SO_3Na$ [2] ...	—	8·46	9·54
$CF_3{\cdot}SO_3Na$ [1] ...	137	7·82 (8·50)	9·60	$Bu{\cdot}SO_3Na$ [2] ...	—	8·50	9·58
$[CH_2(SO_3Na)]_2$ [1]	—	8·45	9·60	n-$C_5H_{11}{\cdot}SO_3Na$ [2]	—	8·53	9·58
$CF_3{\cdot}SO_3Ag$ [1] ...	138	7·9 (8·5)	9·75				

[1] Present work. [2] Raman spectra: Houlton and Tartar, *J. Amer. Chem. Soc.*, 1938, **60**, 544.

* These spectra have been deposited with the Chemical Society. Photocopies may be obtained (price, 3*s.* 0*d.* per copy per spectrum) on application to the General Secretary, quoting the C.S. numbers.

Conductivities.



From potentiometric titration in formic acid, Hammett ("Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 261) concluded that benzenesulphonic acid is stronger than hydrochloric or nitric acid, but weaker than sulphuric or perchloric acid. Replacement of an alkyl or aryl group by a trifluoromethyl group in oxy-acids of phosphorus or arsenic considerably increases the strength of the acid (*J.*, 1954, 551, *et seq.*). There was thus every reason to expect that trifluoromethanesulphonic acid would be one of the strongest known sulphonic acids and probably one of the strongest of all known acids. A comparison with methanesulphonic acid has been obtained from conductivity measurements in aqueous solution. The results are at present inexplicable: dilution of a solution made up initially by weight was accompanied by a slight decrease in the equivalent conductivity (see Experimental part). The plot of equivalent conductivity against square root of concentration shown in the Figure shows only the values obtained from solutions made up directly by weight. By comparison, methanesulphonic acid gives a smooth shallow curve of the expected type (see Figure). That the unexplained variations in the conductivity of trifluoromethanesulphonic acid are caused by the acid and not by the $CF_3{\cdot}SO_3^-$ ion is shown by the conductivity curve for sodium trifluoromethanesulphonate (see Figure) which is a straight line as expected. Extrapolation of this line to infinite dilution leads to a value of 42·3 for the ionic conductivity of $CF_3{\cdot}SO_3^-$, whence the calculated equivalent conductivity at infinite dilution for trifluoromethanesulphonic acid is 392. A straight line drawn through the experimental points for trifluoromethanesulphonic acid (see Figure) gives 388·5 for the equivalent conductivity at infinite dilution, and application of the Onsager equation gives values greater than 1 for the degree of ionisation α; a similar effect has been observed with bistrifluoromethylphosphinic acid (Emeléus, Haszeldine, and Paul, *J.*, in the press). Very approximate values for α and for the ionisation constant K have been calculated from $\alpha = \lambda_c/\lambda_0$ and $K = c\alpha^2/(1 - \alpha)$ by using a smooth curve drawn through the experimental points. These values are shown in Table 2

TABLE 2.

	α	10^5K		α	10^5K		α	10^5K
$CH_3{\cdot}CO_2H$	0·04	1·8	$Ph{\cdot}SO_3H$ [1]	0·96	0·3	$Me{\cdot}SO_3H$	0·96	0·3
$CCl_3{\cdot}CO_2H$	—	0·2	m-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$ [1]	0·97	0·4	$CF_3{\cdot}SO_3H$	0·96	0·3
$CF_3{\cdot}CO_2H$	0·96	0·3						

[1] Wightman and Jones, *Amer. Chem. J.*, 1911, **46**, 56.

with corresponding values similarly calculated for other acids. Trifluoromethanesulphonic acid is clearly a strong acid, but measurements in aqueous solution do not reveal whether it is stronger than other sulphonic acids or sulphuric acid. Preliminary conductivity results (to be reported later) with trifluoromethanesulphonic acid in acetic acid solution, however, show that, as expected, it is distinctly stronger than hydrochloric and sulphuric acid, and can in many ways be regarded as a mineral acid.

EXPERIMENTAL

The preparation of starting materials has been described earlier (Haszeldine and Kidd, *J.*, 1953, 3219). Infra-red spectra were recorded by a Perkin-Elmer Double Beam Instrument, Model 21, with rock-salt optics.

Attempted Oxidation of Bistrifluoromethyl Disulphide.—This disulphide did not react with concentrated nitric acid at 115° during 12 hr.; at 230° (12 hr.) extensive decomposition gave unidentified products. There was no reaction with concentrated sulphuric acid at room temperature, but at 120° (24 hr.) extensive decomposition to sulphur, sulphur dioxide, carbon dioxide, and silicon tetrafluoride.

Trifluoromethanesulphonic Acid.—Bis(trifluoromethylthio)mercury (6·08 g.) and 35% hydrogen peroxide (50 ml.) were heated in a 100-ml. flask under a reflux condenser. At 105°, the evolution of oxygen increased considerably and a yellow solid was deposited; the temperature was kept at 95—105° until the steady evolution of oxygen ceased (2—3 hr.). The yellow solid (1·69 g., 52%) was identified as mercuric oxide contaminated by a small amount of mercuric sulphide, but free from fluoride. The aqueous solution was strongly acid, and gave positive tests for fluoride and sulphate. It was first treated with hydrogen sulphide to precipitate the mercury, filtered, then neutralised with " AnalaR " barium carbonate. After filtration, the solution was evaporated to dryness on a steam-bath to give a white solid; this was extracted with dry acetone and the extract was evaporated to dryness. The resultant white barium salt was completely free from fluoride and sulphate. After drying to constant weight at 100° *in vacuo*, the anhydrous *barium trifluoromethanesulphonate* (4·624 g., 70%) (Found : F, 25·9; S, 14·6; Ba, 31·5. $C_2O_6F_6S_2Ba$ requires F, 26·2; S, 14·7; Ba, 31·5%) was analysed by fusion with sodium. Fluorine was determined by titration with thorium nitrate, and sulphur as sulphate after oxidation with hydrogen peroxide in alkaline solution. Barium was determined as barium sulphate.

In a typical experiment, the salt (5·16 g.) and concentrated sulphuric acid (5 g.) were heated at 10—20 mm., to distil *trifluoromethanesulphonic acid* (3·27 g., 92%), b. p. 42°/1 mm., 81°/37·5 mm., 91°/57·5 mm., 162°/760 mm. (Found: F, 37·3; S, 21·0%; equiv., 149·8. CHO_3F_3S requires F, 37·7; S, 21·2%; equiv., 150). The acid was decomposed by fusion with sodium for analysis. It is a colourless, very hygroscopic, mobile liquid, which fumes copiously in air and burns the skin. Only a qualitative infra-red spectrum could be obtained, since the acid liberated hydrogen chloride from rock salt at room temperature.

Less than 1% decomposition occurred when trifluoromethanesulphonic acid (0·1792 g.) was heated at 100° (24 hr.) with 15% aqueous sodium hydroxide (8 ml.) in a Pyrex tube.

Salts. The barium salt is very soluble in acetone and alcohol, slightly less soluble in water, and very sparingly soluble in ether and benzene. It is slightly hygroscopic, but is readily dried at 100° *in vacuo.*

The barium salt (1·21 g.) was dissolved in water, and the barium was precipitated with dilute sulphuric acid. The solution was neutralised with silver carbonate, filtered, and evaporated to dryness. The residue was extracted with dry acetone, and evaporation of the extracts gave a white residue, dried at 100° *in vacuo*, of *silver trifluoromethanesulphonate* (1·20 g., 84%) (Found : Ag, 41·2. CO_3F_3SAg requires Ag, 42·0%), which darkened in light and was very soluble in water, acetone, alcohol, and ether, and moderately soluble in benzene.

Potentiometric titration of a solution of trifluoromethanesulphonic acid against aqueous sodium hydroxide to pH 5·2, followed by evaporation to drynesss, finally at 100° *in vacuo*, gave *sodium trifluoromethanesulphonate* (Found : Na, 13·45. CO_3F_3SNa requires Na, 13·4%), very soluble in water, moderately soluble in alcohol and acetone, and insoluble in ether and benzene. Fluoride ion was not liberated when the salt (0·120 g.) was heated at 100° (10 hr.) with 15% aqueous sodium hydroxide (8 ml.).

Conductivity Measurements.—Conductivity cells with sealed-in platinised platinum electrodes of conventional type were used. The cells of cell constants 13·29, 4·359, and 0·05338 were used for solutions of concentration >0·01N, 0·01—0·001N, and <0·001N respectively. The solutions used were made up directly by weight, in Pyrex vessels which had been cleaned in chromic acid and then steamed for 24 hr. Conductivity water was stored in a Jena flask. Resistances were measured by means of a standard Wheatstone bridge circuit, with a cathode-ray oscilloscope as null-point detector (Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544); a steady value was reached within 30 min. of placing the cell in the thermostat at 25° ± 0·05°. Further readings were taken with fresh samples of solution until a constant value was obtained.

Trifluoromethanesulphonic acid. The results are given in Table 3 and the Figure. Each solution was made up directly from the acid by weight. The results obtained by dilution of any one solution of the acid were erratic, since dilution gave a decrease in the equivalent conductivity. For example, a 0·005254N-solution made up directly had equivalent conductivity (λ) 378·0, but when diluted by wt. to 0·002479N, had λ 372·2. This effect was reproduced many times and is associated with the process of dilution of a previously prepared solution, not with the preparation of a solution from anhydrous trifluoromethanesulphonic acid. Titration of the diluted solutions showed that the amount of acid present was that which would be expected from the calculated dilution. The acid was stable in aqueous solution as expected, since even strong base at 100° fails to liberate fluoride (see above). The aqueous solutions no matter how prepared showed a steady conductivity, which did not change when the solutions were stored for several days. The possibility of a gross experimental error can be discounted, since similar measurements with the sodium salt, or with methanesulphonic acid (see below), gave excellent results, no matter whether the solutions were made up by dilution or by weight. All normal precautions were taken, and the phenomenon was observed many times. No adequate explanation can be given at the present time, but since the decrease in equivalent conductivity occurs only on dilution, something akin to ion-pair formation may be involved. The fact that sodium trifluoromethanesulphonate behaves normally shows that the $CF_3{\cdot}SO_3^-$ ion is stable in aqueous solution.

TABLE 3.

10^3 Concn. (c) (g.-equiv./l.)...	51·10	36·40	24·98	14·82	7·426	2·630	1·185	0·354
$10^3\sqrt{c}$	226	190·6	158·0	121·7	86·2	51·3	34·4	18·8
Equiv. conductivity λ	366·2	369·1	372·6	377·0	377·9	384·2	384·7	382·0

Sodium trifluoromethanesulphonate. The measurements were made as for the acid; dilution of the aqueous solutions failed to produce anomalous changes in equivalent conductivity, and the results are given in Table 4. Extrapolation to infinite dilution of the λ–$10^3\sqrt{c}$ line gives 92·4 for equivalent conductivity at infinite dilution (λ_0); the ionic conductivity of Na^+ is 50·1 (McInnes, Shedlovsky, and Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2758), hence the ionic conductivity of $CF_3{\cdot}SO_3^-$ is 42·3.

Barium trifluoromethanesulphonate. The barium salt does not behave as a strong electrolyte in aqueous solution (see Table 4).

TABLE 4.

$CF_3{\cdot}SO_3Na$			$(CF_3{\cdot}SO_3)_2Ba$			$CH_3{\cdot}SO_3H$		
10^3c	$10^3\sqrt{c}$	λ	10^3c	$10^3\sqrt{c}$	λ	10^3c	$10^3\sqrt{c}$	λ
21·06	145·1	85·4	10·65	103·2	94·3	187·5	433·0	352·7
14·72	121·4	86·7	7·235	850	96·0	166·1	407·7	354·0
9·268	96·3	87·7	6·738	82·1	96·3	98·97	314·6	361·5
4·654	68·2	89·2	4·333	65·8	98·45	62·77	250·6	367·0
1·024	32·0	90·8	1·755	41·9	103·7	34·53	185·8	372·0
			0·515	22·7	109	16·32	127·8	378·4
						3·172	56·3	387·3
						1·049	32·4	389·6

Methanesulphonic acid (fraction of b. p. 165°/8·5 mm., n_D^{17} 1·4307). Solutions were made up by wt. or by dilution from a solution initially made up by wt. The results are shown in Table 4.

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