Perfluoroalkyl Derivatives of Sulphur. Part II. Trifluoromethane-sulphonic, -sulphinic, and -sulphenic Acid and the Infrared Spectra of Compounds Containing* $-SO_2-$ *and* $>S{:}O$ *Groups.*

By R. N. HASZELDINE and J. M. KIDD.

[Reprint Order No. 6391.]

Trifluoromethanesulphonyl chloride is prepared by oxidation of the sulphenyl chloride with chlorine and water, or from trifluoromethanesulphonic acid and phosphorus pentachloride. The sulphonic acid is obtained from carbon disulphide in 80% yield. Reduction of trifluoromethanesulphonyl chloride with zinc gives trifluoromethanesulphinic acid, isolated as its sodium and zinc salts. Hydrolysis of trifluoromethanesulphenyl chloride gives trifluoromethanesulphenic acid only as unstable intermediate, and bistrifluoromethyl disulphide and trifluoromethanesulphinic acid are the main products; control of the reaction conditions enables trifluoromethyl trifluoromethanethiolsulphonate to be obtained instead of the sulphinic acid. The mechanism of the hydrolyses of trifluoromethanesulphenyl chloride, trifluoromethyl trifluoromethanethiolsulphonate, and bistrifluoromethyl disulphide are discussed.

Infrared spectra of sulphonyl and sulphuryl halides, sulphones, thiolsulphonates, metal sulphonates, thionyl halides, sulphoxides, sulphites, and metal sulphinates are correlated and discussed.

TRIFLUOROMETHANE-THIOL, -sulphenyl chloride, and -sulphonic acid were described earlier; * studies on the preparation of the related trifluoromethane-sulphinic and -sulphenic acid are now described.

Aliphatic sulphinic acids are unstable compounds usually prepared by reaction of sulphur dioxide with a Grignard reagent or by reduction of a sulphonyl chloride; they decompose in air, particularly when heated, to give the corresponding sulphonic acid and thiolsulphonate (von Braun and Weissback, *Ber.*, 1930, **63**, 2836), $3R{\cdot}SO_2H \longrightarrow R{\cdot}SO_3H + R{\cdot}SO_2{\cdot}SR + H_2O$, and are usually isolated as sodium, barium, magnesium, or zinc salts. Salts of trichloromethanesulphinic acid have been prepared by reaction of the sulphonyl chloride with potassium cyanide, sulphur dioxide, or potassium sulphite; they are all water-soluble, but decompose when heated. In view of the experimental difficulties associated with perfluoroalkyl Grignard reagents (*J.*, 1952, 3423; 1953, 1748; 1954, 1273) the route to trifluoromethanesulphinic acid from trifluoromethanesulphonyl chloride was chosen.

Trifluoromethanesulphonyl chloride was synthesised by two methods: from trifluoromethanesulphonic acid by reaction with phosphorus pentachloride, and by oxidation of trifluoromethanesulphenyl chloride. Reaction of the sulphenyl chloride with hydrogen peroxide gives a mixture of bistrifluoromethyl disulphide and trifluoromethanesulphonyl chloride which is difficult to separate. The sulphenyl chloride is readily oxidised by a mixture of chlorine and water at room temperature, however, and this provides an excellent method of synthesis:

$$CF_3{\cdot}SCl + 2Cl_2 + 2H_2O \longrightarrow CF_3{\cdot}SO_2Cl + 4HCl$$

Trifluoromethanesulphonyl chloride is formed quantitatively provided that the chlorine present is in excess of that required by the above equation. This reaction is analogous to the preparation of trichloromethanesulphonyl chloride from carbon disulphide; chlorine yields trichloromethanesulphenyl chloride which in presence of water is oxidised to the sulphonyl chloride (Kolbe, *Annalen*, 1845, **54**, 155). Trifluoromethanesulphonyl chloride is a colourless liquid, b. p. 31·6°, which is almost insoluble in water and only very slowly hydrolysed by it at room temperature. At higher temperatures it is converted into the

---

* Part I, *J.*, 1954, 4228, where references to related work are given.

sulphonic acid within a few hours; hydrolysis by aqueous sodium hydroxide is very rapid, even at room temperature. In this way trifluoromethanesulphonic acid can be synthesised from carbon disulphide by way of bistrifluoromethyl disulphide without the preparation of the bistrifluoromethylthiomercury used in the original synthesis of the acid (Part I, *loc. cit.*) :

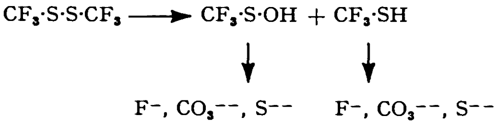
$$CS_2 \xrightarrow{IF_5} CF_3{\cdot}S_2{\cdot}CF_3 \xrightarrow{Cl_2} CF_3{\cdot}SCl \xrightarrow{Cl_2-H_2O} CF_3{\cdot}SO_2Cl \longrightarrow CF_3{\cdot}SO_3H$$

The overall yield from carbon disulphide is >80%, since the last three steps are quantitative.

When trifluoromethanesulphenyl chloride is treated with water and less chlorine than that required by the penultimate stage, bistrifluoromethyl disulphide is also formed, and as the amount of chlorine is progressively decreased so is the yield of trifluoromethanesulphonyl chloride until finally, when no chlorine is present, no sulphonyl chloride is produced; the products formed under such conditions are discussed below.

Reaction of trifluoromethanesulphonyl chloride with zinc dust and water in absence of air, followed by treatment of the resulting aqueous solution with sodium carbonate, gives sodium trifluoromethanesulphinate as a monohydrate. Monohydrate formation is in accord with sodium salts of other sulphinic acids which have general formula $R{\cdot}SO_2Na,H_2O$. The salt is deliquescent and readily soluble in acetone or alcohol. Attempts to isolate a zinc salt of the sulphinic acid less hydrated than $(CF_3{\cdot}SO_2)_2Zn,3H_2O$ have so far been unsuccessful. The infrared spectrum of sodium trifluoromethanesulphinate monohydrate readily distinguishes it from anhydrous sodium trifluoromethanesulphonate which has similar analytical figures. Further distinction is given by their reaction with aqueous sodium hydroxide at 100° : the sulphonate is stable, but the sulphinate evolves fluoroform quantitatively ($CF_3{\cdot}SO_2Na + NaOH \longrightarrow CHF_3 + Na_2SO_3$). Trifluoromethanesulphinic acid is thus the first sulphur compound containing a trifluoromethyl group which liberates fluoroform quantitatively; the others are either stable (*e.g.*, $CF_3{\cdot}S{\cdot}CF_3$) or break down completely (*e.g.*, $CF_3{\cdot}S_2{\cdot}CF_3$, $CF_3{\cdot}SH$). No similar reaction has been observed for alkanesulphinic acids, and trichloromethanesulphinic acid is reported to give the compound $CHCl_2{\cdot}SO_3K$ when heated with aqueous potassium hydroxide (Kolbe, *loc. cit.*; Rathke, *Annalen*, 1872, **161**, 149). Studies on the preparation of trifluoromethanesulphinic acid from its salts will be presented later.

Trifluoromethanesulphenic acid, $CF_3{\cdot}S{\cdot}OH$, was postulated earlier (*J.*, 1952, 2198; 1953, 3219) as an unstable intermediate in the hydrolysis of bistrifluoromethyl disulphide by aqueous base :



$$\begin{array}{ccccc} CF_3{\cdot}S{\cdot}S{\cdot}CF_3 \longrightarrow & CF_3{\cdot}S{\cdot}OH & + & CF_3{\cdot}SH \\ & \downarrow & & \downarrow \\ & F^-, CO_3^{--}, S^{--} & & F^-, CO_3^{--}, S^{--} \end{array}$$

and the preparation of its acid chloride, $CF_3{\cdot}SCl$ (*J.*, 1953, 3219), opened up a possible route to it, although all other sulphenic acids are believed to disproportionate ($2R{\cdot}S{\cdot}OH \longrightarrow R{\cdot}SH + R{\cdot}SO_2H$) and have never been isolated. Trifluoromethanesulphenic acid has not been isolated by aqueous hydrolysis of the sulphenyl chloride, but some knowledge of its stability and reactions has been gained.

The hydrolysis of trifluoromethanesulphenyl chloride by water, which is first considered, is more complicated than indicated by the reaction : $CF_3{\cdot}SCl + H_2O \longrightarrow CF_3{\cdot}S{\cdot}OH + HCl$. A large excess of water (*ca.* 40 : 1 molar ratio) causes the yellow colour of the sulphenyl chloride to disappear after a few hours, and bistrifluoromethyl disulphide (55—60% yield in typical experiments) and a small amount (*ca.* 4%) of carbonyl sulphide are formed. The aqueous solution remaining after the hydrolysis contains fluoride ion (5—10%), and when heated with aqueous sodium hydroxide yields fluoroform (33%). The liberation of fluoroform under these conditions reveals the presence of trifluoromethanesulphinic acid and an approximate scheme may thus be written :

$$3CF_3{\cdot}SCl + 2H_2O \longrightarrow CF_3{\cdot}S_2{\cdot}CF_3\ (66{\cdot}7\%) + CF_3{\cdot}SO_2H\ (33{\cdot}3\%) + 3HCl$$

the facts being borne in mind that the yield of the disulphide is not quite that represented by the equation, and that a small amount of carbonyl sulphide and fluoride ion are also formed. Sulphinic acids are often found as hydrolysis products of other sulphenyl halides (Kharasch, Potempa, and Wehrmeister, *Chem. Rev.*, **1946**, **39**, 269), and it should be noted in particular that neither trifluoromethanesulphonyl chloride nor trifluoromethanesulphonic acid is a reaction product. Two main reaction schemes are put forward to explain the observed hydrolysis. Both require the initial reaction with water to be represented by :

$$CF_3\cdot SCl + H_2O \longrightarrow CF_3\cdot SO^- + Cl^- + 2H^+$$

and both require the ion $CF_3\cdot SO^-$ (from $CF_3\cdot S\cdot OH$) to disproportionate rapidly with formation of $CF_3\cdot S^-$ (from $CF_3\cdot SH$) and $CF_3\cdot SO_2^-$ (from $CF_3\cdot SO_2H$) :

$$2CF_3\cdot SO^- \longrightarrow CF_3\cdot S^- + CF_3\cdot SO_2^-$$

This is analogous to assumptions made for reactions of other sulphenic acids (Kharasch *et al.*, *loc. cit.*).

Scheme I.

$$2CF_3\cdot SCl + 2H_2O \longrightarrow 2CF_3\cdot SO^- + 2Cl^- + 4H^+$$

$$2CF_3\cdot SO^- \longrightarrow CF_3\cdot SO_2^- + CF_3\cdot S^-$$

$$CF_3\cdot SCl + CF_3S^- \longrightarrow CF_3\cdot S\cdot S\cdot CF_3 + Cl^-$$

Overall reaction :

$$3CF_3\cdot SCl + 2H_2O \longrightarrow CF_3\cdot SO_2^-\ (33\cdot 3\%) + CF_3\cdot S_2\cdot CF_3\ (66\cdot 7\%) + 3Cl^- + 4H^+$$

The ion $CF_3\cdot S^-$ is known (*J.*, 1953, 3219, and Part III of this series) to be unstable in water and yields carbonyl sulphide and fluoride; this scheme thus accounts for the formation of fluoride and carbonyl sulphide by breakdown of $CF_3\cdot S^-$ competing with its reaction with trifluoromethanesulphenyl chloride, and this is in accord with the yield of bistrifluoromethyl disulphide being less than expected from the overall reaction equation. Neither the disulphide nor trifluoromethanesulphinic acid yields carbonyl sulphide or fluoride in aqueous solution. It was noted earlier that trifluoromethanethiol reacts slowly with trifluoromethanesulphenyl chloride to give the disulphide (*J.*, 1953, 3219), and it is likely that this reaction is much faster in presence of an ionising solvent.

Scheme II.

$$3CF_3\cdot SCl + 3H_2O \longrightarrow 3CF_3\cdot SO^- + 3Cl^- + 6H^+$$

$$2CF_3\cdot SO^- \longrightarrow CF_3\cdot S^- + CF_3\cdot SO_2^-$$

$$CF_3\cdot SO^- + H_2O \longrightarrow CF_3\cdot S^+ + 2OH^-$$

$$CF_3\cdot S^+ + CF_3\cdot S^- \longrightarrow CF_3\cdot S_2\cdot CF_3$$

Overall reaction :

$$3CF_3\cdot SCl^- + 2H_2O \longrightarrow CF_3\cdot SO_2^- + CF_3\cdot S_2\cdot CF_3 + 3Cl^- + 4H^+$$

This assumes that $CF_3\cdot SO^-$ can also react with water to give $CF_3\cdot S^+$ at approximately the same rate as it disproportionates, so that $CF_3\cdot S^+$ and $CF_3\cdot S^-$ ions are formed in equal amounts. The instability of $CF_3\cdot S^-$ accounts for the carbonyl sulphide and fluoride ion formation as in Scheme I. The reaction $R\cdot SH + R\cdot S\cdot OH \longrightarrow R_2S_2 + H_2O$ has been postulated to explain disulphide formation in other reactions involving hydrolysis of sulphenyl halides.

It can be predicted from both Scheme I and Scheme II that trifluoromethyl trifluoromethanethiolsulphonate should be formed under suitable conditions :

Scheme I :

$$CF_3\cdot SCl + CF_3\cdot SO_2^- \longrightarrow CF_3\cdot SO_2\cdot S\cdot CF_3 + Cl^-$$

Scheme II :

$$CF_3\cdot S^+ + CF_3\cdot SO_2^- \longrightarrow CF_3\cdot SO_2\cdot S\cdot CF_3$$

and this prediction was verified. The concentration of $CF_3\cdot SO_2^-$ ions was maintained as high as possible by treatment of trifluoromethanesulphenyl chloride with consecutive small amounts of water (molar ratio 1 : 0·4) during several days, and under these conditions the thiolsulphonate, which is stable to water, was isolated with approximately equimolar amounts of the disulphide. Incorporation of the last two equations in Schemes I and II respectively gives :

$$4CF_3\cdot SCl + 2H_2O \longrightarrow CF_3\cdot S_2\cdot CF_3\ (50\%) + CF_3\cdot SO_2\cdot S\cdot CF_3\ (50\%) + 4Cl^- + 4H^+$$

for the overall reaction for formation of trifluoromethyl trifluoromethanethiolsulphonate, in good agreement with the experimental yields.

The hydrolysis of trifluoromethanesulphenyl chloride by aqueous sodium hydroxide is next considered. The products depend upon the conditions used : at 70°, fluoride ion (67%), chloride ion (99%), sulphur, and sulphide ion are formed ; at 95°, in addition to the above products in the same yields, fluoroform (33%) is isolated. The scheme :

$$\begin{tikzcd}
3CF_3\cdot SCl + 4NaOH \arrow[r] & CF_3\cdot S_2\cdot CF_3 \arrow[d, "\begin{matrix}NaOH\\70^\circ\end{matrix}"] & + & CF_3\cdot SO_2Na \arrow[d, "\begin{matrix}NaOH\\95^\circ\end{matrix}"] & + 3NaCl + 2H_2O \\
 & (66\cdot6\%)\ CO_3^{--}, F^-, S^{--}, S & & CHF_3\ (33\cdot3\%) &
\end{tikzcd}$$

accounts for this product, since bistrifluoromethyl disulphide is decomposed by aqueous base, whereas the sulphinic acid liberates fluoroform only at 95°. The hydrolysis of other sulphenyl halides has been observed to give disulphide and sulphinic acid in the quantities expected from an equation of the above type (Lecher, Holschneider, Koberle, Spee, and Stocklin, *Ber.*, 1925, **58**, 409 ; Miller and Smiles, *J.*, 1925, 224).

Schemes I and II above thus agree well with the experimental results, and their relation to the aqueous alkaline hydrolysis of bistrifluoromethyl disulphide is next considered. It was postulated earlier that S–S fission occurs, but it is clear that if trifluoromethanesulphenic acid is thus produced it should, according to Scheme I or II, disproportionate to give $CF_3\cdot S^-$ and $CF_3\cdot SO_2^-$. Since trifluoromethanesulphinic acid is stable to aqueous alkali at room temperature and at 50°, and liberates fluoroform only at 95°, the alkaline hydrolysis of bistrifluoromethyl disulphide *via* the sulphenic acid should give trifluoromethanesulphinic acid, and this is inconsistent with the quantitative formation of fluoride ion from bistrifluoromethyl disulphide at 50°. It should be noted, however, that Scheme II, when applied to the alkaline hydrolysis, does not necessarily require the actual formation of the disulphide followed by its decomposition, but only that $CF_3\cdot S^-$ and $CF_3\cdot S^+$ are unstable in alkaline solution. The instability of the first of these is already known from the reactions of trifluoromethanethiol ($CF_3\cdot S^- \xrightarrow{OH^-} CO_3^{--}, F^-, S^{--}$) and $CF_3\cdot S^+$ may well be unstable :

$$CF_3\cdot S^+ + OH^- \longrightarrow S + CF_3\cdot OH \xrightarrow{OH^-} CO_3^{--} + F^-$$

This would also account for the formation of free sulphur during the aqueous alkaline hydrolysis of trifluoromethanesulphenyl chloride.

The liberation of free sulphur in the hydrolysis of bistrifluoromethyl disulphide might indicate C–S bond fission instead of S–S fission :

$$\begin{tikzcd}
OH^- \curvearrowright CF_3{-}S\cdot S\cdot CF_3 \arrow[r] & CF_3\cdot OH \arrow[d] & + & CF_3\cdot S\cdot S^- \arrow[d] \\
 & CO_3^{--}, F^- & & CF_3\cdot S^- \arrow[d] + S \\
 & & & CO_3^{--}, S^{--}, F^-
\end{tikzcd}$$

This fits the experimental observations, would avoid the clash with Scheme I and possibly Scheme II, and also finds support from the hydrolysis of bisheptafluoropropyl disulphide, which can be interpreted in terms of C–S as well as of S–S fission (Part III of this series).

The hydrolysis of trifluoromethyl trifluoromethanethiolsulphonate has also been studied. This ester is stable to water, but decomposed by aqueous alkali, and the products depend upon the conditions : at 50°, fluoride (38%) and sulphide (39%) are formed; at 95°, fluoride (39%), sulphide (99%), and fluoroform (60%) are produced. The appearance of fluoroform at only the higher temperature reveals the formation of trifluoromethanesulphinic acid, formed by S–S bond fission in the thiolsulphonate :

$$CF_3\cdot SO_2\cdot S\cdot CF_3 + OH^- \longrightarrow CF_3\cdot SO_2^- + CF_3\cdot SO^- + H^+$$

This reaction also produces a sulphenate ion which has already been postulated to disproportionate readily. Scheme II can thus be applied to the reaction :

$$\begin{aligned} 3CF_3\cdot SO_2\cdot S\cdot CF_3 + 3OH^- &\longrightarrow 3CF_3\cdot SO_2^- + 3CF_3\cdot SO^- + 3H^+ \\ 2CF_3\cdot SO^- &\longrightarrow CF_3\cdot S^- + CF_3\cdot SO_2^- \\ CF_3\cdot SO^- + H_2O &\longrightarrow CF_3\cdot S^+ + 2OH^- \\ CF_3\cdot S^- + CF_3\cdot S^+ &\longrightarrow CF_3\cdot S_2\cdot CF_3 \end{aligned}$$

Overall reaction :

$$3CF_3\cdot SO_2\cdot S\cdot CF_3 + 3OH^- \longrightarrow (CF_3)_2S_2 + 4CF_3\cdot SO_2^- + H^+ + H_2O$$

$$\begin{array}{cc} \Big\downarrow {\scriptstyle \mathrm{NaOH}\ 50^\circ} & \Big\downarrow {\scriptstyle \mathrm{NaOH}\ 95^\circ} \\ (33\cdot3\%)\ CO_3^{--},\ F^-,\ S^{--},\ S & CF_3H\ (66\cdot7\%) \end{array}$$

The figures, 33·3% of fluoride and 66·7% of fluoroform at 95°, are close to the experimental values. Here again, the scheme does not necessarily require the intermediate formation of the disulphide, but only that $CF_3\cdot S^-$ and $CF_3\cdot S^+$ are unstable as suggested previously. The equation $3R\cdot SO_2\cdot SR + 4NaOH \longrightarrow R_2S_2 + 4R\cdot SO_2Na + 2H_2O$ is analogous to that proposed for hydrolysis of other thiolsulphonates (Otto and Rössing, *Ber.*, 1886, **19**, 1235).

Scheme I can be applied to the hydrolysis of the thiolsulphonate only if the reaction

$$CF_3\cdot S^- + CF_3\cdot SO_2\cdot S\cdot CF_3 \longrightarrow CF_3\cdot SO_2^- + CF_3\cdot S_2\cdot CF_3$$

is possible. Thus, although two reaction schemes can be proposed to explain the hydrolysis of trifluoromethanesulphenyl chloride, Scheme II is preferred, since it is in reasonable agreement with the observed hydrolysis of trifluoromethyl trifluoromethanethiolsulphonate. The hydrolysis of bistrifluoromethyl disulphide is not completely compatible with either Scheme I or II unless C–S bond fission occurs in preference to S–S bond fission.

The structure of trifluoromethyl trifluoromethanethiolsulphonate isolated from the controlled hydrolysis of trifluoromethanesulphenyl chloride follows from its synthesis by interaction of zinc trifluoromethanesulphinate and trifluoromethanesulphenyl chloride :

$$(CF_3\cdot SO_2)_2Zn + 2CF_3\cdot SCl \longrightarrow 2CF_3\cdot SO_2\cdot S\cdot CF_3 + ZnCl_2$$

Attempts to synthesise it by interaction of trifluoromethanesulphonyl chloride and trifluoromethanethiol failed. The compounds $R_2S_2O_2$ have only recently been shown to be thiolsulphonates $R\cdot SO_2\cdot SR$, and not disulphoxides $R\cdot SO\cdot SO\cdot R$ (Zincke and Farr, *Annalen*, 1912, **391**, 57; Child and Smiles, *J.*, 1926, 2696; Gibson, Miller, and Smiles, *J.*, 1925, 1821; Cymerman and Willis, *J.*, 1951, 1332). The infrared spectrum of trifluoromethyl trifluoromethanethiolsulphonate also reveals the $-SO_2-$ group as shown in the Table where it is compared with related compounds. The $-SO_2-$ groups in sulphuryl chloride, trifluoromethanesulphonyl chloride, and trifluoromethyl trifluoromethanethiolsulphonate do not show specific absorption in the ultraviolet region.

Infrared Spectra.—The $-SO_2-$ group in sulphonyl or sulphuryl halides gives rise to symmetric (st.-a.) and asymmetric (st.-s.) stretching vibrations, as does the $-NO_2$ group in *C*-, *O*-, or *N*-nitro-compounds. Increase in electronegativity of the group R in $R\cdot SO_2Cl$ causes a progresive decrease in the wavelength of the st.-a. vibration in the series R = CH_3, CCl_3, Cl, and CF_3 (Table); the st.-s. vibration also decreases in this series provided that 8·07 is taken as this vibration for trifluoromethanesulphonyl chloride. The spectrum of the last compound shows two strong bands, at 8·07 and 8·90 μ, either of which could be

Infrared absorption bands (μ) *of compounds containing* $-SO_2-$ *or* $>SO$ *groups.*

Compound		C.S. No.*	Asymmetric stretching	Symmetric stretching	Compound		C.S. No.*	Asymmetric stretching	Symmetric stretching
				Acid halides.					
SO_2F_2[a]	(v)	—	6·66	7·88	SO_2[e]	(v)	—	7·65	8·65
$CF_3\cdot SO_2Cl$[b]	(v)	218	6·95	8·07 or 8·90	$(C_6H_{11})_2SO_2$	(s)	—	7·62	8·85
SO_2Cl_2[b]	(v)	219	6·96	8·30	Ph_2SO_2[g]	(N)	223	7·59, 7·65 7·73 (t)	8·65
$CH_3\cdot SO_2F$[c]	(v)	—	6·90, 6·97 (d)	8·20	,,	(S)	—	7·48	8·59
$CCl_3\cdot SO_2Cl$	(N)	220	7·12	8·45	$(Ph\cdot SO_2)_2S$[h]	(N)	—	7·35, 7·44 (d)	8·58
,,	(S)	—	7·11	8·42					
,,	(v)	—	7·04	8·35					
$CH_3\cdot SO_2Cl$	(l)[b, d]	—	7·33	8·53					
,,	(v)[b]	221	7·15	8·42					
,,	(S)[b]	—	7·25	8·51					
				Thiolsulphonates, $R\cdot SO_2\cdot SR$.					
R					R				
CF_3[b]	(v)	222	7·03	8·10 or 9·10	*p*-$C_6H_4\cdot CO\cdot NH_2$[h]	(N)	—	7·45	8·67
p-$C_6H_4\cdot CN$[h]	(N)	—	7·45	8·67	Ph[h]	(N)	—	7·51	8·75
				Sulphonates,[i] $R\cdot SO_3^-$.					
$CF_3\cdot SO_3Na$	(N)	137	7·82	9·60	$CH_3\cdot SO_3Na$	(N)	136	8·37	9·50
$(CF_3\cdot SO_3)_2Ba$	(N)	139	7·85	9·62	$CH_3\cdot SO_3H$	(l)	135	8·4	9·44
$CF_3\cdot SO_3Ag$	(N)	138	7·9	9·75	—	—	—	—	—

Compound		C.S. No.*	S:O vibration	Compound		S:O vibration
			Thionyl halides, sulphoxides, sulphites.			
SOF_2[b]	(v)	—	7·49, 7·55 (d)	$(C_6H_{11})(CH_3)SO$[f]	(S)	9·48
$SOCl_2$[j]	(v)	224	7·96, 8·03 (d)	$Ph\cdot SOMe$[f]	(S)	9·48
$(MeO)_2SO$[k]	(l)	—	8·33	Ph_2SO[f]	(S)	9·48
$(EtO)_2SO$[k]	(l)	—	8·33	,,	(N)[h]	9·60
—		—	—	Bu^i_2SO[h]	(S)	9·62
—		—	—	,,	(N)[h]	9·82
			Sulphinates, RSO_2^-.			
$CF_3\cdot SO_2Na$[b]	(N)	225	9·9 (?)	$Ph\cdot SO_2Na$[b]	(N)	9·8
$(CF_3\cdot SO_2)_2Zn$[b]	(N)	226	9·8 (?)	—		—

t = triplet, d = doublet, v = vapour, l = liquid, N = Nujol mull, S = solution in CCl_4.

[a] Perkins and Wilson, *J. Chem. Phys.*, 1952, **20**, 1791. [b] Present work. [c] T. Gramstad, unpublished results; the liquid has corresponding peaks at 7·20 and 8·30 μ. Ham and Hambly (*Austral. J. Chem.*, 1953, **6**, 33) record bands at 7·16 and 8·26 μ in the infrared and 7·14 and 8·26 μ for the Raman spectrum which can be assigned to the SO_2 vibration. [d] T. Gramstad, unpublished results. Ham and Hambly (*loc. cit.*) record bands at 7·31 and 8·51 μ (infrared) and 7·35 and 8·56 μ (Raman) which can be assigned to the SO_2 vibration. [e] Herzberg, "Infrared and Raman Spectra," Van Nostrand, New York, 1947, p. 285. [f] C_6H_{11} = *cyclo*hexyl; Barnard, Fabian, and Koch, *J.*, 1949, 2442; Schreiber (*Analyt. Chem.*, 1949, **21**, 1168) has also examined the spectra of sulphones. [g] Present work; Cymerman and Willis (*loc. cit.*) report 7·58, 7·62, 7·70, and 8·63 μ. [h] Cymerman and Willis, *loc. cit.* [i] Haszeldine and Kidd, *J.*, 1954, 4228. [j] Schreiber (*loc. cit.*) reports 8·08 μ; Cabannes and Rousset (*Ann. Physique*, 1933, **19**, 229) report 8·14 μ (Raman). [k] Matossi and Aderhold, *Z. Physik*, 1931, **68**, 683.

* Spectra bearing C.S. Nos. have been deposited with the Chemical Society. Copies, price 3*s*. 0*d*. each per copy, may be obtained on application, quoting the C.S. No., to the General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

assigned to the st.-s. vibration, and the other to a C–F stretching vibration. The assignment for methanesulphonyl chloride is not open to doubt, since the 7·33 and 8·53 μ bands are the strongest in the spectrum; the assignment for trichloromethanesulphonyl chloride is particularly clear, since there are no C–H vibrations to cause confusion.

In favour of the assignment of the 8·07 μ band to the st.-s. vibration in trifluoromethanesulphonyl chloride are the following points: (*a*) The shift to shorter wavelength for the st.-s. vibration on change of R in $R{\cdot}SO_2Cl$ from CH_3 to CCl_3 indicates an increase in the contribution of $>\mathrm{S{:}O}$ relative to that of $>\overset{+}{\mathrm{S}}\text{–}\mathrm{O}^-$ with increase in inductive effect of R; further shift to shorter wavelength is to be expected when $R = CF_3$. The spectra of methane- and trichloromethane-sulphonyl chloride must be compared for the compounds in similar physical states, in this case as vapours or as solutions in carbon tetrachloride. The spectra of methane- and trifluoromethane-sulphonyl chloride as vapours must similarly be compared to observe the trend. (*b*) Shift to shorter wavelength for the st.-s. vibration also occurs in the series $R{\cdot}SO_2F$ where $R = CH_3$ or F (Table).

In favour of the 8·90 μ band for the st.-s. vibration are the following points: (*a*) Analogy with *C*-nitro-compounds, where it has been shown (*J.*, 1953, 2525) that although the st.-a. band moves to shorter wavelength with increase in negativity of R in $R{\cdot}NO_2$, the st.-s. band moves to longer wavelength. (*b*) Trifluoromethanesulphonyl fluoride shows bands at 6·77 μ (st.-a.) and at 8·07 and 8·69 μ (T. Gramstad, unpublished results). The 8·07 μ band is at the same position as for trifluoromethanesulphonyl chloride, and could plausibly be assigned to a C–F vibration; the 8·69 μ band is shifted relative to the corresponding band (8·90 μ) in trifluoromethanesulphonyl chloride and this could be attributed to the effect on the st.-s. $-SO_2-$ vibration of increase in electronegativity on replacement of chlorine by fluorine.

The spectra of sulphuryl chloride and fluoride, however, also reveal an unambiguous shift of the st.-s. vibration to shorter wavelength, and the assignment of the 8·07 μ band to this vibration for trifluoromethanesulphonyl chloride is thus preferred, particularly when the difference in wavelength (1·0—1·3 μ) between the st.-a. and st.-s. wavelengths is also considered. The sulphones shown in the Table resemble sulphur dioxide, and their st.-a. and st.-s. vibrations lie at longer wavelengths than those of the acid halides. There is thus a shift to shorter wavelength of these vibrations in the series $R{\cdot}SO_2X$ with $X = C_{\text{aliph.}} > C_{\text{arom.}} > S > Cl > F$.

The spectrum of trifluoromethyl trifluoromethanethiolsulphonate shows a marked resemblance to that of trifluoromethanesulphonyl chloride, with strong bands at 7·03, 8·10, and 9·10 μ. Following the assignments for the chloro-compound, the first of these is assigned to the st.-a. vibration, and the second is given preference over the third for the st.-s. vibration. The S:O vibration in a disulphoxide structure $CF_3{\cdot}SO{\cdot}SO{\cdot}CF_3$ for the compound $CF_3{\cdot}S_2O_2{\cdot}CF_3$ would not be at shorter wavelength than that in thionyl fluoride (7·5 μ; Table), where R in $R{\cdot}SO{\cdot}R$ has maximum electronegativity, and would probably lie between 8 and 9 μ; with this structure the 7·03 μ band could not be assigned. The similarity to trifluoromethanesulphonyl chloride and the intensity and position of the 7·03 μ band in the spectrum of $CF_3{\cdot}S_2O_2{\cdot}CF_3$ clearly lead to the thiolsulphonate structure which is in accord with the structure determined by synthesis. Distinct shifts to shorter wavelength of the $-SO_2-$ bands with increase in inductive effect of R in $R{\cdot}SO_2{\cdot}SR$ are apparent.

The $-SO_2-$ vibrations in metal sulphonates are moved to longer wavelength relative to those in sulphones, thiolsulphonates, and sulphonyl halides, just as the C:O vibration of carboxylic acids is moved to longer wavelength in the salt. The assignment of the st.-a. vibration is clear, whereas that of the st.-s. vibration is less certain. When R in $R{\cdot}SO_3^-$ is CF_3 there is the expected shift to shorter wavelength for the st.-a. band (Table), but either the st.-s. band moves to longer wavelength or it must be assigned to other than the strong band near 9·6 μ, presumably to a band in the C–F stretching vibration region (8—9 μ).

The S:O stretching vibration in a sulphoxide is at 9·5 μ, and attachment of the negative oxygen atoms to sulphur as in a dialkyl sulphite causes a marked shift (1·2 μ) to shorter wavelength (Table). This trend is continued for thionyl chloride and fluoride (Table) and the S:O group is more sensitive than the $-SO_2-$ group in this respect. Clear predictions can thus be made for the position of the S:O vibration in R·SO·OMe (8·7—9·1 μ), R·SOCl (8·5—8·9 μ), and R·SOF (8·2—8·8 μ) where R = alkyl or aryl, with shifts of 0·3—0·5 μ to shorter wavelength when R = perfluoroalkyl.

The sulphinates listed in the Table show a strong band at 9·8 μ which is plausibly assigned to the $R{\cdot}SO_2^-$ vibration, but this must be regarded as tentative and may need modification as more examples become available.

EXPERIMENTAL

Bistrifluoromethyl disulphide, trifluoromethanesulphenyl chloride, and trifluoromethanesulphonic acid were prepared as described earlier (*J.*, 1953, 3219; 1954, 4228).

Trifluoromethanesulphonyl Chloride.—(a) *From trifluoromethanesulphonic acid.* The acid (0·714 g.) and phosphorus pentachloride (2·45 g.), heated at 100° (4 hr.) in a 30-ml. Pyrex tube, gave volatile products which were distilled *in vacuo* and identified as phosphorus oxychloride (0·542 g.), b. p. 106°, hydrogen chloride (0·176 g., 99%) (Found : *M*, 37. Calc. for HCl : *M*, 36·5), and *trifluoromethanesulphonyl chloride* (0·504 g., 63%), b. p. 31·6° (isoteniscope) (Found : Cl, 21·2%; *M*, 169. CO_2ClF_3S requires Cl, 21·1%; *M*, 168·5). The sulphonyl chloride freezes to a white solid which sublimes in a high vacuum.

(b) *From trifluoromethanesulphenyl chloride.* Three typical reactions show how the products vary with the relative quantities of reactants taken.

(i) Trifluoromethanesulphenyl chloride (3·70 g., 0·0271 mole), chlorine (5·00 g., 0·0715 mole), and water (5·00 g., 0·278 mole) were vigorously shaken in a 50-ml. Pyrex tube for 7 days, to give trifluoromethanesulphonyl chloride (4·47 g., 98%), b. p. 31·6° (Found : Cl, 21·2%; *M*, 169), and gaseous hydrogen chloride (0·528 g.). The sulphonyl chloride was shown to be identical with the compound prepared from trifluoromethanesulphonic acid by comparison of infrared spectra.

(ii) Trifluoromethanesulphenyl chloride (2·333 g., 0·017 mole), chlorine (1·17 g., 0·0165 mole), and water (4·00 g., 0·222 mole) were vigorously shaken in a 30-ml. Pyrex tube (48 hr.), to give a colourless lower layer. The volatile products were distilled *in vacuo*, to give hydrogen chloride (0·142 g.) and a mixture (1·970 g.; *M*, 177·3), analysed by infrared spectroscopy, of bistrifluoromethyl disulphide (36% yield) and trifluoromethanesulphonyl chloride (47% yield).

(iii) Vigorous shaking of a mixture of trifluoromethanesulphenyl chloride (0·9857 g., 0·0072 mole), chlorine (0·2811 g., 0·0040 mole), and water (3·00 g., 0·167 mole) in a sealed tube caused disappearance of the yellow colour in 2 hr. After 24 hr., distillation gave gaseous hydrogen chloride and a mixture (0·5010 g.; *M*, 184·7) of bistrifluoromethyl disulphide (37% yield) and trifluoromethanesulphonyl chloride (20% yield), analysed by infrared spectroscopy.

A control experiment showed that bistrifluoromethyl disulphide was recovered quantitatively after treatment with chlorine and water at room temperature.

(c) *From oxidation of trifluoromethanesulphenyl chloride by hydrogen peroxide.* The sulphenyl chloride (2·75 g.) was condensed into a 50-ml. flask and 35% hydrogen peroxide (20 ml.) was added carefully. The flask was allowed to warm to room temperature so that the sulphenyl chloride was under reflux (condenser at −78°); the rate of reflux decreased as reaction occurred. After a final heating at 50° for 2 hr. the liquid was colourless. Products more volatile than water were transferred to a gas-manipulation apparatus and distilled *in vacuo* to give a mixture (2·076 g.; *M*, 179·2) shown by infrared spectroscopic analysis to consist of bistrifluoromethyl disulphide (35% yield) and trifluoromethanesulphonyl chloride (40% yield). Examination of the aqueous solution revealed the presence of fluoride (11%) and trifluoromethanesulphonic acid (7%; isolated as its barium salt and identified by means of its infrared spectrum), but no trifluoromethanesulphinic acid.

Hydrolysis of Trifluoromethanesulphonyl Chloride.—Trifluoromethanesulphonyl chloride (0·151 g.) was present as an immiscible layer after being kept with water (1·5 ml.) in a sealed tube at 25° for 4 days. Less than 5% hydrolysis had occurred. Hydrolysis was complete and quantitative after 12 hr. at 75°, and not even traces of fluoride were detected. Quantitative hydrolysis without liberation of fluoride similarly occurred with 15% aqueous sodium hydroxide at 25° (12 hr.). Trifluoromethanesulphonic acid was identified by means of the infrared spectrum of its sodium salt.

Trifluoromethanesulphinic Acid.—(a) *As sodium salt.* Trifluoromethanesulphonyl chloride (1·384 g.), zinc dust (3·0 g.), and water (4·0 ml.) were kept 4 days at 25° in a sealed 30-ml. Pyrex tube. The sulphonyl chloride slowly disappeared, and no volatile products were produced.

The aqueous solution was filtered and the zinc precipitated with " AnalaR " sodium carbonate; filtration followed by freeze-drying gave a white deliquescent solid which was extracted with acetone. The extract was evaporated to dryness at room temperature *in vacuo*, then dried to constant weight at 45° *in vacuo*, to give *sodium trifluoromethanesulphinate monohydrate* (0·551 g., 38%) (Found : CF_3, 39·5; Na, 13·2. $CF_3\cdot SO_2Na,H_2O$ requires CF_3, 39·6; Na, 13·2). The salt was analysed for CF_3 by heating a sample (0·2161 g.) with 15% aqueous sodium hydroxide (5 ml.) at 95° (12 hr.) in a sealed tube; the fluoroform evolved (0·0866 g., 99·8%) (*M*, 70) was identified spectroscopically. Fluoride was not liberated. Sodium was determined as sodium sulphate by treatment of the salt with concentrated sulphuric acid in the usual manner.

(b) *As zinc salt.* Trifluoromethanesulphonyl chloride (0·920 g.), zinc dust (2·5 g.), and water (3 ml.) were allowed to react as above. The aqueous solution was filtered and evaporated to dryness at room temperature *in vacuo*. The residue was extracted with anhydrous ether to remove zinc chloride and the insoluble material was centrifuged three times with more ether. The residual white hygroscopic solid was dried over phosphoric anhydride and shown to be almost pure hydrated zinc trifluoromethanesulphinate (0·3244 g., 15%) [Found : CF_3, 35·1. Calc. for $(CF_3\cdot SO_2)_2Zn,3H_2O$: CF_3, 35·9. Calc. for $(CF_3SO_2)_2Zn,4H_2O$: CF_3, 34·2%]. It was found difficult to repeat this experiment, since separation of zinc chloride by ether-extraction is difficult and tedious.

It should be noted that the yields given above are minimum yields, since if the zinc or sodium salts are not actually isolated a quantitative yield of fluoroform can be obtained by treatment of the aqueous solution with base, showing that trifluoromethanesulphinic acid formation is quantitative. Thus, when trifluoromethanesulphonyl chloride (0·3393 g.) was treated with zinc dust (0·5 g.) and water (3 ml.) as above, and the filtered aqueous solution was heated with sodium hydroxide (1 g.) at 95° (12 hr.), fluoroform (0·1395 g., 99%) (*M*, 70), but no fluoride, was produced.

Hydrolysis of Trifluoromethanesulphenyl Chloride.—(a) *With a large excess of water.* The sulphenyl chloride (1·533 g.) and water (8·0 ml.) were vigorously shaken in a 30-ml. Pyrex tube at room temperature. The yellow colour of the sulphenyl compound disappeared after 3 hr., and shaking was continued for a further 9 hr. The volatile products were distilled *in vacuo*, to give bistrifluoromethyl disulphide (0·647 g., 57%) (*M*, 202), identified spectroscopically, and a more volatile fraction (0·023 g.) (Found : *M*, 60), shown by infrared spectroscopy to be carbonyl sulphide (Calc. for COS : *M*, 60). The aqueous solution was made alkaline with sodium hydroxide and heated at 95° for 12 hr. to give fluoroform (0·258 g., 33%) (*M*, 70) as the only volatile product. The fluoride content of the remaining alkaline solution was equivalent to 6·0% of the trifluoromethanesulphenyl chloride.

In further experiments the yield of the disulphide varied from 55% to 60%, and the fluoride ion from 5% to 10%. The aqueous solution always gave fluoroform in 33% yield on treatment with aqueous base at 95°.

(b) *With small amounts of water.* Trifluoromethanesulphenyl chloride (2·051 g., 0·0150 mole) was treated with successive small portions of water (each *ca.* 0·100 g., 0·0056 mole) at 12—24 hr. intervals in a Pyrex tube at room temperature. When 0·47 g. of water had been added the yellow colour of the sulphenyl halide began to fade and the aqueous globules had a deep yellow colour. When a total of 1·17 g. of water had been added the organic layer was colourless and the aqueous layer deep yellow. Distillation of the volatile products *in vacuo* gave trifluoromethyl trifluoromethanethiolsulphonate (0·206 g., 15%) (Found : *M*, 234. Calc. for $C_2O_2F_6S_2$: *M*, 234), b. p. 69—70° (micro), n_D^{17} 1·3480, spectroscopically identical with the compound synthesised from zinc trifluoromethanesulphinate as described below. A fraction (1·175 g.) (*M*, 212·5) was also isolated and shown to consist of bistrifluoromethyl disulphide (49%) and trifluoromethyl trifluoromethanethiolsulphonate (27%) by spectroscopic analysis. The aqueous solution contained 1% of fluoride ion. The total yield of trifluoromethyl trifluoromethanethiolsulphonate is thus 42%.

(c) *With aqueous sodium hydroxide.* Two typical experiments are given to illustrate the temperature dependence.

(i) Trifluoromethanesulphenyl chloride (0·1516 g.) was heated at 60° with 15% aqueous sodium hydroxide (5 ml.) in a Pyrex tube for 12 hr. A yellow solid (sulphur) formed even at room temperature but dissolved on heating to give a yellow solution. No volatile products were formed, and the aqueous solution contained fluoride (67·0%) and chloride (99·1%), yields being based on the sulphenyl chloride.

(ii) Reaction of trifluoromethanesulphenyl chloride (0·3136 g.) with 15% aqueous sodium hydroxide (8 ml.) rapidly gave a yellow solution with deposition of sulphur. After being heated at 95° (12 hr.) the solution was dark green, and contained fluoride (66·2% based on CF_3·SCl). The volatile product was fluoroform (0·0526 g., 33·2%) (*M*, 70), identified spectroscopically.

Synthesis of Trifluoromethyl Trifluoromethanethiolsulphonate.—Trifluoromethanesulphenyl chloride (2·110 g.) was converted into zinc trifluoromethanesulphinate as described previously; the filtered aqueous solution was evaporated to dryness and the residual solid was dried at 10^{-4} mm. for 24 hr. Reaction of the solid with trifluoromethanesulphenyl chloride (0·555 g.) gave (5 days) the *trifluoromethanethiolsulphonate* (0·641 g., 67% based on CF_3·SCl), b. p. 69—70°, n_D^1 1·3480 (Found: F, 48·0; S, 27·3%; *M*, 234. $C_2F_6O_2S_2$ requires F, 48·7; S, 27·4%; *M*, 234). No other volatile products were formed; some loss of the thiolsulphonate occurred, since it was adsorbed on the solid residue, and could be removed *in vacuo* only with difficulty.

Trifluoromethyl trifluoromethanethiolsulphonate was not formed when trifluoromethanethiol (0·0933 g.) and trifluoromethanesulphonyl chloride (0·1648 g.) were kept in a sealed tube for 5 days.

Bis(trifluoromethylthio)mercury (0·322 g.) dissolved in, but did not react with, trifluoromethanesulphonyl chloride (0·088 g.) at room temperature. Reaction occurred at 55° (3 days) but the products obtained were produced by decomposition of the mercurial and did not contain trifluoromethyl trifluoromethanethiolsulphonate. Thirty-three per cent. of the mercurial was recovered.

Hydrolysis of Trifluoromethyl Trifluoromethanethiolsulphonate.—This compound is stable to water but hydrolysed by aqueous sodium hydroxide. The annexed Table summarises reactions carried out with 15% aqueous sodium hydroxide in sealed Pyrex tubes for 12 hr. at the temperature shown. The fluoride and sulphide (including polysulphide and free sulphur) present in the resulting aqueous solution were determined in the usual manner, and the fluoroform was characterised by b. p., molecular weight, and infrared spectroscopy.

Temp.	CHF_3 (%)	F^- (%)	S^{--} (%)	Temp.	CHF_3 (%)	F^- (%)	S^{--} (%)
50°	—	38	39	95°	60·3	39·6	99·6
75	34·2	33·9	68	95	59·3	39·7	99·5

Spectra.—A Perkin-Elmer Model 21 Spectrophotometer with rock-salt optics was used for the infrared spectra. The thionyl fluoride was an analytically pure sample (*J.*, 1953, 3219); thionyl and sulphuryl chlorides were redistilled commercial samples. A 10-cm. gas cell was used for the majority of the vapour spectra. Solids were examined as mulls in Nujol and hexachlorobutadiene, and solutions were in carbon tetrachloride. Sodium and zinc trifluoromethanesulphinates are hydrated and show bands caused by water at 3 and 6 μ.

CF_3·SO_2Cl (vapour)	λ	240	230	220	210
	ε	3	15	45	130
CF_3·SO_2·S·CF_3 (vapour)	λ	260	250	240	230
	ε	13	21	32	41
SO_2Cl_2 (vapour)	λ	250	240	230	—
	ε	98	190	280	—

The ultraviolet spectra given in the annexed Table were determined with a Unicam Spectrophotometer.

One of the authors (J. M. K.) is indebted to the Department of Scientific and Industrial Research for a Maintenance Allowance (1950—1953) during the tenure of which this work was carried out.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, May 4th*, 1955.]