The Preparation and Some Reactions of Nitryl Fluoride.

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A new and simple method of preparing nitryl fluoride, NO_2F, in quantity is described. It is obtained in almost quantitative yield from sodium nitrite by the action of fluorine. The reactions of the compound with many elements and with some non-metallic fluorides and oxides are detailed. It is shown that certain of these reactions lead to new compounds: dinitronium hexafluorogermanate, and nitronium pentafluoroselenite, pentafluorotellurite, and hexafluoroiodate have been prepared.

Although Moissan and Lebeau (*Compt. rend.*, 1905, **140**, 1621) claimed to have prepared nitryl fluoride, NO_2F, and the compound has been the subject of a number of communications, there is apparently no report of a simple method for its preparation in quantity. Moissan and Lebeau thought they obtained the material as the result of the spontaneous combustion of nitric oxide and fluorine; but as they also mentioned (*ibid.*, p. 1573) that fluorine did not react with nitrogen peroxide, what they actually had is open to doubt. Ruff, Menzel, and Neumann (*Z. anorg. Chem.*, 1932, **208**, 293) prepared nitryl fluoride from fluorine and nitrogen peroxide, and the qualitative reactions of their preparation differed so greatly from those given by Moissan and Lebeau that they concluded that the earlier workers were really handling a mixture of nitrosyl fluoride (m. p. −132·5°, b. p. −59·9°) and fluorine. This method of preparation does not give a pure product; and, in order to reduce contamination by silicon, Faloon and Kenna (*J. Amer. Chem. Soc.*, 1951, **73**, 2937) used a lower temperature and treated nitrogen peroxide, liquefied in a Fluorothene vessel, with fluorine. In a further attempt to avoid impurity Schmeisser and Elisher (*Z. Naturforsch.*, 1952, **7**, *b*, 583) passed a stream of nitryl chloride over silver fluoride in a platinum tube at 240°, but obtained only a 5% conversion.

Previous workers differ about the behaviour of nitryl fluoride towards glass. We have found the attack on glass at room temperature to be so slow as to be negligible in the times required for an experiment, but at higher temperatures it is appreciable Faloon and Kenna (*loc. cit.*) stated that nitryl fluoride in a glass vessel becomes contaminated with silicon tetrafluoride, but this is unlikely since, as we show below, silicon tetrafluoride combines with nitryl fluoride to form the white, solid dinitronium hexafluorosilicate which is insoluble in nitryl fluoride.

We have found that fluorine reacts with slightly warm, dry sodium nitrite to give an almost quantitative conversion of the nitrogen into nitryl fluoride, and that since this reaction can be carried out in glass, it forms the most convenient means of preparing the compound. We have made 50 g. per run but this amount could be increased indefinitely by using more nitrite, always provided the temperature is controlled by adjusting the fluorine flow. The reaction may be formally represented by the successive stages

$$2NaNO_2 + F_2 \longrightarrow 2NaF + 2NO_2$$
$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

but its quantitative character suggests that the sequence is a rapid one and that it probably takes place on the surface of the reaction solid and may possibly be, in the main, a single reaction. The relatively low temperature involved makes the use of glass apparatus possible, and fractionation in a vacuum readily rids the product of the excess of fluorine and traces of nitrogen peroxide whichare condensed with it. Thus treated, nitryl fluoride is a colourless liquid freezing to a white solid.

Reactions of Nitryl Fluoride with Elements.—(*a*) *Metals.* According to their behaviour with nitryl fluoride, metals fall into three groups: (i) those which form an oxide and a fluoride, (ii) those which form an oxyfluoride, and (iii) those which do not react below about 300°.

The first group is by far the largest; and the fact that the gases issuing from the reaction show, on condensation, the blue colour of dinitrogen trioxide indicates that the reaction takes place in at least two stages:

$$M + 2NO_2F \longrightarrow MF_2 + 2NO_2$$
$$M + NO_2 \longrightarrow MO + NO$$
$$NO_2 + NO \longrightarrow N_2O_3$$

The metals chromium, molybdenum, tungsten, and uranium constitute the second group. The oxides of these metals react with nitryl fluoride to give the oxyfluorides. This suggests consecutive reactions involving formation of oxide and leading to the overall result represented by $M + 2NO_2F \longrightarrow MO_2F_2 + 2NO$, provided the temperature is kept below a certain maximum. Above that point oxides and fluorides are formed and the oxyfluoride itself is decomposed.

Examples of the third group are beryllium, magnesium, calcium, and gold.

(*b*) *Non-metals.* So many of these react with nitryl fluoride to give nitronium salts as to make the reaction almost a general method of preparation. Exceptions are bromine and tellurium. The compounds we have prepared are nitronium tetrafluoroborate, $(NO_2)BF_4$; dinitronium hexafluoro-silicate, $(NO_2)_2SiF_6$, and -germanate, $(NO_2)_2GeF_6$; nitronium hexafluorometa-phosphate, -arsenate, and -antimonate, $(NO_2)PF_6$, etc.; nitronium pentafluoroselenite, $(NO_2)SeF_5$, and hexafluoroiodate, $(NO_2)IF_6$. There seems little doubt that the fluoride is first formed and that this reacts with the appropriate number of molecules of nitryl fluoride; *e.g.*,

$$Si + 4NO_2F \longrightarrow SiF_4 + 4NO_2$$
$$SiF_4 + 2NO_2F \longrightarrow (NO_2)_2SiF_6$$

since we have shown that the fluorides combine thus with nitryl fluoride. Several of these nitronium compounds have been prepared previously by other methods which may well have involved nitryl fluoride as the active agent. Thus Woolf and Emeléus (*J.*, 1950, 1050) obtained $(NO_2)BF_4$, $(NO_2)PF_6$, $(NO_2)AsF_6$, and $(NO_2)SbF_6$ by the action of nitrogen peroxide together with bromine trifluoride on a suitable compound of the non-metal; and Schmeisser and Elisher (*loc. cit.*) made $(NO_2)BF_4$ and $(NO_2)_2SiF_6$ by adding a mixture of anhydrous hydrofluoric acid and the appropriate fluoride to a solution of dinitrogen pentoxide in nitromethane.

The distribution of known nitronium fluoro-compounds in relation to the Periodic Table is set out below.

Gp. I	Gp. II	Gp. III	Gp. IV	Gp. V	Gp. VI	Gp. VII
		$(NO_2)BF_4$				
			$(NO_2)_2SiF_6$	$(NO_2)PF_6$		
			$(NO_2)_2GeF_6$	$(NO_2)AsF_6$	$(NO_2)SeF_5$	$[(NO_2)BrF_4]$
			$(NO_2)_2SnF_6$	$(NO_2)SbF_6$	$[(NO_2)TeF_5]$	$(NO_2)IF_6$
$(NO_2)AuF_4$						

Two of the compounds, shown in square brackets, are of special interest. The tellurium compound has been made, not from the element but from the dioxide, TeO_2, which (unlike the trioxide) reacts readily with nitryl fluoride. The nitronium fluoroselenite can also be made in this way as well as from the element. The reaction of nitryl fluoride with elementary tellurium is being further investigated because of the anomalous results obtained under what appear to be identical conditions (see p. 1123).

When nitryl fluoride is bubbled through bromine trifluoride the liquid becomes yellow and viscous. We have not been able to separate a solid by cooling, but we believe the material contains $(NO_2)BrF_4$, the unstable base first postulated by Woolf and Emeléus (*loc. cit.*). The yellow colour is doubtless due to the nitronium ion. Incidentally, the same colour is observed when selenium tetrafluoride and iodine pentafluoride are severally treated with nitryl fluoride. The difficulty of isolating $(NO_2)BrF_4$ is understandable in view of the properties of the nitronium hexafluoroiodate; this exhibits a high dissociation pressure even at room temperature, but is stable enough at lower temperatures. It is hydrolysed by water almost quantitatively according to the equation $(NO_2)IF_6 + 4H_2O = HNO_3 + HIO_3 + 6HF$, there being no more than a trace of free iodine in the final solution.

EXPERIMENTAL

Preparation of Nitryl Fluoride.—This was conveniently prepared by passing a stream of fluorine (about 4 g./hr.), diluted with nitrogen (1 : 1 by vol.), over sodium nitrite (50 g.), dried by heating to 140° before charging and then flamed out in a vacuum in the glass reaction tube. The optimum concentration of fluorine depends upon the amount and distribution of the nitrite; if it is too great a yellow flame appears—probably of nitrogen peroxide burning in fluorine—and there is much attack on the glass. The gaseous product, which consisted of nitryl fluoride contaminated with a little nitrogen peroxide and the excess of fluorine, was condensed in a trap by means of liquid air and fractionated in a vacuum to free it from fluorine and nitrogen peroxide (Found: N, 21·2; F, 29·1%; *M*, 64·6. Calc. for NO_2F: N, 21·5; F, 29·2%; *M*, 65). The colourless liquid boiled between −73° and −72° under atmospheric pressure, and at *ca.* −160° froze to a white solid.

Reaction of Nitryl Fluoride with Elements.—In the case of solids, nitryl fluoride was passed over the element spread in a glass tube, and, when necessary, heat was applied to start the reaction. The solid residue, except where otherwise stated, was examined by qualitative chemical tests and *X*-ray. *X*-Ray powder photographs were taken with use of Co-$K\alpha$ radiation, the samples being mounted in Pyrex capillaries. In the case of potassium, in addition to the spectrum of potassium fluoride, the *X*-ray evidence included lines which could be ascribed to potassium dioxide, KO_2, and the yellow colour of the solid was in keeping with this. Qualitatively, the material reacted with water, showed strong oxidising properties, and gave evidence of a peroxide. The presence of some of the peroxide, K_2O_2, is not excluded. Again the traces of the highest oxide, mentioned in connection with phosphorus, arsenic, and antimony, were all displayed in the *X*-ray photographs and established by qualitative chemical tests. In every instance blue dinitrogen trioxide was seen in the condensate, indicating a reduction of nitrogen peroxide consequent on oxide formation. Data for the mercury fluorides do not appear in the S.M.T. Index but the greenish colour and the qualitative reactions all pointed to the material's being mercurous fluoride.

The volatile products were condensed or frozen in traps and examined qualitatively.

The results tabulated call for remarks on three elements only. Bismuth formed neither oxide nor nitronium compound: the white solid contained neither BiF_3 nor Bi_2O_3, and qualitative tests showed the presence of fluoride and the absence of nitrogen. On the other hand, uranium which first glowed white-hot produced a sublimate of green uranium tetrafluoride. If the current of nitryl fluoride was then stopped, the original solid was found to have increased many times in bulk and become black. When the reaction was started again, this solid glowed red and the greyish final product consisted mainly of uranyl fluoride with a little U_3O_8. Provided the reaction temperature was kept below 300° the oxyfluoride was formed from either metal or oxide.

Tellurium behaves peculiarly; the reaction which started spontaneously at room temperature and evolved much heat gave, under what appeared to be identical conditions, either tellurium tetrafluoride (Found: Te, 61·1; F, 36·3. Calc. for TeF_4: Te, 62·7; F, 37·3%) or a yellow liquid which could be separated into two fractions, b. p. 85—86° and 121—122°, the former being the main constituent. The reaction with tellurium is being further examined with a view to define the conditions leading to the two types of product and to establish the nature of the compounds present in the liquid product.

The behaviour of sulphur and carbon, both of which are attacked by nitryl fluoride, was so obviously complex as to call for a more detailed study which we reserve for the future.

Element	Temperature conditions to initiate reaction	Observation	Products of reaction
H_2	200—300°	Explodes	—
Li	200—300	Burns with red flame	LiF
Na	Room temp.	Burns with yellowish-white flame	NaF, Na_2O_2 (traces of $NaNO_3$, $NaNO_2$)
K	Room temp.	Burns with lilac flame	KF, KO_2
Cu	Up to 300°	No obvious reaction	Some Cu_2O, CuO
Ag	Mild warming	First turns black then yellow	Ag_2O first formed; further heating gives AgF
Au	Up to 300°	No reaction	—
Be	Up to 300°	No reaction	—
Mg	Up to 300°	No reaction	—
Ca	Up to 300°	No reaction	—
Zn	Mild warming	Glows red and burns with yellow flame	ZnF_2, ZnO
Cd	Mild warming	Glows red	CdF_2, CdO
Hg	Mild warming	—	Hg_2F_2
B	Room temp.	Glows red	$(NO_2)BF_4$
Al	Mild warming	Glows white	AlF_3, Al_2O_3
Ti	Mild warming	Glows white	TiF_4, TiO_2
Zr	Room temp.	Glows white	ZrF_4, ZrO_2
Th	Room temp.	Glows white	ThF_4, ThO_2
Si	Room temp.	Glows red	$(NO_2)_2SiF_6$
Ge	Mild warming	No obvious heating	$(NO_2)_2GeF_6$
Sn	Mild warming	Metal melts	SnF_4, SnO_2
Pb	Mild warming	Meltal melts	PbF_2, PbO
V	Mild warming	Glows red	$(NO_2)VOF_4$, $(NO_2)VF_6$
P (red)	Room temp.	Glows red	$(NO_2)PF_6$, trace P_2O_5
As	Room temp.	—	$(NO_2)AsF_6$ trace As_2O_5
Sb	Mild warming	Becomes very hot, first forms drops of SbF_5	$(NO_2)SbF_6$ trace Sb_2O_5
Bi	200—300°	White solid forms	BiF_5 (probably)
Cr	Mild warming	—	CrO_2F_2, trace CrF_3
Mo	Room temp.	Glows white	MoO_2F_2, $MoOF_4$
W	Mild warming	Glows red	WOF_4
U	Room temp.	(*a*) Glows white, then (*b*) glows red	(*a*) UF_4, U_3O_8, UO_2; (*b*) UO_2F_2
Se	Room temp.	First forms drops of SeF_4	$(NO_2)SeF_5$
Te	Room temp.	Much heat evolved	(i) TeF_4; (ii) yellow liquids
Mn	200—300°	Glows red	MnF_2, and probably Mn_2O_3
Br	Room temp.	No reaction	—
I	Mild warming	First forms drops of IF_5	$(NO_2)IF_6$
Fe	Mild warming	Glows red	FeF_3, Fe_2O_3
Co	Mild warming	Glows red	CoF_2
Ni	Mild warming	Glows red	NiF_2, NiO

Reactions of Nitryl Fluoride with Non-Metallic Fluorides.—(i) Boron trifluoride, prepared by heating calcium fluoride with boron trioxide in concentrated sulphuric acid, was mixed with gaseous nitryl fluoride. The exothermic reaction produced white, solid nitronium tetrafluoroborate. It was analysed by dissolving it in cold aqueous sodium hydroxide and estimating the nitrogen as ammonia after reduction with Devarda's alloy. The products of hydrolysis, nitric and fluoroboric acids, were determined as the mixed nitron salt [Found: N, 9·9. Calc. for $(NO_2)BF_4$: N, 10·5%. Found, for nitron salt: C, 61·9; H, 4·86; N, 16·45. Calc. for $C_{20}H_{16}N_4HNO_3 + C_{20}H_{16}N_4HBF_4$: C, 61·9; H, 4·4; N, 16·2%].

(ii) Prepared from its elements, silicon tetrafluoride combined strongly exothermally with nitryl fluoride to give white, solid dinitronium hexafluorosilicate. Nitrogen was determined as above, and fluorine as lead chlorofluoride. Silicon was obtained by fusion with sodium carbonate–potassium nitrate, dissolving the melt in water, evaporating to dryness with hydrochloric acid, and weighing as SiO_2 [Found: Si, 11·6; F, 47·7; N, 11·8. Calc. for $(NO_2)_2SiF_6$: Si, 12·0; F, 48·7; N, 12·0%].

(iii) Germanium tetrafluoride, obtained by heating barium fluorogermanate to 700° in a silica bulb, combined in the gaseous phase with nitryl fluoride with evolution of heat to give a white solid, *dinitronium hexafluorogermanate*. Germanium was determined as the dioxide, and fluorine as lead chlorofluoride, after the original solid had been decomposed with aqueous sodium hydroxide solution [Found: Ge, 25·5; F, 41·4; N, 10·4. $(NO_2)_2GeF_6$ requires Ge, 26·1; F, 40·9; N, 10·1%].

(iv) Phosphorus pentafluoride and nitryl fluoride gave, with slight evolution of heat, white nitronium hexafluorophosphate. Phosphorus was determined in the aqueous extract of a sodium carbonate–potassium nitrate fusion as ammonium phosphomolybdate [Found: P, 16·0; N, 7·6. Calc. for $(NO_2)PF_6$: P, 16·2; N, 7·3%].

(v) Arsenic pentafluoride, resulting from the fluorination of arsenious oxide, reacted with nitryl fluoride with slight evolution of heat to give white, solid nitronium hexafluoroarsenate. Arsenic was determined as silver arsenate from the aqueous extract of a sodium carbonate–potassium nitrate fusion [Found: As, 31·4; N, 6·3. Calc. for $(NO_2)AsF_6$: As, 31·9; N, 6·0%].

(vi) Antimony pentafluoride, from the action of fluorine on the trioxide, reacted extremely vigorously with nitryl fluoride (the pentafluoride was caused to boil) to produce white, solid nitronium hexafluoroantimonate. Passage of nitryl fluoride over the solid was continued until all the pentafluoride was consumed, after which the reaction vessel was heated at 100° under vacuum for some time. Antimony was determined as the sulphide and fluorine as calcium fluoride [Found: Sb, 43·8; F, 41·0; N, 4·6. Calc. for $(NO_2)SbF_6$: Sb, 43·2; F, 40·4; N, 5·0%].

(vii) Selenium tetrafluoride, obtained by interaction of the elements at 0°, was treated with nitryl fluoride. It became viscous and, in time, gave white, solid *nitronium pentafluoroselenite.* The compound was heated at 100° under vacuum to remove residual selenium tetrafluoride. Selenium was determined by reduction to the element with sulphur dioxide, and fluorine as lead chlorofluoride after distillation from 50% sulphuric acid [Found: Se, 36·5; F, 43·9; N, 6·4. $(NO_2)SeF_5$ requires Se, 35·9; F, 43·2; N, 6·4%].

(viii) Bromine trifluoride, prepared from its elements, was treated with a stream of nitryl fluoride. The liquid became yellow, then viscous, and appeared to have some solid in suspension. Attempts to separate this solid or to increase its amount by cooling the liquid were unavailing, as was also evaporation in a vacuum which gave a white solid containing bromine, fluorine, nitrogen, and silicon, but of indefinite composition.

(ix) Iodine pentafluoride, prepared from the elements, and saturated with nitryl fluoride, first became yellow and then yielded white, solid *nitronium hexafluoroiodate.* This was stable at low temperatures but at room temperature showed appreciable dissociation into nitryl fluoride and iodine pentafluoride. Iodine was determined by reduction with sulphur dioxide and precipitation as silver iodide, and fluorine as calcium fluoride [Found: I, 45·2; F, 40·2; N, 4·6. $(NO_2)IF_6$ requires I, 44·3; F, 39·7; N, 4·9%]. The discrepancy in the analyses corresponds to, and is probably due to, the presence of iodine pentafluoride arising from decomposition, to the extent of 7% molar.

Reactions of Nitryl Fluoride with Oxides.—(i) Vanadium pentoxide, slightly warmed in nitryl fluoride, first became a darker red, then yellow, and finally white; this material melted and rapidly reacted with more nitryl fluoride to give a vapour which froze to a white solid further along the tube. By stopping the reaction at intermediate stages, it was shown that the primary products were vanadium oxyfluoride and pentafluoride. These individually reacted with the molecule of nityl fluoride to give a mixture of the new *nitronium tetrafluoro-oxyvanadate*(v) and *nitronium hexafluorovanadate*(v) as the composite sublimate [Found: V, 25·0; F, 43·9; N, 6·8. $(NO_2)VOF_4$ requires V, 27·0; F, 40·2; N, 7·4. $(NO_2)VF_6$ requires V, 24·2; F, 54·0; N, 6·6%):

$$\begin{tikzcd} V_2O_5 \arrow[r] & VOF_3 \arrow[r] \arrow[d] & VF_5 \arrow[d] \\ & (NO_2)VOF_4 & (NO_2)VF_6 \end{tikzcd}$$

These findings agree with those of Sharpe (*J.*, 1951, 798) who says in reference to his use of nitrogen peroxide and bromine trifluoride: "Attempts to obtain . . . nitronium hexafluorovanadates gave products intermediate in composition between the tetrafluoro-oxyvanadates and hexafluorovanadates."

(ii) Sulphur trioxide, strictly anhydrous, reacted exothermally with nitryl fluoride, first melting, then becoming yellow—owing possibly to its dissolving the nitronium ion—and finally colourless. The white solid left on cooling after the reaction was nitronium fluorosulphonate [Found: S, 23·0; F, 13·7; N, 9·6. Calc. for $(NO_2)SO_3F$: S, 22·1; F, 13·1; N, 9·7%], which had been prepared by treating sulphur trioxide with nitrogen peroxide and bromine trifluoride (Woolf, *J.*, 1950, 1053).

(iii) Selenium dioxide reacted with nitryl fluoride at room temperature to give, first, selenium tetrafluoride which then combined with more nitryl fluoride to give white, crystalline *nitronium pentafluoroselenite* [Found : Se, 36·7. $(NO)_2SeF_5$ requires Se, 35·9%].

(iv) The reaction between tellurium dioxide and nitryl fluoride proceeded steadily after being started by slight initial warming. The considerable evolution of heat kept the product, *nitronium pentafluorotellurite,* molten (m. p. ~110°). It set to a white solid on cooling [Found : Te, 47·8; F, 36·0; N, 4·9. $(NO_2)TeF_5$ requires Te, 47·5; F, 35·4; N, 5·2%]. It is noteworthy that nitryl fluoride had no action on tellurium trioxide.

(v) Nitryl fluoride had little effect on glass at room temperature, but, on slight warming, attacked it appreciably. Nitrogen dioxide was evolved and a feathery white solid was deposited on the surface of the glass. This solid was insoluble in nitryl fluoride and contained nitrogen, fluorine, silicon, and boron. Silicon and nitrogen were determined, as above, and also fluorine on a sample not subjected to fusion, in an attempt to estimate the amount of $(NO_2)_2SiF_6$ present. The analyses clearly indicate a mixture of nitronium fluorosilicate and fluoroborate, the rather high fluorine content being due to hydroysis of the BF_4^- ion [Found: Si, 11·0; F, 48·7; N, 11·8. Calc. for 90% $(NO_2)_2SiF_6$ + 10% $(NO_2)BF_4$: Si, 10·8; F, 43·7 (BF_4^- ion being assumed to be undissociated) : N, 11·9%].

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