481. *The Preparation of Complex Fluorides by Use of Sulphur Tetrafluoride as Fluorinating Agent.*

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Sulphur tetrafluoride converts mixtures of alkali-metal fluorides and metal oxides, sulphides, and carbonyls into complex fluorides. Silver, thallous, and ammonium salts can also be prepared by use of this reagent.

Recent work [1] has shown that sulphur tetrafluoride is a versatile fluorinating agent for the preparation of binary fluorides from inorganic oxides and sulphides. It has now been found that by using this reagent it is possible to prepare alkali-metal, ammonium, thallous, and silver(I) fluoroborates, hexafluorosilicates, hexafluorogermanates, hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates, hexafluorotitanates, hexafluoroniobates, hexafluorotantalates, hexafluoromolybdates(V), hexafluorotungstates(V), and hexafluorouranates(IV) (see Table). Sulphur tetrafluoride is a particularly convenient reagent since the other product from the reaction with oxides is thionyl fluoride which is volatile, and there is no solvolysis such as occurs when other non-aqueous fluorinating solvents (bromine trifluoride, iodine pentafluoride, selenium tetrafluoride, etc.) are used. Sulphur tetrafluoride also has the advantages that it may be prepared without the use of elementary fluorine [2] and that the reactants are not necessarily oxidised to the maximum valency state.

Sulphur tetrafluoride is a Lewis base and forms many adducts with other fluorides.[1,3] In the present work it has been found that previously unreported adducts are formed with niobium, tantalum, and molybdenum pentafluorides but, apart from molybdenum pentafluoride where a very approximately 1 : 1 adduct is formed, the stoicheiometries of the adducts do not correspond to a simple ratio between the Lewis acid and the Lewis base.

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[1] Oppegard, Smith, Muetterties, and Engelhardt, *J. Amer. Chem. Soc.*, 1960, **82**, 3835.
[2] Tullock, Fawcett, Smith, and Coffman, *J. Amer. Chem. Soc.*, 1960, **82**, 539.
[3] Seel and Detmer, *Z. anorg. Chem.*, 1959, **301**, 113.

Reactants	Reaction temp.	Solid products	Analysis (%)		X-Ray data (Å) *
			Found	Calc.	
$2KF : 1B_2O_3$	200°	KBF_4	BF_4, 68·1	BF_4, 69·0	O,[a] a = 7·84, b = 5·68, c = 7·37
$2AgF : 1B_2O_3$	175	$AgBF_4$	Ag, 54·5	Ag, 55·4	O,[b] a = 7·75, b = 5·54, c = 7·16
$2NH_4F : 1B_2O_3$	180	NH_4BF_4	BF_4, 83·6	BF_4, 82·8	O,[c, d] a = 8·89, b = 5·68, c = 7·21
$2NaF : 1SiO_2$	350	Na_2SiF_6	Si, 14·0	Si, 14·8	H,[e] a = 8·86, c = 5·02
$2NaF : 1GeO_2$	350	Na_2GeF_6	Ge, 30·1	Ge, 31·2	H,[e] a = 9·10, c = 5·13
$2NaF : 1P_2S_5$	350	$NaPF_6$,S			N,[f, g] a = 7·60
$2KF : 1As_2O_3$	350	$KAsF_6$	As, 33·8	As, 32·9	R,[f] a = 4·92, α = 97·2
$2NaF : 1Sb_2O_3$	350	$NaSbF_6$	Sb, 46·3	Sb, 47·1	N,[h] a = 8·18
$2NaF : 1TiO_2$	350	Na_2TiF_6	Ti, 22·9	Ti, 23·1	H,[e] a = 9·21, c = 5·15
$2NaF : 1Nb_2O_5$	350	$NaNbF_6$	Nb, 39·8	Nb, 40·4	N,[f] a = 8·27
$2NaF : 1Ta_2O_5$	350	$NaTaF_6$	Ta, 56·1	Ta, 56·9	N,[f] a = 8·26
$1LiF : 1Mo(CO)_6$	165	$LiMoF_6$	Mo, 44·5	Mo, 44·2	R,[i] a = 5·44, α = 57·0°
$2NaF : 1Mo(CO)_6$	200	$NaMoF_6$,NaF	Mo, 34·1	Mo, 34·9	N,[j] a = 8·19
$2NaF : 1MoO_2$	250	$NaMoF_6$,NaF			N,[j] a = 8·20
$2NaF : 1MoS_2$	400	$NaMoF_6$,NaF, MoS_2, S			N,[j] a = 8·19
$1CsF : 1Mo(CO)_6$	200	$CsMoF_6$	Mo, 29·5	Mo, 28·0	R,[j] a = 5·29, α = 96·0°
$1TlF : 1Mo(CO)_6$	165	$TlMoF_6$	Mo, 24·0	Mo, 23·2	R,[i] a = 5·12, α = 96·6°
$2NaF : 1W(CO)_6$	200	$NaWF_6$,NaF	M, 50·1	W, 50·7	N,[i] a = 8·18
$1CsF : 1W(CO)_6$	200	$CsWF_6$	W, 41·9	W, 42·7	R,[j] a = 5·31, α = 95·5°
$2NaF : 1UO_2$	350	Na_2UF_6	U, 60·1	U, 59·8	Several phases present
Nb_2O_5	350	NbF_5,0·54SF_4	Nb, 37·8	Nb, 37·8	
Ta_2O_5	350	TaF_5,0·39SF_4	Ta, 56·8	Ta, 56·8	
$Mo(CO)_6$	165	MoF_5,0·69SF_4	Mo, 36·1	Mo, 36·1	

[a] Pesce, *Gazzetta*, 1930, **60**, 936. [b] Sharp and Sharpe, *J.*, 1956, 1855. [c] Hoard and Blair, *J. Amer. Chem. Soc.*, 1935, **57**, 1985. [d] Klinkenberg and Ketelaar, *Rec. Trav. chim.*, 1935, **54**, 959. [e] Cox, *J.*, 1954, 3251. [f] Cox, *J.*, 1956, 876. [g] Bode and Teufer, *Z. anorg. Chem.*, 1952, **268**, 20. [h] Schrewelius, *Z. anorg. Chem.*, 1938, **238**, 241. [i] Kemmitt and Sharp, unpublished results. [j] Hargreaves and Peacock, *J.*, 1957, 4212.

* Structure type is indicated by: H (hexagonal), O (orthorhombic), N (NaCl) and R (rhombohedral).

All sulphur tetrafluoride adducts are unstable in the presence of basic fluorides: the fluoride ion is a better Lewis base than sulphur tetrafluoride. The decomposition of SF_4,BF_3 with potassium fluoride has been suggested as a method of preparing pure sulphur tetrafluoride.[3]

Most of the complexes resulting from these reactions contain elements in the same valency state as the starting materials. However, fluorination of a mixture of alkali fluoride and molybdenum hexacarbonyl, molybdenum dioxide, or molybdenum disulphide gives molybdenum(v) complexes. It has previously been reported [1] that fluorination of molybdenum disulphide gives molybdenum tetrafluoride which was characterised as its dimethyl sulphoxide adduct. We suggest that the actual product from the fluorination of molybdenum disulphide is MoF_5,SF_4 (molybdenum tetrafluoride would most probably form a 1 : 2 adduct with sulphur tetrafluoride) and that this dissociates and disproportionates to MoF_4 and MoF_6 in solution with dimethylsulphoxide. Similar disproportionation occurs when molybdenum pentachloride forms complexes with oxygen-containing ligands.[4] The action of sulphur tetrafluoride on a mixture of alkali fluoride and tungsten hexacarbonyl also gives quinquevalent complexes.

EXPERIMENTAL

Alkali fluorides were dried by heating them in a platinum crucible. Thallous fluoride was prepared from thallous carbonate and hydrofluoric acid; silver(I) fluoride was prepared by the method of Andersen, Bak, and Hillebert.[5] "AnalaR" ammonium fluoride was used as supplied. Metal oxides were dried at 130° and molybdenum and tungsten carbonyls were resublimed before use. Sulphur tetrafluoride was used directly from cylinders of the gas, which were kindly supplied by E.I. du Pont de Nemours and Co. Inc. and Imperial Chemical Industries Limited.

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[4] Gunduz and Sharp, unpublished observations.

[5] Andersen, Bak, and Hillebert, *Acta Chem. Scand.*, 1953, **7**, 236.

Alkali fluoride–metal oxide, sulphide, or carbonyl mixtures in various ratios (see Table) were fluorinated with an excess of sulphur tetrafluoride at autogenous pressures in a stainless-steel bomb which was rocked and heated overnight. The gaseous products were pumped off and the solid complexes were subsequently handled in the dry box. All solid products were analysed (see Table). *X*-Ray powder photographs of samples sealed in Lindemann glass capillaries were taken with Cu-K_α or Co radiation; measured values of $\sin^2 \theta$ were compared with values obtained from lattice constants recorded in the literature.

We thank Murex and Co. Ltd. for the gift of chemicals, the Chemical Society for a grant from the research fund, and the Department of Scientific and Industrial Research for a maintenance grant (to R. D. W. K.).

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[*Received, January* 17*th*, 1961.]