250. *The Alkyl- and Aryl-substituted Fluorides of Sulphur, Selenium, Tellurium, and Iodine.*

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A number of new aryl and alkyl fluorides of sulphur, selenium, and tellurium of the type $RXHal_3$, R_2XHal_2 and R_3XHal have been prepared and characterised, together with the new *compound* Ph_2IF and the silicofluorides of certain of these bases. It is shown that the substituted fluorides of sulphur, selenium, 'and tellurium are much less stable than their other halides. Stability increases from fluorine to iodine, and, in all the halides, with the number of organic radicals in the molecule. There is also an increase in stability in all the series of compounds in passing from sulphur to tellurium. The silicofluorides are more stable than the fluorides.

The fluorides of sulphur, selenium, and tellurium show decided differences from the other halides of these elements. For instance, in all three cases the maximum covalency of 6 is reached in combination with fluorine, but not with the other halogens, even at low temperatures. The hexafluorides are exceptionally stable, whereas the other halides, including the fluorides, easily hydrolyse and dissociate when heated. Indeed, some doubt exists as to the formation of lower fluorides of selenium and tellurium. Considerable interest, therefore, attaches to the preparation and properties of the alkyl- and aryl-substituted fluorides of these elements. Experiments are described below which seem to show that substituted hexafluorides such as RSF_5 are not stable. Certain di- and tri-substituted fluorides have been prepared, and general conclusions are drawn about the stability of these compounds and their relation to the unsubstituted halides. In the table below are given the formulæ of the relevant compounds known previously, and, in italics, those of new compounds now described. The table does not include a number of new silicofluorides which were prepared and characterised.

Valency 2.

X.	$XHal_2$.	X_2Hal_2.	XMeHal.	XPhHal.
S	SCl_2, SF_2	S_2Cl_2, S_2Br_2	—	SPhCl, SPhBr
Se	—	Se_2Cl_2, Se_2Br_2	—	SePhCl, SePhBr
Te	$TeCl_2$, $TeBr_2$	—	—	—

Valency 4.

X.	$XHal_4$.	$XMeHal_3$.	XMe_2Hal_2.	XMe_3Hal.	$XPhHal_3$.	XPh_2Hal_2.	XPh_3Hal.
S	SF_4, SCl_4, SBr_4	—	SMe_2Cl_2, SMe_2Br_2, $SeMe_2I_2$	SMe_3Cl, SMe_3Br, $SeMe_3I$, $\mathit{SMe_3F}$	—	SPh_2Cl_2, SPh_2Br_2, SPh_2I_2	SPh_3Cl
Se	$SeCl_4$, $SeBr_4$	($SeEtBr_3$)	$SeMe_2Cl_2$, $SeMe_2Br_2$, $SeMe_2I_2$	$SeMe_3Cl$, $SeMe_3Br$, $SeMe_3I$, $\mathit{SeMe_3F}$	$SePhCl_3$, $SePhBr_3$	$SePh_2Cl_2$, $SePh_2Br_2$	$SePh_3Cl$, $SePh_3Br$, $SePh_3I$, $\mathit{SePh_3F}$
Te	$TeCl_4$, $TeBr_4$, TeI_4	$TeMeBr_3$, $TeMeI_3$ $\mathit{TeMeF_3}$ *	$TeMe_2Cl_2$, $TeMe_2Br_2$, $TeMe_2I_2$ $\mathit{TeMe_2F_2}$,	$TeMe_3Cl$, $TeMe_3Br$, $TeMe_3I$, $\mathit{TeMe_3F}$	—	$TePh_2Cl_2$, $TePh_2Br_2$, $TePh_2I_2$, $\mathit{TePh_2F_2}$	$TePh_3Cl$, $TePh_3Br$, $TePh_3I$, $\mathit{TePh_3F}$

* Not obtained pure.

The resemblance between polyvalent iodine and tellurium has often been discussed. Tervalent iodine forms a series of aryl-substituted halides corresponding in properties to the tellurium compounds; *e.g.*, $PhICl_2$ is non-polar, and Ph_2ICl salt-like. The fluoride $PhIF_2$ was prepared by Dimroth and Bockemüller (*Ber.*, 1931, **64**, 522), but Ph_2IF, which was also prepared in the course of this work, has not been described before.

Experimental.

Since the direct reaction of fluorine with organic substances usually leads to destruction of the organic nucleus, even when the conditions are controlled (Bigelow *et al.*, *J. Amer. Chem. Soc.*, 1933, **55**, 4614; Fredenhagen and Cadenbach, *Ber.*, 1934, **67**, 928), fluorine had to be introduced by indirect procedures, such as the interaction of another halide with a metallic fluoride or anhydrous hydrogen fluoride, or the action of aqueous hydrogen fluoride upon the appropriate oxide or hydroxide. In all the successful preparations described here, the fluorinating agent was silver fluoride or aqueous hydrogen fluoride.

Silver fluoride was made by dissolving the freshly-precipitated and washed oxide in excess of 40% hydrofluoric acid, and evaporating the solution to dryness on a sand-bath. The product was several times alternately powdered and heated for an hour or so at 200° in a high vacuum. It was stored in a desiccator. Aqueous solutions were filtered before use to remove a little silver and silver oxide. The silver fluoride was employed either in aqueous solution for double decompositions, or anhydrous for preparing non-salt-like fluorides. In the former case the stoicheiometric amount was required, and could be weighed, since the material was almost pure. In the latter case an excess was needed, because of the inefficient contact between the reagents, especially when iodides were being fluorinated and a mixture of silver fluoride and iodide was formed. (This disadvantage in the use of silver fluoride was first noted by Swarts.) The halide to be fluorinated was often dissolved in an inert organic solvent, either because it decomposed below its m. p., or in order to make the reaction less violent.

Analytical Methods.—The classical gravimetric method of fluorine determination, precipitation as calcium salt, was abandoned after a few trials because it was tedious, and also not accurate enough where only small quantities of material were available, which was usually the case. An improved form of the volumetric procedure of Willard and Winter (*Ind. Eng. Chem. Anal.*, 1933, **5**, 7; and numerous later articles) was found to be rapid and reliable. The organic compound was dissolved in water, or, if insoluble, hydrolysed with dilute sodium hydroxide solution, giving a solution containing 2—10 mg. of fluorine. The solution was diluted to 30—40 c.c., and 3 drops of 0·05% aqueous sodium alizarinsulphonate solution added. The acidity was adjusted with very dilute hydrochloric acid or sodium hydroxide, so that the indicator was just yellow. 0·5 C.c. of Hoskins–Ferris buffer solution of pH 3·5 (Rowley and Churchill, *ibid.*, 1937, **9**, 551) was added. The sample was titrated with a thorium nitrate solution containing about 6 g. of the commercial salt per l., from a 10-c.c. burette. Good lighting was essential, and it was found that a daylight lamp held close to the flask was satisfactory. The end-point was marked by a permanent pink colour (the thorium–alizarin lake). It was more easily detected by allowing the precipitate of thorium fluoride, which adsorbs the lake, to settle. The thorium nitrate was standardised against pure sodium fluoride. With about 5 mg. of fluorine the estimated titration error was ±0·6%. In this way samples of the organic substance no larger than 0·05 g. were satisfactorily analysed. The titration succeeds whether the fluorine is present as fluoride or as silicofluoride.

Fluorination of the Substituted Dihalides.—No fluorine derivatives in this series were isolated. Attempts were made to replace chlorine by fluorine in PhSCl, *o*-$NO_2{\cdot}C_6H_4{\cdot}SCl$, *o*-$NO_2{\cdot}C_6H_4{\cdot}SBr$, and *p*-$NO_2{\cdot}C_6H_4{\cdot}SCl$, with silver, mercurous, mercuric, and hydrogen fluoride. All these substances reacted with the metallic fluorides, but the product always consisted mostly of the corresponding disulphide, mixed with tarry matter containing some fluorine; hydrogen fluoride was evolved during the reaction. The *p*-$NO_2{\cdot}C_6H_4{\cdot}SCl$ reacted with liquid anhydrous hydrogen fluoride giving a similar mixture of products, but also a small quantity of mixed crystals of *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_2F$, for the formation of which atmospheric oxidation may have been responsible; the *o*-isomer did not react. PhSeBr reacted vigorously with silver fluoride, but the product was a mixture of high-boiling substances, and no fluorine compound was present which distilled at a lower temperature than the bromide. Antimony trifluoride and ammonium fluoride did not fluorinate PhSeBr.

Fluorination of the Monosubstituted Tetrahalides.—$PhSeBr_3$ in benzene solution did not react appreciably with silver fluoride during several hours' heating at 70°, nor did the solid bromide react with liquid anhydrous hydrogen fluoride, with or without antimony pentachloride. An ethereal solution reacted with mercuric fluoride but the product was a crystalline substance containing mercury, probably as a double salt; on the supposition that $PhSeF_3$ might be more salt-like than the other halides, solutions were prepared, which might be expected to contain the fluoride, by double decomposition of the tribromide with silver fluoride in water, and by treating benzeneseleninic acid with excess of 40% hydrofluoric acid, in which it is freely soluble. When allowed to evaporate, these solutions yielded unchanged acid which at first contained a little fluorine, but which lost it on recrystallisation from water.

Methyltellurium Trifluoride, $TeMeF_3$.—This compound was not prepared pure but there is evidence that it may exist. The tri-iodide was prepared by Drew's method (*J.*, 1929, 565), and 2·6 g. were added gradually to 10 c.c. of boiling anhydrous acetone containing 6 g. of dry silver fluoride. After 20 minutes, the solution, at first brown, had become colourless. It was filtered and evaporated in a vacuum desiccator. An oil which would not crystallise remained, which had the smell of methyl telluride, and fumed slightly in moist air. A specimen was analysed by hydrolysis and titration (Found: F, 20·7. Calc. for $TeMeF_3$: F, 29·0%). The oil reacted at once with water, precipitating an amorphous white solid (probably the " anhydride " of methanetellurinic acid). After standing for 3 days in a high vacuum, the substance had become converted into a pasty crystalline solid mixed with some liquid, which could not be satisfactorily recrystallised from organic solvents. The initial product was almost certainly impure $TeMeF_3$, which probably disproportionated on standing according to the equation: $2TeMeF_3 \longrightarrow TeF_4 + TeMe_2F_2$. The inaccessibility of $TeMeI_3$ made it impracticable to repeat this preparation.

Fluorination of the Disubstituted Tetrahalides.—Because the sulphur compounds in this series, and the methylselenium compounds, are very unstable and decompose at, or slightly above, room temperature, no attempt was made to fluorinate these. Attention was concentrated on the diphenylselenium dihalides and the dimethyl- and diphenyl-tellurium dihalides, in which cases new fluorine compounds were isolated.

Phenyl selenide was first prepared by the methods of Leicester and Bergstrom (*J. Amer. Chem. Soc.*, 1929, **51**, 3587; improved method, *Org. Synth.*, Coll. Vol. 2, 238). In order to prepare $SePh_2Cl_2$, the crude Ph_2Se was dissolved in concentrated nitric acid, concentrated hydrochloric acid added, and the precipitate filtered off, drained, air-dried, and recrystallised from benzene. Ph_2SeBr_2 was prepared from the selenide and bromine (Krafft and Vorster, *Ber.*, 1893, **26**, 2818). $SePh_2O,H_2O$ was obtained by boiling the dichloride for a minute with a small excess of 10% sodium hydroxide solution and recrystallised from benzene. $SePh_2Cl_2$ and $SePh_2Br_2$ were rather inert towards fluorides. In unsuccessful attempts to make them react in benzene or toluene solution with silver fluoride, they both reacted preferentially with the solvent and vapours of hydrogen chloride or bromide mixed with hydrogen fluoride and silicon tetrafluoride were evolved. There was no organic product containing more than a trace of fluorine.

Diphenylselenoxide Hydrofluoride, $SePh_2O,HF$.—The compound $SePh_2O,H_2O$ was extremely soluble in 40% hydrofluoric acid, as was the seleninic acid. Both compounds behave differently towards the other halogen acids, with which sparingly soluble dihalides are formed. The hydrogen fluoride solutions of the hydrated selenoxide when evaporated on the steam-bath yielded a syrup which crystallised on cooling to a mass of elongated prisms. A quantity of this product was made by pumping off the water and excess acid from such a solution in a waxed vacuum desiccator, and recrystallising it twice from benzene in platinum vessels (Found: F, 6·6, 6·4. $C_{12}H_{10}OSe,HF$ requires F, 7·1%). The *substance* hydrolysed slowly in moist air, forming the hydrated selenoxide. It seems reasonable, therefore, to assign it the formula $SePh_2O,HF$ or $SePh_2F{\cdot}OH$. The m. p. was 75°. The compound was readily soluble in benzene. The solutions instantly attacked glass, forming two new substances, one consisting of large, thin, crystalline plates ($2SePh_2O,H_2SiF_6$), and the other of microscopic, rectangular plates ($3SePh_2O,H_2SiF_6$), both of which were insoluble in benzene.

The former compound was obtained in good yield when a solution of the hydrated selenoxide in excess of 40% hydrofluoric acid was left to evaporate over sulphuric acid in an unwaxed vacuum desiccator, the walls of which presumably supplied the silicon tetrafluoride for the reaction. The product was washed well with benzene to remove $SePh_2O,HF$. It did not melt when heated, but charred gradually above 250°. It was freely soluble in water and the solution gave a gelatinous precipitate with potassium salts, showing that SiF_6'' was present (Found : F, 17·7; Se, 23·1. $2C_{12}H_{10}OSe,H_2SiF_6$ requires F, 17·8; Se, 24·5%). The result for selenium (method of Bauer, *Ber.*, 1915, **48**, 507) was low because of adsorption upon gelatinous silica formed by fluoride attack on the walls of the Carius tube. The *substance* lost hydrogen fluoride on standing in moist air, and fell to a microcrystalline powder, consisting of the silicofluoride described next.

The *compound* $3Ph_2SeO,H_2SiF_6$ (above) was prepared in better yield by boiling the hydrated selenoxide with 10% hydrofluosilicic acid for a few minutes, filtering off the insoluble white solid, and recrystallising it twice from boiling ethanol. It consisted then of minute, well-formed, thin, rectangular plates, which were only slightly soluble in cold but appreciably soluble in boiling water. The solution gave the silicofluoride test with potassium sulphate solution. For analysis the substance was dissolved in dilute nitric acid and titrated (Found : F, 12·1, 12·0, 12·4; Se, 25·3. $3C_{12}H_{10}OSe,H_2SiF_6$ requires F, 12·8; Se, 26·5%).

Dimethyltellurium Difluoride, Me_2TeF_2.—The di-iodide was prepared by Vernon's method (*J.*, 1920, **117**, 90). 3 G. were dissolved in 15 c.c. of anhydrous acetone, and a large excess (6 g.) of silver fluoride was added to the boiling solution. There was a vigorous reaction and the solution became colourless after 20 minutes' boiling and shaking. The silver salts were filtered off, and the filtrate evaporated in a desiccator at the filter-pump. The white flakes of the *difluoride* remaining were recrystallised from 8 c.c. of boiling light petroleum to which 1·5 c.c. of absolute ethanol had been added. The product consisted of sparkling, colourless leaves, which were analysed by dissolving in water and titrating (Found : F, 19·6, 19·8. $C_2H_6F_2Te$ requires F, 19·6%). The difluoride was very soluble in water, ethanol, and acetone, but insoluble in petroleum. It smelt like methyl telluride. Water solutions were acid to methyl-red, so the substance was probably strongly hydrolysed. It was, however, perfectly stable in moist air. The m. p. was 84° and decomposition began at 208° with formation of a black residue (probably tellurium).

Diphenyltellurium Difluoride.—The phenyl telluride required was present in the ethereal solution from the preparation of triphenyltellurium iodide (see below), which was dried over calcium chloride and evaporated to a small bulk. An ethereal solution of 3 g. of iodine was added gradually until the di-iodide had precipitated completely and the solution was yellow. The precipitate was filtered off and washed with ether. The di-iodide was added in small portions to a refluxing mixture of 15 c.c. of dry toluene and 2 g. of dry silver fluoride. Each addition was made when the red colour due to the last had disappeared. The hot solution was filtered at the pump, and immediately deposited small colourless crystals of the *difluoride*, which were filtered off, washed with toluene, and recrystallised from benzene. For analysis, the substance was hydrolysed by boiling with 2N-sodium hydroxide for a short time. [The telluroxide first formed redissolved after a little boiling, perhaps as $TePh_2(OH)_2$.] (Found : F, 12·1, 11·8. $C_{12}H_{10}F_2Te$ requires F, 11·9%). The difluoride formed small rhombs, moderately soluble in benzene and toluene and very soluble in chloroform. It was unaffected by the atmosphere and insoluble in water. It melted at 154° and began to decompose at 290°. This compound could be prepared similarly from the dibromide and silver fluoride in boiling benzene, but the reaction is slower.

The Trisubstituted Tetrahalides.—The compounds in this series were salt-like. Nearly all the fluorides can be prepared. The chief experimental difficulties arose from their very great solubility in water, accompanied usually by extreme deliquescence and a tendency to separate from organic solvents in a liquid form. The silicofluorides, which were well-crystallised and stable, were prepared and examined in cases where the fluorides were difficult to purify. In all cases the fluorine analyses were performed by dissolving the salts in water and titrating them with thorium nitrate.

Trimethylsulphonium Fluoride.—The iodide was prepared by mixing 6 g. of methyl sulphide and 14 g. of methyl iodide. After standing for 24 hours, the solid cake which had formed was recrystallised once from ethanol, giving an almost theoretical yield of the sulphonium iodide, from which a trace of iodine was removed by ether washing. 4·3 G. of silver fluoride were dissolved in 10 c.c. of water, the solution filtered, and to it was gradually added the equivalent quantity of the sulphonium iodide (7 g.), dissolved in a little water, until precipitation of silver iodide was just complete. The latter was filtered off in the cold, and the filtrate evaporated in a platinum dish in a vacuum desiccator. Crystallisation began after 2 days and was complete after 4 days over phosphoric oxide in a second vacuum desiccator. A dry specimen was analysed (Found : F, 17·0, 16·7. C_3H_9SF,H_2O requires F, 16·8. C_3H_9SF requires F, 19·8%). The fact that the *substance* decomposed at 123° without melting showed that the water was present as crystal water and not as free water. The fluoride was extremely soluble in water and liquefied in moist air as quickly as phosphoric oxide. It was very soluble in ethanol and insoluble in anhydrous acetone or ether. It separated as a liquid from acetone–ethanol mixtures in attempts at recrystallisation.

Trimethylsulphonium Silicofluoride.—A standard solution of the silver salt was made by digesting a weighed excess of silver oxide with 10% hydrofluosilicic acid and filtering off, washing, drying, and weighing the excess oxide. The equivalent quantity of trimethylsulphonium iodide, dissolved in a little water, was added to a measured volume of the silver solution, and the mixture was boiled, filtered, and evaporated to dryness on the steam-bath. The residue was recrystallised once from 95% ethanol. The *silicofluoride* formed colourless needles which did not deliquesce. It was very soluble in water, sparingly soluble in ethanol and insoluble in acetone or ether. It decomposed at 323° without melting (Found : F, 39·3. $C_6H_{18}S_2F_6Si$ requires F, 38·6%).

Triethylsulphonium Fluoride.—This compound was less stable than the methyl analogue and was not prepared pure. A solution of the iodide was subjected to double decomposition with silver fluoride in the same way as for the methyl compound. During the evaporation, after crystallisation had begun, ethyl sulphide vapour was evolved. The product consisted of sticky crystals which could not be dried (Found : F, 22·1, 21·8. Calc. for $C_6H_{15}SF$: F, 13·8%. Calc. for $C_6H_{15}SF,HF$: F, 24·0%). An aqueous solution of the crystals was acid to methyl-red. The normal fluoride may decompose thus : $Et_3S^+ \longrightarrow Et_2S + Et^+$; $Et^+ + OH^- \longrightarrow EtOH$; $Et_3SF + H^+ + F^- \longrightarrow Et_3SF,HF$. $SePh_3F$ was found to decompose similarly (see below).

Triethylsulphonium silicofluoride was prepared like the methyl compound but with evaporation in a vacuum instead of on the steam-bath, because solutions of this silicofluoride are unstable at 100°. The product was recrystallised by adding dry ether to its solution in acetone–ethanol (10 : 1). It separated in small colourless needles (Found : F, 29·9. $C_{12}H_{30}S_2F_6Si$ requires F, 30·0%). The salt was very soluble in water and ethanol, insoluble in acetone and ether, and, unlike other silicofluorides, very deliquescent. It decomposed at 208° without melting.

Trimethylselenonium Fluoride.—Me_3SeI,I_2 was made from black selenium and methyl iodide (Scott, *Proc.*, 1904, **20**, 156). It was dissolved in a little ethyl acetate and precipitated with ether, filtered off, washed with ether, and redissolved in ethyl acetate. Water was added, and hydrogen sulphide passed in until the solution was colourless. The mixture was filtered and the iodide precipitated by adding much acetone.

The iodide was only slightly soluble in water. The fluoride and silicofluoride were therefore made from the free base. 7 G. of trimethylselenonium iodide were ground with silver oxide and water, and the solution filtered. It was neutralised to phenolphthalein with very dilute hydrofluoric acid in a platinum dish. The solution was evaporated in a vacuum over sulphuric acid and then over phosphoric oxide for several days. The crystals were dissolved by adding the minimum of absolute ethanol to their suspension in boiling anhydrous acetone. The salt did not crystallise on cooling, but separated as colourless needles when ether was added to the cold solution. If ether was added to an ethanol solution it separated as a liquid. Analysis showed that the product was a *monohydrate* (Found, in two preparations: F, 11·9, 11·8. C_3H_9SeF,H_2O requires F, 11·8%). The substance was very deliquescent and very soluble in water or ethanol but only slightly soluble in acetone and ether. It decomposed without melting at 124°.

Trimethylselenonium Silicofluoride.—A solution of the hydroxide, prepared as described above, was neutralised to methyl-red with hydrofluosilicic acid. The residue after evaporation on the steam-bath was recrystallised from 80% ethanol. The *salt* then consisted of well-formed rhombs, very sparingly soluble in absolute ethanol, but freely soluble in water and not deliquescent. It decomposes at 300° without melting (Found: F, 29·5. $C_6H_{18}Se_2F_6Si$ requires F, 29·4%).

Triphenylselenonium Fluoride.—$SePh_3Cl,2H_2O$ was prepared by the method of Leicester and Bergstrom (*loc. cit.*). The *fluoride* was obtained by double decomposition in aqueous solution with the equivalent of silver fluoride. Upon evaporation in a vacuum large anhydrous octahedra slowly crystallised out (Found: F, 5·65, 5·6, 5·6. $C_{18}H_{15}SeF$ requires F, 5·8%). The fluoride was very deliquescent, very soluble in water, ethanol, and chloroform, and moderately soluble in anhydrous acetone. It decomposed at 145° without melting.

No satisfactory method of recrystallisation was found. When solutions of this fluoride were evaporated on the steam-bath, it did not crystallise out. Instead, the syrupy residue separated into a lower viscous layer and an upper mobile layer. The latter was identified as phenyl selenide by conversion into the chloride, m. p. 179°. The lower layer solidified to a mass of brown needles when heating was continued; these consisted of the acid fluoride $SePh_3F,HF$ (below). The hydrolysis reaction recalls that of SEt_3F.

Triphenylselenium Hydrogen Fluoride, Ph_3SeF,HF.—A solution of the normal fluoride was filtered into a platinum dish and treated with one equiv. of 40% hydrofluoric acid, which was weighed out in a platinum crucible. The solution crystallised easily when evaporated in a vacuum. The *substance* recrystallised from anhydrous acetone in colourless needles, m. p. 99° (Found: F, 10·3. $C_{18}H_{15}SeF,HF$ requires F, 10·9%); a specimen made by decomposition of an aqueous normal salt solution (Found: F, 10·5; Se, 21·6. Calc.: F, 10·9; Se, 22·6%) had m. p. 100°; mixed m. p. 98—99°.

Triphenylselenonium Dihydrogen Fluoride, $SePh_3F,2HF$.—This *compound* resulted when an excess of 40% hydrofluoric acid was added to a solution of the normal fluoride and the solution was evaporated in platinum upon the steam-bath. The product was recrystallised from dry acetone in platinum vessels; colourless needles, m. p. 117—120°, were obtained (Found: F, 15·2. $C_{18}H_{15}SeF,2HF$ requires F, 15·5%). The compound was more soluble in acetone than the mono-acid salt; the solution attacked glass rapidly, forming a shower of minute crystals of the silicofluoride.

Triphenylselenonium Silicofluoride.—A solution of the chloride dihydrate was decomposed with silver silicofluoride, and the filtered product evaporated on the steam-bath. The residue, recrystallised from acetone containing a little water, separated in small hexagonal tablets (decomp. 228°), very soluble in water and ethanol, but insoluble in acetone and ether (Found: F, 15·6. $C_{36}H_{30}Se_2F_6Si$ requires F, 15·0%). A small quantity of this *compound* was found in the products of the hydrolytic decomposition of the fluoride.

Trimethyltelluronium Fluoride.—$TeMe_3I$ and $TeMeI_3$ were prepared by Drew's method (*J.*, 1929, 565). The former was recrystallised once from water; 2·5 g. were converted into the base by grinding in a mortar with excess of silver oxide and a little water. One half of the filtered base solution was neutralised to phenolphthalein with dilute hydrofluoric acid in a platinum dish and evaporated in a vacuum over sulphuric acid. The white cake remaining after 24 hours was recrystallised from anhydrous acetone containing the minimum of absolute ethanol to dissolve the salt. The fluoride separated in thin leaves. The crystals obtained from moist specimens were long needles, stable in ordinary air, efflorescent in a desiccator, and deliquescent in moist air. The anhydrous *salt* (Found: F, 9·5. C_3H_9TeF requires F, 9·65%) was deliquescent. By analogy with the corresponding sulphur and selenium compounds, the hydrate is probably a monohydrate. The fluoride was very soluble in water and ethanol and insoluble in acetone and ether. It decomposed at its m. p., 128°, disappearing completely and producing an odour of methyl telluride.

Trimethyltelluronium Silicofluoride.—The other half of the hydroxide solution (above) was neutralised to methyl-red with hydrofluosilicic acid and evaporated to dryness on the steam-bath. The residue was recrystallised from 80% ethanol, from which the *silicofluoride* separated in large thin rhombs (Found: F, 23·7. $C_6H_{18}Te_2F_6Si$ requires F, 23·5%), insoluble in acetone and ether, slightly soluble in alcohol and freely soluble in water. The crystals did not deliquesce; they decrepitated at 210° and decomposed at 320—336°.

Triphenyltelluronium Fluoride.—Tellurium tetrachloride (Michaelis, *Ber.*, 1887, **20**, 1780) was converted by reaction with phenylmagnesium bromide into the telluronium bromide (Lederer, *Ber.*, 1911, **44**, 2289), which was obtained in better yield than by Lederer by recrystallising it from ethanol instead of converting it into the iodide. The bromide was converted into the base by treatment with silver oxide in cold water. (If the mixture was boiled, as Lederer describes, the base instantly decomposed.) The base solution was neutralised with hydrofluoric acid and evaporated in a vacuum. The *fluoride* was recrystallised from dry acetone, in which it was moderately soluble (Found: F, 5·2. $C_{18}H_{15}TeF$ requires F, 5·05%). This was the most stable fluoride of the series. It did not deliquesce or separate as a liquid from solutions. The crystals were stumpy prisms, very soluble in water and ethanol, but insoluble in ether. Decomposition began near 190° and at 203° the compound melted and decomposed suddenly.

Diphenyliodonium Fluoride, Ph_2IF.—15 G. of phenyliodonium chloride were ground with a small excess of 5% sodium hydroxide solution and the paste shaken for 24 hours in a stoppered bottle. The yield of iodosobenzene after collection and washing was only 5 g. Some of the material had become converted into soluble salts and 3·5 g. of diphenyliodonium iodide were precipitated from the filtrate by adding excess of potassium iodide solution.

6·5 G. of iodoxybenzene were prepared from 10 g. of iodobenzene by Ortoleva's method (*Chem. Zentr.*, 1900, I, 723). The iodoso- and iodoxy-benzene were used to prepare diphenyliodonium iodide (Hartmann and Meyer, *Ber.*, 1894, **27**, 502); yield 3·5 g.

The two yields of this iodide were shaken with an excess of silver oxide and 30 c.c. of water for 6 hours. The resulting solution of iodonium hydroxide was filtered off and divided into two parts. One portion of the base solution was neutralised to phenolphthalein with dilute hydrofluoric acid, and the solution evaporated to small bulk on the steam-bath. The evaporation was completed over sulphuric acid and then over phosphoric oxide in a vacuum. The *fluoride* was recrystallised twice from dry acetone, separating in large colourless rhombs, which deliquesced in moist air (Found: F, 6·3, 6·3. $C_{12}H_{10}FI$ requires F, 6·35%). It was very soluble in water and in ethanol and insoluble in ether; it melted with decomposition at 85° and decomposed quickly at 110°, and it was photosensitive, becoming dark brown after a few days in daylight.

Diphenyliodonium Silicofluoride.—The second portion of the base solution (above) was neutralised to methyl-red with hydrofluosilicic acid and evaporated to dryness on the steam-bath. The residue was recrystallised twice from absolute ethanol. The *silicofluoride* formed small pointed prisms which were not deliquescent (Found: F, 16·5. $C_{24}H_{20}I_2F_6Si$ requires F, 16·2%), but were easily soluble in water, sparingly soluble in ethanol, and insoluble in acetone and ether; m. p. 187° (decomp.). The salt was stable to light.

Higher-substituted Fluorides.—No analogues of the compounds SRF_3, SRF_5 and $SeRF_5$ exist for the other halogens. It was therefore necessary to choose methods of preparation other than by way of the usual metal fluorides or hydrogen fluoride. Experiments were made on the following lines: (1) The action of Grignard reagents upon sulphur tetra- and hexa-fluoride. (2) The action of fluorine, or phenyliodonium fluoride, upon the organic disulphides and diselenides

(1) Gaseous sulphur hexafluoride bubbled through an ethereal solution of phenylmagnesium bromide did not react below the b. p. of ether. Liquid "sulphur tetrafluoride," prepared in an impure state from cobaltic fluoride and sulphur (Fischer and Jaenckner, *Z. angew. Chem.*, 1929, **42**, 810), reacted violently with phenylmagnesium bromide in ether at −60°. The products, however, contained no volatile fluorine compound and apparently consisted of PhSBr and bromine, which were not, however, positively identified. Phenylmagnesium iodide reacted to give iodine as the only volatile product. The following mechanism may be suggested:

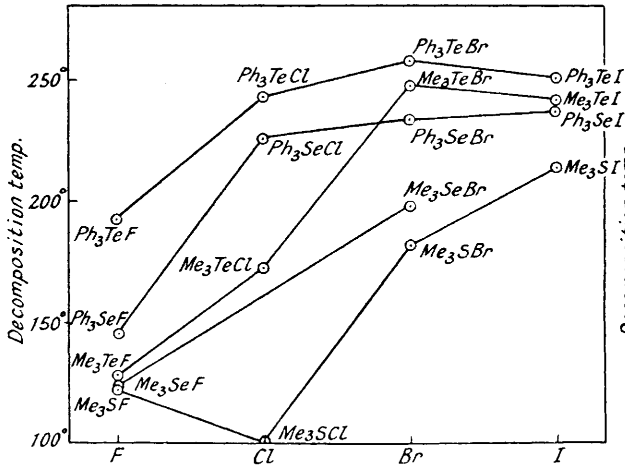
$$PhMgBr(I) + SF_4 \longrightarrow PhSF_3 + MgBr_2(I_2) + MgF_2$$
$$PhSF_3 + MgBr_2(I_2) \longrightarrow PhSBr_3(I_3) + MgF_2$$
$$PhSBr_3 \longrightarrow PhSBr + Br_2$$
$$PhSI_3 \longrightarrow Ph_2S_2 + I_2 \text{ (PhSI does not exist)}$$

(2) The reaction at 0° between fluorine–nitrogen mixtures and chloroform solutions of diphenyl diselenide or *o*- or *p*-nitrophenyl disulphide yielded only hydrogen fluoride and tarry or high-boiling condensation products. Phenyliodonium fluoride, prepared by Dimroth and Bockemüller's method (*Ber.*, 1931, **64**, 522), reacted similarly, although it was established by separate experiments that the analogous reactions of the iodonium chloride with phenyl selenide gave excellent yields of phenylselenonium dichloride.

DISCUSSION.

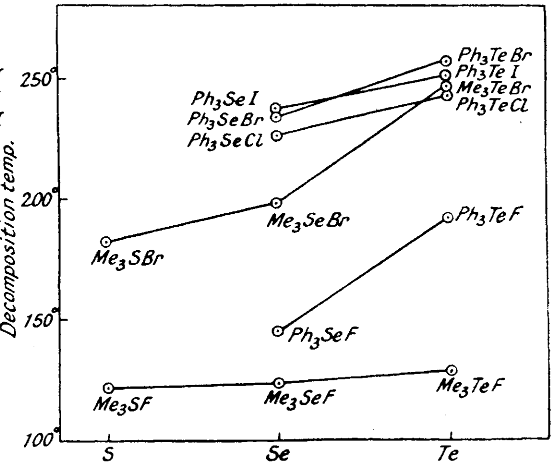
From the work described, the following conclusions emerge: (1) The substituted fluorides of sulphur, selenium, and tellurium are much less stable than the other halides. Stability increases from fluorine to iodine. (2) Stability increases in all the halides with the number of organic radicals in the molecule, and most noticeably in the fluorides. (3) Stability increases from sulphur to tellurium.

FIG. 1.



Influence of halogen on thermal stability.

FIG. 2.



Influence of central atom on thermal stability.

Therefore, in those cases where the chlorine derivatives are on the verge of decomposition at room temperature, it seems unlikely that fluorine derivatives could be prepared. It was only with tellurium that more than one atom of another halogen was replaced by fluorine, and stable compounds ($TeMe_2F_2$ and $TePh_2F_2$) obtained. In experiments designed to prepare corresponding compounds of sulphur and selenium, hydrogen fluoride was evolved and the organic residues were complex, pointing to condensation reactions between the ·SF and ·SeF grouping and the organic nucleus. The chlorides and bromides decompose similarly but less easily.

The salt-like substituted halides of sulphur, selenium, tellurium and iodine always decompose in the same way, *e.g.*, $SMe_3I \longrightarrow SMe_2 + MeI$; $Ph_2ICl \longrightarrow PhI + PhCl$, forming on the one hand an aryl iodide or a dialkyl or diaryl sulphide, selenide, or telluride, and on the other hand an alkyl or aryl halide. Et_3OBF_4 decomposes similarly, behaving as a compound of Et_3OF and BF_3: $Et_3OBF_4 \longrightarrow Et_2O,BF_3 + EtF$ (Meerwein *et al.*, *J. pr. Chem.*, 1937, **147**, 257).

The decomposition could take place by either of two mechanisms. The cation may disrupt, giving a free organic radical with unit positive charge, which afterwards combines with the anion; or an intermediate covalent form of the substance in which the central atom has a decet valency group may be formed. Fajans's principle excludes the latter hypothesis, for such a covalent form would result most easily in the case of the most easily deformed anion, that is, in the iodides, and least easily in the fluorides. Actually (see Fig. 1) the iodides are the most stable thermally, and the fluorides the least stable. On the other hypothesis, the crucial factors deciding decomposition are the intrinsic strength or weakness of the cation structure and the degree of deformation it suffers from the neighbouring anions. The fluoride ion produces the greatest deformation, and the cations containing sulphur, with its relatively small tendency to assume a positive charge, break up more easily than those containing the more metallic tellurium, because in the former the ionic charge will be located less centrally and more peripherally than in the latter. The observations are shown in Fig. 2, which illustrates the influence of the central atom on the thermal stability, and are in accordance with this idea. The decomposition temperatures in these diagrams are not individually well defined, but they show very definite trends. The decomposition of a typical compound XR_3Hal probably takes place thus: $(R_3X)^+Hal^- \longrightarrow R_2X + X^+ + Hal^-$; $X^+ + Hal^- \longrightarrow XHal$. Lucas, in studying the decomposition of *o*-tolyliodonium iodide, came to the same conclusion through a different argument (*J. Amer. Chem. Soc.*, 1936, **58**, 157).

The greatest changes in thermal stability should be produced by correspondingly great changes in ionic radius, *i.e.*, in passing from fluorine to chlorine and from oxygen to sulphur. In fact, the fluorides are much less stable than the chlorides and the oxonium salts are so much less stable than the sulphonium salts that Et_3OI, in theory the most stable oxonium halide, cannot be prepared (Meerwein, *loc. cit.*). The silicofluorides, in which the small free F^- ion is replaced by the large SiF_6^{--} ion with its relatively small distorting power, are highly stable.

With sulphur and selenium, octet valency groups are usual in combination with the heavier halogens and in combination with fluorine the duodecet is the only stable grouping. The lower sulphur fluorides disproportionate very easily so as to restore the duodecet. Tellurium alone forms stable tetrahalides with a decet valency group, although sulphur and selenium show a weak tendency towards the decet. The results of the attempts to fluorinate the phenyl sulphur halides can be explained as follows: The phenyl sulphur fluoride first formed disproportionated to a mixture of the disulphide and a higher fluoride [*e.g.*, *p*-$NO_2{\cdot}C_6H_4{\cdot}SF$ to (*p*-$NO_2{\cdot}C_6H_4{\cdot}S)_2$ and *p*-$NO_2{\cdot}C_6H_4{\cdot}SF_3$ or *p*-$NO_2{\cdot}C_6H_4{\cdot}SF_5$]; the latter then decomposed by intermolecular condensations to hydrogen fluoride and tarry products. Similarly for selenium. With tellurium, however, the stability of the decet facilitated the formation of diphenyl- and dimethyl-tellurium difluorides.

According to Pauling, even the bonds between non-metals and fluorine can be strongly ionic. When $SePh_2O$ and $Ph{\cdot}SeO_2H$ are treated with aqueous hydrochloric, hydrobromic, or hydriodic acid, insoluble covalent compounds are formed but these two bases are freely soluble in aqueous hydrofluoric acid, probably because the fluorine remains ionised instead of assuming a predominantly covalent binding like the other halogens. Upon evaporation the ions Ph_2Se^{++} and $PhSe^{+++}$ separate as $Ph{\cdot}SeO_2H$ or $SePh_2O,HF$, because the small solubility products of the bases are exceeded first. The weakness of hydrofluoric acid, making for a higher concentration of hydroxyl ions, is a contributory factor.

Previous experiments on the fluorination of sulphur halides by Ruff (*Ber.*, 1906, **39**, 4310) with antimony pentafluoride, Moissan (*Bull. Soc. chim.*, 1891, **5**, 456) with silver fluoride, and Guntz (*Compt. rend.*, 1884, **98**, 819) with lead fluoride, and of selenium tetrachloride by Prideaux and Cox (*J.*, 1928, 1603) all gave indefinite results. According to work described above, it seems that the substituted halides are generally rather resistant to conversion into fluorides, only vigorous reagents, such as silver fluoride, being effective. The halides of bivalent sulphur and selenium are the most reactive; the mono- and di-substituted tetrahalides of quadrivalent tellurium are moderately reactive, and $SePhBr_3$ could not be fluorinated by silver fluoride. Together with Thiel's observation that sulphur tetrachloride is not converted into fluoride by silver fluoride or antimony trifluoride (Thesis, Berlin, 1905), these facts support the theory that fluorinations take place through co-ordination of fluoride ions with the central atom of the halide. Sulphur tetrachloride and $PhSeBr_3$ lose some of their halogen very easily and could not therefore be expected to attach further radicals by co-ordination. $SHal_6^{--}$ ions do not exist, $SeHal_6^{--}$ ions are unstable, and $TeHal_6^{--}$ ions fairly stable, showing the relative ease of co-ordination of halogen ions.

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