216. *The Preparation of Nitrosyl Complex Fluorides and of Fluorosulphonates by Means of Bromine Trifluoride.*

By A. A. Woolf.

Nitrosyl complex fluorides have been prepared by the reaction of bromine trifluoride with mixtures of nitrosyl chloride and compounds capable of functioning as "acids" in bromine trifluoride solution. Nitrosyl fluorosulphonate, made by fluorinating nitrosyl pyrosulphate, can undergo replacement reactions with both "acids" and "bases" in bromine trifluoride, to yield nitrosyl salts and fluorosulphonates, respectively. The latter were also formed from "bases" and solutions of sulphur trioxide in bromine trifluoride, in which the sulphur trioxide reacted as $BrF_2^+SO_3F^-$. The following new *salts* have been prepared by these methods: $AgSO_3F$, $(NO)SO_3F$, $(NO_2)SO_3F$, $(NO)AuF_4$, $(NO)PF_6$, $(NO)_2GeF_6$, $(NO)_2SnF_6$.

Nitronium salts have been prepared by the interaction of dinitrogen tetroxide and "acids" in bromine trifluoride (Woolf and Emeléus, preceding paper). The interaction of nitric oxide and "acids" should similarly yield nitrosyl salts; in practice nitrosyl chloride was used as the source of NO^+ ions because of the inconvenience of handling the volatile and readily oxidised nitric oxide. The presence of dinitrogen tetroxide in the latter would lead to the contamination of the reaction products with nitronium salts.

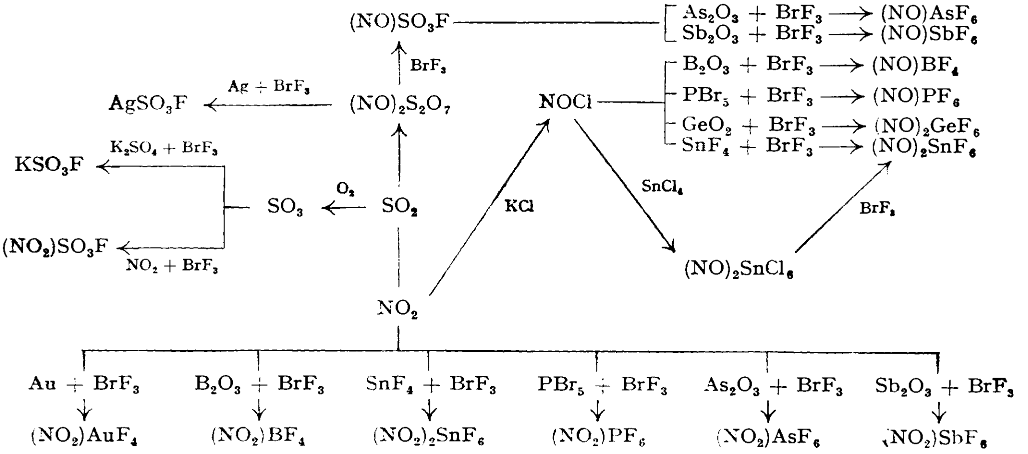
Nitrosyl (or more correctly nitrosonium) *tetrafluoroaurate*, tetrafluoroborate, *hexafluorogermanate*, *hexafluorostannate*, and *hexafluorophosphate* have been prepared as illustrations of the use of this method. The ionic nature of these compounds is indicated by the mode of preparation and by the presence of two nitrosyl groups in the tin and germanium compounds. There is little doubt that the compounds would also enhance the conductivity of bromine trifluoride. The tin compound is analogous to the complex chloride $(NO)_2SnCl_6$ (Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749) from which it can be prepared by fluorination with bromine trifluoride. The compound $(NO)BiCl_4$ (Sudborough, *J.*, 1891, 662) is, however, converted into bismuth trifluoride. This difference in behaviour is explained by the insolubility of bismuth trifluoride in bromine trifluoride and the consequent inability to form an "acid" in this solvent. The conversion of nitrosyl chlorostannate into the fluorostannate probably involves a neutralization reaction between the "acid" $(BrF_2)_2SnF_6$ (Woolf and Emeléus, *J.*, 1949, 2865) and a "base" $(NO)BrF_4$. By analogy it would be expected that $(NO)AuCl_4$ would be converted into $(NO)AuF_4$ by bromine trifluoride, since a "gold acid" $(BrF_2)AuF_4$ is known (Sharpe, *J.*, 1949, 2901), whereas $(NO)AlCl_4$ would yield aluminium trifluoride which is insoluble in bromine trifluoride.

The compound "nitrosyl sulphuric anhydride" provides an interesting link between nitrosyl compounds and fluorosulphonates since, by simple replacement reactions, it is converted into the former by reaction with "acids", and into the latter by "bases" in bromine trifluoride. Bromine trifluoride alone converts the "anhydride" into *nitrosyl fluorosulphonate*, a reaction which does not necessarily justify its formulation as the pyrosulphate $(NO)_2S_2O_7$, although it has been shown that alkali-metal pyrosulphates are converted into fluorosulphonates by bromine trifluoride (Emeléus and Woolf, *J.*, 1950, 164). Nitrosyl fluorosulphonate contaminated with nitrosyl hydrogen sulphate has been prepared from dinitrogen trioxide and fluorosulphonic acid (Lange, *Ber.*, 1927, **60**, 967). Modification of this method (reaction of nitrosyl chloride or dinitrogen tetroxide with excess of fluorosulphonic acid, and the latter with excess of dinitrogen tetroxide) also gave impure nitrosyl fluorosulphonate. The analogous reaction of dinitrogen tetroxide with chlorosulphonic acid, on the other hand, gave nitrosyl hydrogen sulphate free from nitrosyl chlorosulphonate (Jones, Price, and Webb, *J.*, 1929, 312). The last-mentioned compound has probably been prepared from nitrosyl chloride and sulphur trioxide (Weber, *Jahresber.*, 1864, 157).

Replacement reaction of nitrosyl fluorosulphonate with "acids" in bromine trifluoride go to completion only in the case of fluoroarsenates and fluoroantimonates. The reaction which probably occurs for the latter is: $(NO)SO_3F + (BrF_2)SbF_6 = (NO)SbF_6 + (BrF_2)SO_3F$. The "acid" $(BrF_2)SO_3F$ has not yet been isolated in a pure state, but a solid of approximately this composition may be isolated by dissolving sulphur trioxide in bromine trifluoride and removing excess of solvent in a vacuum at room temperature. This reaction resembles the formation of fluorosulphonic acid from hydrogen fluoride and sulphur trioxide. The compound dissociates readily and may be volatilised completely above 60°. Partial replacement of the fluorosulphonate ion was observed in the reaction of nitrosyl fluorosulphonate with boric oxide (which yields the BF_4^- ion) in bromine trifluoride, while with stannic fluoride the product was a mixture of nitrosyl fluorosulphonate and the partly decomposed " tin acid." Experiments with potassium fluorosulphonate reveal a similar behaviour in that the products of reaction with " acids " in bromine trifluoride, when the excess solvent is removed at room temperature, contain sulphur and bromine. Replacement reactions can occur with other compounds containing the tetrahedral SO_3 group. Thus potassium dinitrososulphite, $K_2(SO_3)(NO)_2$, the structure of which has recently been determined by Cox, Jeffrey, and Stadler (*J.*, 1949, 1783), is converted by bromine trifluoride into an equimolecular mixture of potassium fluorobromite and fluorosulphonate, just as are potassium sulphate, pyrosulphite, and thiosulphate (Emeléus and Woolf, *loc. cit.*). In the reaction between potassium dinitrososulphite, mixed with excess of arsenious oxide, and bromine trifluoride, however, the product was an equimolecular mixture of potassium and nitrosyl fluoroarsenates, instead of the expected mixture of potassium fluorosulphonate and potassium and nitrosyl fluoroarsenates (1 : 1 : 2). A displacement reaction with elimination of BrF_3,SO_3 may have occurred. Sulphites behave differently in their reaction with bromine trifluoride and there is no evidence of formation of BrF_3,SO_3. They probably decompose to sulphur dioxide, or more probably sulphuryl fluoride, and oxygen in a similar manner to carbonates, which eliminate only one-third of their oxygen as such (Emeléus and Woolf, *loc. cit.*).

The replacement reactions of " bases " and nitrosyl fluorosulphonate enable metal fluorosulphonates to be prepared. Thus, silver and nitrosyl pyrosulphate gave *silver fluorosulphonate.* An attempt to prepare silver fluorosulphonate by a neutralisation reaction between silver nitrate and nitrosyl fluorosulphonate in liquid dinitrogen tetroxide failed, the reactants being recovered unchanged. This may be compared with the reaction in this solvent between silver nitrate and nitrosyl chloride: $AgNO_3 + NOCl = AgCl + N_2O_4$ (Addison and Thompson, *J.*, 1949, S 218). Fluorosulphonates were also formed by a more direct reaction of " bases " with solutions of sulphur trioxide in bromine trifluoride. Excess of dinitrogen tetroxide and sulphur trioxide produced *nitronium fluorosulphonate* quantitatively, and potassium sulphate and sulphur trioxide (1 : 1) yielded two molecules of potassium fluorosulphonate. These reactions can be explained in terms of neutralisation processes involving the " acid " $BrF_2^+SO_3F^-$. The relationship of some of the reactions leading to nitrosyl and nitronium complex fluorides and to fluorosulphonates is shown diagrammatically.

Production of nitrosyl and nitronium complex fluorides and fluorosulphonates with bromine trifluoride.



Experimental.

Nitrosyl chloride, prepared by the method of Whittaker, Lundstrom, and Merz (*Ind. Eng. Chem.*, 1931, **23**, 1410), was stored in a bulb attached to a measuring tube. In each experiment a 40% excess of nitrosyl chloride was condensed at −10° into the measuring tube and transferred by vacuum-distillation to a silica reaction flask which held the substance capable of forming an " acid " in bromine trifluoride. The reaction vessel was detached from the vacuum line, and bromine trifluoride added while it was still cooled by liquid air. The mixture was allowed to reach room temperature and then heated to complete the reaction. Excess of solvent was distilled off *in vacuo* in the usual way.

Methods of analysis are given below only when they have not been previously described.

Nitrosyl Fluoroborate.—Nitrosyl chloride and boric oxide with bromine trifluoride gave a 96% yield of nitrosyl fluoroborate [Found: N, 11·9; F, 64·6. Calc. for $(NO)BF_4$: N, 12·0; F, 65·0%]. This white solid, in common with the other nitrosyl salts, decolorized aqueous solutions of potassium permanganate and liberated iodine from potassium iodide solution. It was first prepared by Wilke-Dörfurt and Balz (*Z. anorg. Chem.*, 1926, **159**, 197) by the action of dinitrogen trioxide on fluoroboric acid.

Nitrosyl Fluorophosphate.—Red phosphorus was converted into the pentabromide with bromine, and the excess of nitrosyl chloride was condensed on to the cooled mixture before reaction with bromine trifluoride. The yield of *nitrosyl fluorophosphate* was 88% on the phosphorus taken (Found : N, 7·9; F, 64·6. $NOPF_6$ requires N, 8·0; F, 65·2%). Lange suspected that the solid obtained from nitrosyl fluoride and phosphorus pentafluoride was nitrosyl fluorophosphate but no analytical figures were given (*Ber.*, 1928, **61**, *B*, 794).

Nitrosyl Fluorogermanate.—Germanium dioxide and nitrosyl chloride gave an 84% yield of the *fluorogermanate* when treated with bromine trifluoride. The germanium was determined as dioxide (Johnson and Dennis, *J. Amer. Chem. Soc.*, 1925, **47**, 790) after decomposition of the salt with aqueous sodium carbonate solution, and the fluorine precipitated as calcium fluoride in a separate portion [Found : N, 11·6; Ge, 29·6; F, 46·8. N : Ge : F = 2·03 : 1·00 : 6·04. $(NO)_2GeF_6$ requires N, 11·4; Ge, 29·5; F, 46·3%]. A second experiment gave a ratio N : Ge : F = 1·93 : 1·00 : 6·00.

Nitrosyl Fluorostannate.—Stannous chloride was first converted into stannic fluoride and then treated with nitrosyl chloride and bromine trifluoride to give the *fluorostannate* [Found : N, 9·2; Sn, 40·6; F, 38·2%; equiv., 288. $(NO)_2SnF_6$ requires N, 9·6; Sn, 40·6; F, 39·0%; equiv., 293).

Nitrosyl Fluorosilicate.—Silica and excess of nitrosyl chloride after treatment with bromine trifluoride left a white solid which contained nitrogen, silicon, and fluorine but was free from bromine. The yield was 4·8% and was insufficient for quantitative analysis. Contamination of other nitrosyl salts with the fluorosilicate produced by attack on the reaction vessel was negligible since the average loss of flask weight was 40 mg. in the preparation of gram quantities.

Nitrosyl Fluoroaurate.—Metallic gold and nitrosyl chloride with bromine trifluoride left the *fluoroaurate* [Found : N, 4·4; Au, 63·6; F, 23·5; equiv., 312. N : Au : F = 1·00 : 1·01 : 3·91. $(NO)AuF_4$ requires N, 4·6; Au, 65·1; F, 25·1%; equiv., 303] as a yellow solid which rapidly blackened on exposure to air. With water the compound gave an immediate black precipitate, only part of which was soluble in concentrated hydrochloric acid. The filtrate contained traces of nitrous acid. It appears that the nitrous acid formed on hydrolysis reduced tervalent gold to the metal. The nitronium salt behaves quite differently in that it is hydrolysed to auric hydroxide and nitric acid.

Nitrosyl Fluorotitanate.—Titanium powder was dissolved in bromine trifluoride and most of the excess of solvent removed *in vacuo* at 80°. Excess of nitrosyl chloride and bromine trifluoride were then added. The white product, which contained appreciable amounts of bromine, was decomposed with sodium hydroxide solution. The precipitate was ignited to titania and an aliquot of the filtrate used to determine nitrogen and fluorine [Found : N, 10·9; Ti, 23·3; F, 52·0. Calc. for $(NO)_2TiF_6$: N, 12·6; Ti, 21·6; F, 51·4%. Calc. for TiF_4 : Ti, 38·7; F, 61·3%]. These figures show that the product was essentially the nitrosyl salt contaminated with $TiF_4,xBrF_3$. It is significant that no pure fluorotitanates have been prepared with bromine trifluoride.

The Fluorination of Nitrosyl Complex Chlorides.—(*a*) $(NO)BiCl_4$. This yellow salt was prepared by the action of nitrosyl chloride on bismuth at room temperature (Sudborough, *J.*, 1891, 662) and was converted by bromine trifluoride into white, non-hygroscopic, water-insoluble bismuth trifluoride.

(*b*) $(NO)_2SnCl_6$. A two-fold excess of nitrosyl chloride was condensed on to a solution of 1 g. of stannic chloride in 10 c.c. of carbon tetrachloride and maintained at −20° for ½ hour (Rheinboldt and Wasserfuhr, *Ber.*, 1927, **60**, *B*, 732). The excess of reactants was removed *in vacuo*; some of the solid also distilled over. The product which remained after fluorination consisted of $(NO)_2SnF_6$ together with some stannic fluoride which resulted from decomposition of the former [Found : N, 8·8; Sn, 43·1; F, 39·0%; equiv., 271. Calc. for 88% of $(NO)_2SnF_6$ + 12% of SnF_4 : N, 9·1; Sn, 43·1; F, 39·0%; equiv., 271].

Nitrosyl Fluorosulphonate.—Nitrosyl pyrosulphate was prepared by treating equal volumes of nitrogen dioxide and sulphur dioxide at room temperature in a sealed tube (Jones, Price, and Webb, *loc. cit.*). The excess of gases was removed *in vacuo* [Found : N, 11·8; S, 27·8. Calc. for $(NO)_2S_2O_7$: N, 11·9; S, 27·2%]. This salt was freely soluble in bromine trifluoride and left a white hygroscopic solid on removal of excess of solvent. Its solution in water was free from sulphate and contained a trace of bromine. The fluorine content was determined by a thorium nitrate titration after distillation as fluorosilicic acid from 50% sulphuric acid. The sulphur was determined as barium sulphate after evaporation of all fluoride with hydrochloric acid [Found : N, 10·4; S, 23·6; F, 14·2%; equiv., 130. N : S : F = 1·01 : 1·00 : 1·01. $(NO)SO_3F$ requires N, 10·8; S, 24·9; F, 14·7%; equiv., 129].

Attempted Preparation of $(NO)SO_3F$ *from Fluorosulphonic Acid.*—Excess of fluorosulphonic acid was added to nitrosyl chloride and the solution heated. The excess of acid was distilled off at room temperature *in vacuo*; the temperature was raised to 80° to remove the last traces. A solution of the residue in water contained sulphate as well as fluorosulphonate [Found : N, 11·1; S, 24·8; F, 9·7. Calc. for $(NO)HSO_4$: N, 11·0; S, 25·2. Calc. for $(NO)SO_3F$: N, 10·8; S, 24·9; F, 14·7%]. On addition of nitrogen dioxide to fluorosulphonic acid a white gelatinous precipitate formed. The mixture was left overnight at 0° and excess of dioxide removed *in vacuo*. The product contained about 90% of nitrosyl fluorosulphonate (Found : N, 10·6; S, 25·5; F, 13·5%). In an experiment with nitrogen dioxide and excess of acid the product contained only 2·4% of fluorine.

Replacement Reactions with " Acids."—Nitrosyl pyrosulphate together with excess of arsenic trioxide was dissolved in bromine trifluoride. The residue had an equivalent weight of 239 after being kept at 50° for 6 hours *in vacuo*, and 216 after 3 more hours at 100° [Found : N, 6·4; As, 34·7; F, 50·3%; equiv., 216. Calc. for $(NO)AsF_6$: N, 6·5; As, 34·6; F, 52·6%; equiv., 217]. Nitrosyl pyrosulphate with an equivalent amount of antimonous oxide behaved similarly [Found : N, 5·3; F, 42·5%; equiv., 270. Calc. for $(NO)SbF_6$: N, 5·3; F, 42·9%; equiv., 266]. Nitrosyl fluoroarsenate and antimonate have been prepared by the action of nitrosyl fluoride on the corresponding pentafluorides (Ruff, Stauber, and Graff, *Z. anorg. Chem.*, 1908, **58**, 325). Excess of boric oxide gave a partial replacement; the product contained sulphur as well as boron [Found: F, 31·0%; equiv., 124. Calc. for $(NO)BF_4$: F, 65·0%; equiv., 117. Calc. for $(NO)SO_3F$: F, 14·7%; equiv., 129]. Stannous chloride however brought about no displacement. The product, after evacuation at 90°, contained bromine as well as sulphur and had a composition $(NO)SO_3F + SnF_4 + 0{\cdot}08BrF_3$, calculated from the equivalent weight 463 (Found: Br, 1·0; S, 12·5. Calc.: Br, 1·4; S, 13·8%).

Reactions with Potassium Dinitrososulphite.—The reaction of bromine trifluoride with this salt, prepared from potassium sulphite and nitric oxide (Weitz and Achtenberg, *Ber.*, 1933, **66**, 1718), gave an equimolecular mixture of potassium fluorobromite and fluorosulphonate (Found: Br, 24·7; F, 29·7%; equiv., 338. Calc. for $KSO_3F + KBrF_4$: Br, 24·0; F, 28·5%; equiv., 333). When the salt was mixed with an excess of arsenious oxide and treated with bromine trifluoride the sulphur, but not the nitrogen, was eliminated [Found: N, 2·8; As, 32·0; F, 50·5%; equiv., 898. Calc. for $2(KAsF_6 + NOAsF_6)$: N, 3·15; As, 33·6; F, 51·2%; equiv., 890].

Replacement Reactions with "Bases."—Silver and nitrosyl pyrosulphate in equivalent proportions were converted into silver fluorosulphonates with bromine trifluoride. This *salt* crystallised in shiny hygroscopic plates which were readily soluble in water (Found: Ag, 51·0; S, 15·5; F, 9·1%; equiv., 212. $AgSO_3F$ requires Ag, 52·1; S, 15·6; F, 9·2%; equiv., 207). The aqueous solution gave no precipitate with barium nitrate until it was acidified and boiled, but gave an immediate precipitate with nitron acetate. The elimination of nitrosyl fluoride in this reaction was shown by the loss of 35 mg. in flask weight compared with 1 mg. in the "acid" replacement reactions, and 5 mg. in the reaction of nitrosyl pyrosulphate alone.

Reaction of Bromine Trifluoride with Sulphur Trioxide.—Sulphur trioxide, prepared by passing sulphur dioxide and oxygen dried with concentrated sulphuric acid over platinized asbestos at 650°, was stored over phosphoric oxide and distilled directly into the reaction flask before use. It dissolved in bromine trifluoride without evolution of oxygen or liberation of bromine, and after 8 hours' evacuation at room temperature left a sticky white solid. This solid scarcely fumed in air, in marked contrast to sulphur trioxide, and was decomposed without violence by water and alcohol in contrast to bromine trifluoride. The solid analysed as $SO_3 + 0{\cdot}7BrF_3$ (equiv., 176) (Found: S, 16·0; Br, 29·2; F, 22·6. Calc. for $SO_3 + 0{\cdot}7BrF_3$: S, 18·2; Br, 31·8; F, 22·7%). In an experiment with excess of sulphur trioxide the product after 8 hours' evacuation was a pale yellow liquid which was only a little more viscous than bromine trifluoride and had the composition $BrF_3 + 1{\cdot}37SO_3$.

The experiments described above give some indication of the existence of a compound BrF_3,SO_3 which may well be $BrF_2^+SO_3F^-$. Reactions of sulphur trioxide with "bases" in bromine trifluoride provide more certain evidence for the existence of this "acid."

Reactions of Sulphur Trioxide Solutions.—Sulphur trioxide was distilled into the reaction flask and weighed. An equivalent of potassium sulphate was added and the mixture dissolved in bromine trifluoride. The product which remained after removal of solvent was potassium fluorosulphonate (Found: K, 28·0; F, 14·1%; equiv., 277. Calc. for $2KSO_3F$: K, 28·3; F, 13·8%; equiv. 276). The reactions which are believed to occur are:

$$K_2SO_4 \xrightarrow{BrF_3} 2KBrF_4 + (BrF_2)SO_3F$$

$$SO_3 \xrightarrow{BrF_3} (BrF_2)SO_3F$$

$$2KBrF_4 + 2(BrF_2)SO_3F = 2KSO_3F + 4\,BrF_3$$

Sulphur trioxide and excess of nitrogen dioxide left a white solid after treatment with bromine trifluoride. This *compound* dissolved in water to give a solution free from nitrite and bromide [Found: N, 9·53; S, 21·8; F, 13·4%; equiv., 144. N : S : F = 1·00 : 1·00 : 1·03. $(NO_2)SO_3F$ requires N, 9·65; S, 22·2; F, 13·1%; equiv., 145]. Nitrosyl fluorosulphonate could be prepared similarly from nitrosyl chloride and sulphur trioxide. This method would be more convenient than the preparation from nitrosyl pyrosulphate.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

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