Reactions of Oxides of Nitrogen with the Group V Pentafluorides and Stannic Fluoride

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The pentafluorides of phosphorus, arsenic, and antimony have been treated with *inter alia*, nitric oxide, dinitrogen trioxide, nitrogen dioxide, and dinitrogen pentoxide, and stannic fluoride has been treated with nitrogen dioxide. Nitric oxide does not combine chemically with phosphorus pentafluoride, and yields only a single involatile phase, $NOAsF_6$, with arsenic pentafluoride. The other reactions yield complex mixtures, all of which contain nitrosonium and/or nitronium salts. Evidence is presented for the formation of complex oxyfluoride species containing anions of general formula $[MOF_4]^-$ (M = P, As, Sb). The $[Sb_2F_{11}]^-$ anion is frequently formed in reactions involving antimony pentafluoride.

Antimony pentafluoride reacts with oxides of nitrogen in the liquid phase to form nitrito- or nitrato-fluorides, and stannic fluoride also forms a nitrato-fluoride when treated with liquid dinitrogen tetroxide.

Materials of composition SbF_5,NO_2 and AsF_5,NO_2 were first reported by Aynsley *et al.*[1] as products of the interactions of the appropriate pentafluorides with gaseous nitrogen dioxide. SbF_5,NO_2 was described as a white, moisture-sensitive solid which dissociated without melting into the parent compounds at 150°. The arsenic compound, which was also reported by Schmeisser, Fink, and Brändle[2] had similar properties to its antimony analogue. Material of composition PF_5,NO_2 was first reported by Tassel[3] and later by Muetterties *et al.*[4]

The related nitrogen oxide–boron trifluoride systems have been studied in great detail, particularly by Evans *et al.*[5] and Ray.[6] Reactions (1)—(3) were suggested by these workers, although the formation of NO_2BF_4 in reaction (2) was disputed by Ray. Morrow and Young[7] have recently carried out an incomplete investigation of the arsenic pentafluoride–nitrogen dioxide system, and have suggested the formation of ionic nitroxy-species in this system also.

$$3N_2O_3 + 8BF_3 \longrightarrow 6NOBF_4 + B_2O_3 \qquad (1)$$

$$3N_2O_4 + 8BF_3 \longrightarrow 3NOBF_4 + 3NO_2BF_4 + B_2O_3 \qquad (2)$$

$$3N_2O_5 + 8BF_3 \longrightarrow 6NO_2BF_4 + B_2O_3 \qquad (3)$$

We report here the results of treating oxides of nitrogen with the pentafluorides of phosphorus, arsenic, and antimony. To obtain essential background information, the reaction between nitrogen dioxide and stannic fluoride has also been studied. The reaction products have been characterised chiefly by i.r. spectroscopy and *X*-ray powder diffraction.

RESULTS

At −196° phosphorus pentafluoride interacts with nitric oxide to give a brilliant red colour. Intense colours have been observed[8] under similar conditions in the related boron trifluoride–nitric oxide system, and are believed to be due to a charge-transfer complex. The colour fades on warming. At room temperature there is no evidence of reaction, and the starting materials can be recovered unchanged.

Phosphorus pentafluoride reacts with dinitrogen trioxide, nitrogen dioxide, and dinitrogen pentoxide to give white, moisture-sensitive solids. Phosphorus oxytrifluoride is formed as a volatile product in all cases. The solid products evidently either decompose on standing or react with the glass storage vessels with the evolution of brown fumes.

Treatment of arsenic pentafluoride with nitric oxide at

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[1] E. E. Aynsley, R. D. Peacock, and P. L. Robinson, *Chem. and Ind.*, 1951, 1117.

[2] M. Schmeisser, W. Fink, and K. Brändle, *Angew. Chem.*, 1957, **69**, 780.

[3] E. Tassel, *Compt. rend.*, 1890, **110**, 1264.

[4] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nuclear Chem.*, 1960, **16**, 52.

[5] J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, 1964, **3**, 857.

[6] A. B. Ray, *Inorg. Chem.*, 1967, **6**, 110.

[7] S. I. Morrow and A. R. Young, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 349.

[8] G. R. Finlay, *J. Chem. Educ.*, 1947, **24**, 149; W. Bues, *Angew. Chem.*, 1952, **64**, 621.

low temperatures also leads to a brilliant red colour (*cf.* PF_5). On warming to 25°, however, the colour disappears and the white solid $NOAsF_6$ is formed, together with volatile arsenic trifluoride ($2NO + 3AsF_5 \longrightarrow 2NOAsF_6 + AsF_3$). The remaining nitrogen oxides react with arsenic pentafluoride to form white, moisture-sensitive solids that remain stable in glass for long periods. Volatile products are not formed.

The reactions of the oxides of nitrogen with antimony pentafluoride are more complicated than the foregoing. With nitric oxide, gaseous nitrogen dioxide, and dinitrogen pentoxide white, moisture-sensitive solids are formed. There is no evidence of volatile products. With liquid dinitrogen trioxide and liquid nitrogen dioxide, reactive yellow solids are formed which, under vacuum, lose nitrogen dioxide slowly at 25°, and rapidly at 100°, to give stable, white, moisture-sensitive solids.

The i.r. absorption frequencies and *X*-ray powder data of the products are shown in Tables 1—6, in which comparison is made with authentic samples of nitrosonium and nitronium salts.

DISCUSSION

(*a*) *Reactions of Phosphorus Pentafluoride.*—From Tables 1 and 2 the products of reactions (4)—(6) can be identified. These complex species, however, are stable under anhydrous conditions, and the presence of additional less stable species is suggested by the instability of the products, and the decomposition of the nitronium species initially formed by the reaction of phosphorus pentafluoride with nitrogen dioxide.

$$PF_5 + N_2O_3 \longrightarrow NOPF_6 \qquad (4)$$

$$PF_5 + NO_2 \longrightarrow NOPF_6 \qquad (5)$$

$$PF_5 + N_2O_5 \longrightarrow NO_2PF_6 \qquad (6)$$

TABLE 1

I.r. absorption frequencies of solid products of reactions of PF_5 with nitrogen oxides (cm.$^{-1}$)

PF_5 + N_2O_3	PF_5 + NO_2[a]	PF_5 + NO_2[b]	PF_5 + N_2O_5	$NOPF_6$	NO_2PF_6	Assignment
	2373s	2375w	2372s		2373s	$\nu(NO_2^+)$
2340m	2340m	2340m		2340m		$\nu(NO^+)$
840vs[c]	840vs[c]	840vs[c]	840vs[c]	830vs	830vs	$\nu_3(PF_6^-)$
	600m		602m		601m	$\delta(NO_2^+)$
558ms	555ms	555ms	552ms	555ms	554ms	$\nu_4(PF_6^-)$

[a] Immediately after reaction. [b] After several weeks. [c] Absorption very broad with ill-defined shoulders between 900 and 1000 cm.$^{-1}$.

TABLE 2

Debye *X*-ray powder data for solid products from reactions of PF_5 with nitrogen oxides (*d* spacings in Å)

$PF_5 + N_2O_3$	$PF_5 + NO_2$	$PF_5 + N_2O_5$	$NOPF_6$	NO_2PF_6
	5·75w			
5·07w				
		4·65s		4·67s
4·56s	4·54s		4·55s	
		4·31w		4·31w
3·95s	3·95s	3·95s	3·95s	3·95s
	3·78w	3·76s		3·74s
	3·49w			
	3·34m			
	3·06w	3·05m		3·06m
		2·80w		2·80w
2·78m	2·79m		2·79m	
		2·72w		2·72w
		2·58w		2·57w
2·38w	2·38m	2·38w	2·38w	
		2·30m		2·29m
2·27w	2·28m		2·27w	
2·17w				
		2·15m		2·15m
		1·96m		1·96m
	1·80m			
		1·79w		1·79w
		1·77w		1·77w
1·76w	1·76w		1·76w	
		1·63w		1·63w
1·61w	1·61m		1·61w	

(b) *Reactions of Arsenic Pentafluoride.*—From Tables 3 and 4 the products of reactions (7)—(10) can be identified. Further study of Tables 3 and 4, however, shows that these products are not single compounds, but mixtures (except for the product formed from nitric

$$AsF_5 + NO \longrightarrow NOAsF_6 \qquad (7)$$

$$AsF_5 + N_2O_3 \longrightarrow NOAsF_6 \qquad (8)$$

$$AsF_5 + NO_2 \longrightarrow NOAsF_6 \qquad (9)$$

$$AsF_5 + N_2O_5 \longrightarrow NO_2AsF_6 \qquad (10)$$

TABLE 3

I.r. absorption frequencies of solid products from reactions of AsF_5 with nitrogen oxides (cm.$^{-1}$)

AsF_5 + NO	AsF_5 + N_2O_3	AsF_5 + NO_2	AsF_5 + N_2O_5	$NOAsF_6$	NO_2-AsF_6	Assignment
		2368ms	2365ms		2365ms	$\nu(NO_2^+)$
2334m	2332m	2334m		2334m		$\nu(NO^+)$
	895s	900s	900s			
700vs	700vs	700vs	700vs	700vs	700vs	$\nu_3(AsF_6^-)$
		601m	596s		602ms	$\delta(NO_2^+)$

TABLE 4

Debye *X*-ray powder data for solid products from reactions of AsF_5 with nitrogen oxides (*d* spacings in Å)

AsF_5 + NO	AsF_5 + N_2O_3	AsF_5 + NO_2	AsF_5 + N_2O_5	$NOAsF_6$	NO_2-AsF_6
			5·10m		5·11ms
			4·85s		4·88s
	4·94s				
4·70s	4·65s	4·73s		4·67s	
			4·52s		4·54s
4·06s	4·06s	4·08s		4·06s	
	3·85ms	3·84m	3·87s		
	3·65m				
			3·55s		3·54s
			3·38w		3·38m
	3·32m				
	3·17ms	3·13w			
			2·91w		2·91m
2·88s	2·88ms	2·87s		2·87s	
			2·69vw		2·69w
2·45m	2·45w	2·45w	2·45w	2·45w	2·45m
2·34ms	2·34w	2·34m		2·34m	
			2·32w		2·32m
	2·25w				
			2·21m		2·21s
			2·06vw		2·06w
2·02m	2·03m	2·03w	2·02vw	2·02w	2·02w
	1·99w				
			1·92vw		1·92vw
1·86ms	1·86w	1·87w		1·86m	
			1·85w		1·85w
1·81ms	1·81m	1·82m		1·81m	
			1·78w		1·78m
			1·69w		1·69m
1·65ms	1·65w	1·65mw		1·65m	
1·56ms	1·56w	1·56mw		1·56m	

oxide). The nitronium species formed in the reaction with nitrogen dioxide is apparently not NO_2AsF_6, and the strong i.r. absorptions at 890—900 cm.$^{-1}$ cannot be attributed to the AsF_6^- ion.

(c) *Reactions of Antimony Pentafluoride*.—(i) *With nitric oxide*. Although the nitrosonium ion can be identified in the i.r. spectrum (Table 5) of the product, there is no evidence of the SbF_6^- ion, or of $NOSbF_6$ in the *X*-ray powder pattern (Table 6). The stoicheiometry of the reaction suggests that the principal components are $NOSb_2F_{11}$ and $SbF_5(SbF_3)_2$, formed in reaction (11) (Found: N, 2·2; F, 41·1. $N_4O_4Sb_{11}F_{55}$ requires N, 2·2; F, 40·5%).

$$4NO + 11SbF_5 \longrightarrow 4NOSb_2F_{11} + SbF_5(SbF_3)_2 \quad (11)$$

Certain of the i.r. absorption frequencies of this product agree closely with those of other $[Sb_2F_{11}]^-$ systems recently isolated. Thus J. K. Ruff[9] reports absorptions at 490—520 cm.$^{-1}$ and 690—710 cm.$^{-1}$ for $[N_2F]^+[Sb_2F_{11}]^-$ and $[N_2F_3]^+[Sb_2F_{11}]^-$, and Weidlein and Dehnicke[10] report similar absorptions for $[VO_2]^+$-$[Sb_2F_{11}]^-$. The formation of $SbF_5(SbF_3)_2$, previously prepared by O. Ruff and Plato,[11] is difficult to confirm since it has no clear i.r. absorption and is practically amorphous to *X*-rays. However, qualitative tests show the presence of antimony(III) in the product, and the *X*-ray powder data show SbF_3 to be absent.

TABLE 5

I.r. absorption frequencies of solid products from reactions of SbF_5 with nitrogen oxides (cm.$^{-1}$)

SbF_5 + NO	SbF_5 + NO_2(gas)	SbF_5 + N_2O_5	SbF_5 + N_2O_3 [a]	SbF_5 + N_2O_3 [a]	SbF_5 + N_2O_4 [b]	SbF_5 + N_2O_4 [b]	$NOSbF_6$	NO_2SbF_6	Assignment
	2372ms	2375s			2375s	2377s		2375s	(NO_2^+)
2337m	2338m		2340ms	2340ms	2340m	2341m	2339m		(NO^+)
			2280w		2265w				
			1865w						
			1745m						
					1672w				
			1600w						
					1580m				
			1295m		1300m				
	840w		840ms	840ms	845m	850m			
	770m,sh	765m,sh				770s,sh			
	722vs	720} vs,b	720vs	720vs	725s	720s			
690vs	690vs	655}							($Sb_2F_{11}^-$)
	660vs		660vs	660vs	660vs	665vs	665vs	668vs	(SbF_6^-)
	594m	594m			600m	600m		597ms	(NO_2^+)
	555m	555m	560m	560m	560m	560m			
498m	490m	485m							($Sb_2F_{11}^-$)
			460m		460m				

[a] SbF_5 + liquid nitrogen oxide (yellow product). [b] Product (*a*) heated (white).

(ii) *With gaseous nitrogen dioxide and dinitrogen pentoxide*. Bands due to the $[Sb_2F_{11}]^-$ ion are also evident in the spectra of the products of these reactions. The products of reactions (12) and (13) can be identified.

$$SbF_5 + NO_2 \longrightarrow NOSbF_6 + NOSb_2F_{11} \quad (12)$$

$$SbF_5 + N_2O_5 \longrightarrow NO_2SbF_6 + NO_2Sb_2F_{11} \quad (13)$$

Antimony pentafluoride treated with a nitrogen oxide for a short time only shows evidence of a greater proportion of $[Sb_2F_{11}]^-$ than a sample treated for longer which, in turn, contains a considerable proportion of SbF_6^-. As was found in the corresponding reactions of arsenic pentafluoride, however, these products alone cannot account for all the observed i.r. absorptions, and the products appear to be mixtures.

(iii) *With liquid nitrogen dioxide and dinitrogen trioxide*. The products obtained by thermal decomposition of the yellow substances initially formed in these reactions both clearly contain $NOSbF_6$. These products appear to be closely related to those described in section (ii) although $[Sb_2F_{11}]^-$ species cannot be identified in either product. I.r. spectra of the products of the reactions of antimony pentafluoride with gaseous and liquid nitrogen dioxide both show bands attributable to an unknown nitronium species, and several other bands are also visible in both spectra. It appears that the final products of both reactions are very similar, although the mechanisms leading to their formation are quite different.

It is evident from physical properties alone that the yellow products formed in the reactions of the liquid nitrogen oxides contain compounds of a different type to those described previously. The i.r. spectra of these products indicate the nature of these additional compounds. Thus the absorptions at 2265 and 2280 cm.$^{-1}$ can be assigned to the nitrosonium ion, and the absorptions at 1300 cm.$^{-1}$ and 1500—1900 cm.$^{-1}$ are in the regions associated with covalent nitroxy-groups. The product of the reaction with nitrogen dioxide, in particular, has bands in these regions which resemble closely those of antimony fluoride nitrates, which have been prepared by Weidlein and Dehnicke (Table 7).[12]

Further identification of the covalent nitroxy-compounds can only be carried out with great difficulty, owing to the instability of the species. However the fluoride nitrates of tin are considerably more stable than

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[9] J. K. Ruff, *Inorg. Chem.*, 1966, **5**, 1791.

[10] J. Weidlein and K. Dehnicke, *Z. anorg. Chem.*, 1966, **348**, 278.

[11] O. Ruff and W. Plato, *Ber.*, 1904, **37**, 680.

[12] J. Weidlein and K. Dehnicke, *Chem. Ber.*, 1965, **98**, 3053.

those of antimony.[12,13] The reaction of liquid nitrogen dioxide with stannic fluoride has therefore been studied.

Stannic fluoride reacts with liquid nitrogen dioxide to yield an unstable, moisture-sensitive, oily yellow solid which evolves nitrogen dioxide in a vacuum at room temperature, and on heating becomes colourless and more stable, although still moisture-sensitive. The i.r. absorption frequencies of these two products are in Table 8. In the spectrum of the final product can be identified NO_2^+, NO^+, and a fluoride nitrate which is apparently $SnF_3(NO_3)$. The first product clearly contains a nitrosonium species. We believe that this is the 2 : 1 adduct $NO^+[SnF_4(NO_3)]^-$, since stannic chloride,[14] under similar conditions, forms the analogous complex $NO^+[SnCl_4(NO_3)]^-$. On heating this can then decompose with the formation of SnF_3NO_3.

TABLE 6

Debye *X*-ray powder data for solid products from reactions of SbF_5 with nitrogen oxides (*d* spacings in Å)

$SbF_5 + NO$	$SbF_5 + N_2O_3$ [b]	$SbF_5 + NO_2$ [a]	$SbF_5 + NO_2$ [b]
5·39m			
5·18m			
	5·04s	5·01s	5·07s
4·70m			
3·93s	3·91ms	3·95s	
3·57m	3·57s	3·57s	3·59s
3·44s			
		3·13w	
	2·92w	2·98w	2·94w
2·80w		2·81w	
2·72w	2·72vw	2·72w	
2·50w		2·50w	
2·45w		2·46w	
2·39w	2·39vw	2·39w	
	2·27m	2·27w	2·27w
	2·07m	2·08m	2·08m
2·03–1·62 } Many very weak lines			
	1·80m	1·80m	1·80m
	1·69m	1·70m	1·69m
	1·60m	1·61m	1·61m
	1·53m	1·54m	1·53m
	1·48w	1·47w	1·47w
	1·41m	1·42m	1·41m
	1·36m	1·37m	1·36m

$SbF_5 + N_2O_5$	$SbF_5 + NOF$ [c]	$NOSbF_6$	NO_2SbF_6	SbF_3
5·71ms			5·80ms	
	5·39w			
5·04m	5·04s	5·04s	5·04m	
4·64m			4·62m	
4·07ms			4·06s	
3·95ms	3·93ms		3·97s	
3·74s			3·76s	
3·64m			3·65m	3·68ms
	3·60s	3·57s	3·59w	3·57s
3·44m			3·44m	3·29vw
	3·15w		3·17m	2·70vw
	2·93w	2·95w		2·59w
	2·82w			2·46w
	2·72w			2·21m
	2·51w			2·11m
	2·46w			2·08ms
	2·39w			2·03m
	2·27m	2·27w	2·30w	1·98w
2·15w				1·89m
	2·07m	2·08m		1·86vw
	2·03w			1·82m
2·02w			2·00ms	1·78ms
	1·80m	1·80m		1·65vw
	1·69m	1·69m		1·62m
	1·61m	1·60m		1·57m
	1·54m	1·54m		
	1·47w	1·48w		
	1·41m	1·41m		
	1·36m	1·36m		

[a] SbF_5 + gaseous nitrogen oxide. [b] SbF_5 + liquid nitrogen oxide and heat. [c] SbF_5 in excess.

TABLE 7

I.r. absorption frequencies in the region 1250—2000 cm.⁻¹ of antimony fluoride nitrates and the products formed by reaction of antimony pentafluoride with liquid oxides of nitrogen

Reaction products		Antimony fluoride nitrates [a]	
SbF_5 + liquid N_2O_3	SbF_5 + liquid NO_2	$SbF_3(NO_3)_2$	$NO_2^+[SbF_3O(NO_3)]^-$
1865			
1745	1672	1668	1670
1600	1580	1600	1590
		1358	
1295	1300	1309	1295

[a] Ref. 12.

TABLE 8

I.r. absorption frequencies of the products of the reaction of stannic fluoride with nitrogen dioxide, and the fluoride nitrates SnF_3NO_3 and $SnF_2(NO_3)_2$ (cm.⁻¹)

$SnF_4 + NO_2$ [a]	$SnF_4 + NO_2$ [b]	SnF_3-(NO_3) [c]	SnF_2-$(NO_3)_2$ [d]	Assignment
2375s	2375s			$\nu(NO_2^+)$
2290vs	2340m,sh			$\nu(NO^+)$
1970m				
	1672w,sh		1673s	
			1610vs	
	1555s	1555vs	1572vs	
			1363s	
	1300s	1287vs	1305vs	
			1250m	
	970s	965s	990s	
	770m	780m	787s	
	615vs,b	608s	630vs	
	550vs,b	555s	578s	$\nu(SnF_6^{2-})$

[a] Yellow solid complete absorption below 1700 cm.⁻¹. [b] White solid. [c] Ref. 12. [d] Ref. 13.

On the above evidence, we suggest the scheme shown in reactions (14)—(17). The nitronium species known

$$3SnF_4 + 6NO_2 \longrightarrow 3NO^+[(SnF_4(NO_3)]^- \tag{14}$$

$$2NO^+[SnF_4(NO_3)]^- \longrightarrow 2SnF_3(NO_3) + 2NOF \tag{15}$$

$$2NOF + NO^+[SnF_4(NO_3)]^- \longrightarrow (NO)_2SnF_6 + 2NO_2 \tag{16}$$

$$3SnF_4 + 4NO_2 \longrightarrow 2SnF_3(NO_3) + (NO)_2SnF_6 \tag{17}$$

to be present in the product is probably formed by some rearrangement of the $SnF_3(NO_3)$ to an ionic form $NO_2^+[SnOF_3]^-$ during heating. Such a rearrangement is typical of many fluoride nitrates.[12]

Using the reaction scheme (14)—(17) we can suggest similar schemes for the reactions of the Group V pentafluorides. The reactions of antimony pentafluoride with

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[13] K. Dehnicke, *Chem. Ber.*, 1965, **98**, 280.

[14] C. C. Addison and W. B. Simpson, *J. Chem. Soc.* (*A*), 1966, 775.

liquid nitrogen dioxide has many similarities to the analogous reaction of stannic fluoride, and we believe that the first-formed yellow product is the complex $\mathrm{NO^+[SbF_5(NO_3)]^-}$, a structure which is consistent with the i.r. data. On heating, decomposition can take place to $\mathrm{SbF_4NO_3}$, which can then rearrange to the more stable ionic form $\mathrm{NO_2{}^+[SbOF_4]^-}$. The scheme of reactions (18)—(22) is suggested.

$$\begin{array}{rr}
\mathrm{2SbF_5 + 4NO_2 \longrightarrow 2NO^+[SbF_5(NO_3)]^-} & (18)\\
\mathrm{NO^+[SbF_5(NO_3)]^- \longrightarrow SbF_4(NO_3) + NOF} & (19)\\
\mathrm{NOF + NO^+[SbF_5(NO_3)]^- \longrightarrow NOSbF_6 + NO_2} & (20)\\
\mathrm{SbF_4(NO_3) \longrightarrow NO_2{}^+[SbOF_4]^-} & (21)\\
\hline
\mathrm{2SbF_5 + 2NO_2 \longrightarrow NO_2SbOF_4 + NOSbF_6} & (22)
\end{array}$$

The heteropolar dissociation of liquid nitrogen dioxide (dinitrogen tetroxide) to $\mathrm{NO^+}$ and $\mathrm{NO_3{}^-}$ has been noted previously,[15] and provides a simple path for the formation of the ionic complexes $\mathrm{NO^+[MF_{\mathit{x}}(NO_3)]^-}$.

The reaction of antimony pentafluoride with liquid dinitrogen trioxide can occur similarly to the reaction with liquid nitrogen dioxide. The heteropolar dissociation of dinitrogen trioxide occurs [16] with the formation of $\mathrm{NO^+}$ and $\mathrm{NO_2{}^-}$ ions. Thus we believe that the yellow product isolated from the reaction of antimony pentafluoride with liquid dinitrogen trioxide is the complex $\mathrm{NO^+[SbF_5(NO_2)]^-}$ (with the i.r. bands at 1295 cm.$^{-1}$ and 1600—1900 cm.$^{-1}$ attributable to the nitrite group), and the overall reaction scheme to be (23)—(27).

$$\begin{array}{rr}
\mathrm{2SbF_5 + 2N_2O_3 \longrightarrow 2NO^+[SbF_5(NO_2)]^-} & (23)\\
\mathrm{NO^+[SbF_5(NO_2)]^- \longrightarrow SbF_4(NO_2) + NOF} & (24)\\
\mathrm{NOF + NO^+[SbF_5(NO_2)]^- \longrightarrow} & \\
\mathrm{NOSbF_6 + N_2O_3} & (25)\\
\mathrm{SbF_4(NO_2) \longrightarrow NO^+[SbOF_4]^-} & (26)\\
\hline
\mathrm{2SbF_5 + N_2O_3 \longrightarrow NOSbF_6 + NOSbOF_4} & (27)
\end{array}$$

The nitrogen oxide presumably cannot ionise in the gas phase, so that in the reactions of the gaseous nitrogen oxides the intermediate nitrosonium complexes are not observed. The reactions of nitrogen dioxide in the gas phase might also involve the monomeric nitrogen dioxide molecule, and not the dimeric dinitrogen tetroxide form, which is likely to be the more abundant species in the liquid. The simple dissociative mechanism is therefore not operative in the gas phase.

We have noted the close relationship of the final products formed whether antimony pentafluoride reacts with the nitrogen oxide in the gas or the liquid phase. The i.r. spectra also indicate a close relationship between the reactions of all three pentafluorides. In the absence of any effects caused by the heteropolar dissociation of the liquid nitrogen oxides, we now suggest reactions (28)—(30) where M = P, As, or Sb. When M = Sb, $\mathrm{Sb_2F_{11}{}^-}$ species are also formed.

$$\begin{array}{rr}
\mathrm{N_2O_3 + 2MF_5 \longrightarrow NOMF_6 + NOMOF_4} & (28)\\
\mathrm{2NO_2 + 2MF_5 \longrightarrow NOMF_6 + NO_2MOF_4} & (29)\\
\mathrm{N_2O_5 + 2MF_5 \longrightarrow NO_2MF_6 + NO_2MOF_4} & (30)
\end{array}$$

The i.r. spectra are consistent with these suggestions. Compounds containing anions of the type $\mathrm{[AsOF_4]^-}$ and $\mathrm{[SbOF_4]^-}$ have been prepared by Kolditz *et al.*[17–20] These are polymeric anions, and several species including dimers and higher polymers have been isolated. Few i.r. data have been published for these compounds. The $\mathrm{[SbOF_4]_2{}^{2-}}$ anion absorbs at 540—565 cm.$^{-1}$ said to be owing to a metal–oxygen bond vibration, and has an absorption assigned to the Sb–O–Sb bridge [20] at 870 cm.$^{-1}$. The analogous arsenic–oxygen bond absorbs at 595—635 cm.$^{-1}$, but figures for the As–O–As bridge are not available. The oxyfluorides $\mathrm{AsOF_3}$ and $\mathrm{SbOF_3}$ are also believed to be oxygen-bridged polymeric systems,[21] and absorptions associated with the metal–oxygen bonds have been reported in the compounds at 860 and 830 cm.$^{-1}$ respectively. The P–O–P system in phosphorus oxyfluoride compounds has also been studied, and absorptions occur in the 935—1050 cm.$^{-1}$ region.[22]

Although the evidence is far from conclusive, we tentatively assign the strong bands at 895—900 cm.$^{-1}$ in the spectra of the products of the arsenic pentafluoride reactions to the arsenic–oxygen bonds of an $\mathrm{[AsOF_4]_{\mathit{n}}{}^{\mathit{n}-}}$ ion, and the bands at 555—560 cm.$^{-1}$ and 845—850 cm.$^{-1}$ in the spectra of the antimony pentafluoride reaction products to the antimony–oxygen bonds of an $\mathrm{[SbOF_4]_{\mathit{n}}{}^{\mathit{n}-}}$ ion. No clear band attributable to phosphorus oxyfluoride anions is present in the spectra of the phosphorus pentafluoride products. However, bands associated with such anions may account for the breadth and asymmetry of the absorptions at 840 cm.$^{-1}$. The absorptions due to the metal–fluorine vibrations in these anions appear to be largely obscured by the strong absorptions of the $\mathrm{MF_6{}^-}$ ions, although the strong absorption at 720 cm.$^{-1}$ in products of antimony pentafluoride reactions is probably attributable to such an $\mathrm{[SbOF_4]^-}$ ion.

Although compounds containing $\mathrm{[AsOF_4]^-}$ and $\mathrm{[SbOF_4]^-}$ ions are well known, there is little evidence to support the existence of the $\mathrm{[POF_4]^-}$ ion. The reactions of alkali-metal fluorides with $\mathrm{POF_3}$ yield only the $\mathrm{[PO_2F_2]^-}$ and $\mathrm{PF_6{}^-}$ salts.[23] The instability of such species as $\mathrm{NOPOF_4}$ and $\mathrm{NO_2POF_4}$ is therefore expected, and would account for the reactivity of the products formed in the reactions of phosphorus pentafluoride with

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the oxides of nitrogen, and the decomposition of the nitronium species in the product of the reaction with nitrogen dioxide in the manner shown in reactions (31)—(33).

$$NO_2 + PF_5 \longrightarrow NOPF_6 + NO_2POF_4 \qquad (31)$$

$$NO_2POF_4 \longrightarrow NO_2F + POF_3 \qquad (32)$$

$$NO_2F \xrightarrow{\text{glass}} NO_2 + SiF_4 \qquad (33)$$

EXPERIMENTAL

Arsenic and antimony pentafluorides were prepared directly from the elements. Phosphorus pentafluoride was prepared by the thermal decomposition of Phosfluorogen A ($ClC_6H_4N_2PF_6$, Ozark-Mahoning Co.). All the pentafluorides were purified by distillation under vacuum.

Stannic fluoride was prepared by treating metallic tin with bromine and bromine trifluoride, and thermally decomposing the $SnF_4,2BrF_3$ so formed.[24]

Nitric oxide (Matheson) was freed from moisture and other oxides of nitrogen by passage through a trap at −78°. Nitrogen dioxide was prepared by the direct oxidation of nitric oxide in a flow-system. Dinitrogen trioxide was prepared by repeated condensation of nitrogen dioxide and excess of nitric oxide at −196°, and warming to −78°. N_2O_3 separated as a deep blue liquid at −78°, and excess of nitric oxide was pumped off at this temperature. Dinitrogen pentoxide was prepared by the dehydration of nitric acid with phosphoric oxide; the method was similar to that described by Gruenhut *et al.*[25] Nitrosyl fluoride was prepared by the fluorination of nitric oxide in a flow system. Nitryl fluoride was prepared by the fluorination of sodium nitrite as described by Aynsley *et al.*[26]

Apparatus and Techniques. Because of the moisture-sensitive nature of many of the reactants and products, the reactions were carried out in Pyrex high-vacuum systems. Wherever possible the use of lubricated joints was avoided, and break-seal techniques were employed. Absolute dryness was essential, and before an experiment the apparatus was flamed under a vacuum to remove moisture. Solids were prepared for physical measurements in a nitrogen-filled dry-box. I.r. spectra of gaseous products were obtained in a 10 cm. cell fitted with potassium bromide windows. Spectra of the solid products were taken on sodium-dried Nujol or Fluorolube mulls mounted between silver chloride plates, and were recorded in the range 3000—410 cm.$^{-1}$ on a Perkin-Elmer 225 spectrometer. Samples for X-ray powder diffraction study were finely ground, and loaded into 0·5 mm. diameter glass capillary tubes which were then sealed. The photographs were recorded with a 114·6 mm. diameter camera with Ni-filtered Cu-K_α radiation. In very few cases were elemental analyses carried out. In view of the complex nature of the products, which were usually mixtures, it was considered that analysis would give no real indication of the exact natures of the products.

Reactions of PF_5 *and* AsF_5 *with Nitrogen Oxides.*—500 ml. bulbs were filled with the pentafluoride and the gaseous nitrogen oxide. The two gases were condensed together at −196° and warmed to the reaction temperature. Alternatively, in the reactions of the less stable N_2O_3 and N_2O_5, the pentafluoride was condensed on excess of nitrogen oxide. After reaction, gas samples were removed for i.r. study, then remaining volatile materials were pumped off. Further details are in Table 9.

TABLE 9

	Reaction conditions	Product(s)
$PF_5 + NO$	−196°	Red solid
	25°	No reaction
$AsF_5 + NO$	−196°	Red solid
	25°	White solid ($NOAsF_6$) AsF_3 as volatile product[a]
$PF_5 + N_2O_3$	−23°	White solid ($NOPF_6$, $NOPOF_4$) POF_3 as volatile product[b]
$AsF_5 + N_2O_3$	−23°	White solid ($NOAsF_6$, $NOAsOF_4$)
$PF_5 + NO_2$	−23°	White solid ($NOPF_6$, NO_2POF_4) POF_3 as volatile product[b]
$AsF_5 + NO_2$	−23°	White solid ($NOAsF_6$, NO_2AsOF_4)
$PF_5 + N_2O_5$	−78° (1 hr.) Slowly raised to 0°	White solid (NO_2PF_6, NO_2POF_4) POF_3 as volatile product[b]
$AsF_5 + N_2O_5$	−78° (1 hr.) Slowly raised to 0°	White solid (NO_2AsF_6, NO_2AsOF_4)

[a] Identified by i.r. spectrum: 738 and 701 cm.$^{-1}$. [b] Identified by i.r. spectrum: 1415, 990, 873, and 485 cm.$^{-1}$.

Reactions of SbF_5 *with Nitrogen Oxides.*—(a) $SbF_5 + NO$. (b) SbF_5 + *gaseous* NO_2. Excess of gaseous nitrogen oxide was admitted to a bulb containing SbF_5 (5 g.). After the immediate reaction the mixture was warmed to complete the reaction. A gas sample was removed for i.r. analysis, then unchanged starting materials were pumped off. The product from (a) was a white solid [$NOSb_2F_{11}$, $SbF_5(SbF_3)_2$] and from (b) was a white solid ($NOSbF_6$, $NOSb_2F_{11}$, NO_2SbOF_4).

(c) $SbF_5 + N_2O_3$, (d) SbF_5 + *liquid* NO_2, (e) $SbF_5 + N_2O_5$. Excess nitrogen oxide was condensed on SbF_5 (5 g.) at −196° and reaction was induced by warming. Nitrogen oxide was then pumped off and the mixture was warmed to room temperature. The procedure was repeated several times. Finally a gas sample was removed for i.r. study, then volatile materials were pumped off. Further details are in Table 10.

TABLE 10

	Reaction conditions	Products
$SbF_5 + N_2O_3$	−78°	Yellow solid [$NO,SbF_5(NO_2)$]
	Dynamic vacuum 100°	White solid ($NOSbF_6$, $NOSbOF_4$)
$SbF_5 + NO_2$	25°	Yellow solid [$NO,SbF_5(NO_3)$]
	Dynamic vacuum 100°	White solid ($NOSbF_6$, NO_2SbOF_4)
$SbF_5 + N_2O_5$	0°	White solid (NO_2SbF_6, NO_2SbOF_4, $NO_2Sb_2F_{11}$)

Preparation of $NOMF_6$ *and* NO_2MF_6 *Salts.*—The salts were prepared by interaction of the pentafluoride with nitrosyl

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fluoride or nitryl fluoride. The methods of Woolf and Emeléus [27, 28] with bromine trifluoride frequently gave impure products, often mixtures of nitrosonium and nitronium salts. This may account for differences between i.r. frequencies reported here and those in previous reports.[29]

Reaction of Stannic Fluoride with Nitrogen Dioxide.—A large excess of NO_2 was condensed on SnF_4 (2 g.) and warmed to room temperature. The liquid NO_2 was held over the tetrafluoride for 1 hr., then removed to leave an oily yellow solid. The solid became colourless under a dynamic vacuum at 190°.

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