CONTRIBUTION FROM THE CHEMICAL PHYSICS RESEARCH LABORATORY,
THE DOW CHEMICAL COMPANY, MIDLAND, MICHIGAN

The Structures of Nitrogen Oxide–Boron Trifluoride Complexes

BY J. C. EVANS, H. W. RINN, S. J. KUHN, AND G. A. OLAH

Received November 12, 1963

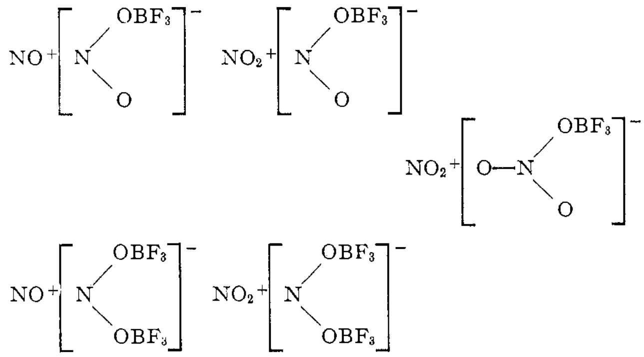
Raman and infrared spectra and X-ray powder diffraction patterns of the reaction products of BF_3 with N_2O_3, N_2O_5, and N_2O_4 have established that the predominant products are, respectively, $NOBF_4$, NO_2BF_4, and a mixture of these two ionic compounds. No evidence for the existence of the complex anions previously postulated was obtained.

Introduction

White, stable but moisture-sensitive, solid products are obtained when the nitrogen oxides react with boron trifluoride under anhydrous conditions.[1,2] Various investigators have proposed the existence of the complexes

$N_2O_3 \cdot BF_3$	$N_2O_4 \cdot BF_3$	$N_2O_5 \cdot BF_3$
$N_2O_3 \cdot 2BF_3$	$N_2O_4 \cdot 2BF_3$	

with the postulated structures[2-4]



Evidence for these structures is based on the chemical behavior of the products, *i.e.*, their nitrating and nitrosating properties, and on their physical properties, *i.e.*, infrared absorption spectra, X-ray powder diffraction patterns, electrical conductivities, and magnetic susceptibilities.

Further study of these structures appeared to be desirable and, in particular, a study of the Raman spectra of these structures promised to be informative since differentiation of the nitryl and nitrosyl ions is not conclusive by the infrared spectra alone, especially in the presence of complicated anions. The nitrosyl ion, NO^+, being diatomic and heteropolar, has one vibrational mode which is Raman and infrared active. This mode is rather sensitive to the nature of its environment and frequency values in the range 2390–2165 cm.$^{-1}$ have been reported.[5-7] The antisymmetric stretching mode of the triatomic, linear ion $[ONO]^+$ is infrared active but Raman inactive and occurs in the nitrosyl ion frequency range; unambiguous proof of the origin of an infrared band in this region is not possible. However, the observation of an infrared band in the 500–600 cm.$^{-1}$ region which may arise from the nitryl ion bending mode[8] and of a band near 3750 cm.$^{-1}$ assignable to a combination tone[9] of the symmetric and asymmetric stretching modes does constitute good evidence for the presence of the nitryl ion. The Raman spectrum of the nitryl ion consists of one very strong band at 1400 cm.$^{-1}$, the infrared-inactive, symmetric stretching mode[10]; no ambiguity arises if a strong Raman band is observed in the 2350 cm.$^{-1}$ region. Knowledge of both infrared and Raman spectra should then enable a conclusive determination of the presence of either the NO^+ or the NO_2^+ ions or both. In addition, these spectra should indicate whether or not the proposed complex anions are present; for these, rich infrared and Raman spectra would be expected.

During this investigation it became apparent that the earlier work[2] on the physical properties of these solids was complicated by effects produced by inadequate protection from moisture. The large number of infrared bands reported, *e.g.*, bands due to nitric acid, indicate this, while the fact that the products gave the same intense lines in their X-ray powder diffraction patterns[2] indicates a common predominant constituent. For this reason the X-ray patterns of the products were re-examined under dry conditions.

Experimental

Preparation of Nitrogen Oxide–Boron Trifluoride Complexes.—The nitrogen oxide–boron trifluoride complexes investigated during the present study were prepared by allowing the reagents to react in solution.

(a) **Sulfur Dioxide Solution.**—Nitrogen oxide (N_2O_3, N_2O_4, or N_2O_5) (0.2 mole) was dissolved in 100 g. of sulfur dioxide and into these solutions boron trifluoride gas was introduced at 20° in different mole ratios, in order to obtain nitrogen oxide·BF_3 and nitrogen oxide·$2BF_3$ complexes. In separate experiments excess BF_3 gas was introduced into the solutions until no more BF_3 was absorbed. The reaction vessel was protected from atmospheric moisture. After the addition of the boron trifluoride was completed, SO_2 was distilled off and the solid white residue was pumped dry. Suitable amounts of the complexes

---

[1] F. Kuhlman, *Ann.*, **39**, 320 (1891).

[2] R. W. Sprague, A. B. Garrett, and H. H. Sisler, *J. Am. Chem. Soc.*, **82**, 1059 (1960). Earlier studies are summarized.

[3] G. B. Bachman and T. Hokama, *ibid.*, **79**, 4370 (1957).

[4] G. B. Bachman and J. L. Dever, *ibid.*, **80**, 5871 (1958).

[5] H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **72**, 21 (1953).

[6] D. J. Millen and D. Watson, *J. Chem. Soc.*, 1369 (1957).

[7] D. W. A. Sharp and J. Thorley, *ibid.*, 3557 (1963).

[8] R. Terashini and J. C. Decius, *J. Chem. Phys.*, **22**, 896 (1954).

[9] R. A. Marcus and J. M. Fresco, *ibid.*, **27**, 564 (1957).

[10] C. K. Ingold, D. J. Millen, and H. G. Poole, *J. Chem. Soc.*, 2576 (1950).

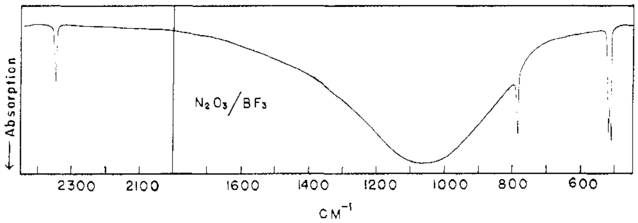


Fig. 1.—The infrared absorption spectrum of the solid reaction product of N_2O_3 with BF_3. Samples were mulled with Fluorolube (3800–1330 cm.$^{-1}$) and with Nujol (1330–450 cm.$^{-1}$) and mounted between AgCl plates. Absorption bands of the mulling agents are not reproduced.

were transferred into Raman tubes in a drybox and the tubes were sealed.

(b) **Nitromethane Solution.**—Nitrogen oxide (N_2O_3, N_2O_4, N_2O_5) (0.2 mole) was dissolved in 50 g. of nitromethane and boron trifluoride gas was introduced at 10° according to 1:1, 1:2 (nitrogen oxide : BF_3) mole ratios or the solutions were saturated with excess BF_3. The precipitated solids were filtered in a drybox, washed with Freon 113, pumped dry, and transferred into the Raman tubes.

Authentic samples of $NOBF_4$ were prepared by the reaction of NOF and BF_3,[11] and of NO_2BF_4 by reaction of NO_2F and BF_3.[12]

Spectroscopic Observations.—Raman spectra of the solid powders were recorded photographically using a Hilger spectrograph (*f*/5.7, 16 Å./mm.) with 4358 Å. (mercury) excitation. Excessive stray radiation arising from reflections from the many crystal faces of the sample was removed by the use of narrow-band interference filters used in a complementary arrangement.[13] Exposure times of 5 hr. or more were required.

Infrared spectra of mulls (Fluorolube and Nujol) of the solid powders, prepared in a drybox and mounted between silver chloride plates, were recorded in the 3800–450 cm.$^{-1}$ range using a prism-grating instrument.[14] Alkali halide supporting plates are rapidly attacked by these compounds resulting in additional, confusing absorption bands.

X-Ray Powder Diffraction Patterns.—Samples were loaded in a drybox into glass capillary tubes, which then were sealed. X-Ray patterns were recorded with a 143.2-mm. diameter camera using Cu Kα radiation.

Results and Discussion

N_2O_3–BF_3.—Several preparations, using different reactant proportions and different solvents, yielded samples which gave the same Raman and the same infrared spectra. The wave number data are collected in Table I and the infrared spectrum is drawn in Fig. 1. Comparison of these with the spectra obtained from an authentic sample of $NOBF_4$ showed complete agreement in both infrared and Raman spectra. The same was true of the X-ray powder patterns, details of which are given in Table II. However, neither the derived unit cell dimensions nor the infrared wave number value of the NO^+ stretching vibration agreed with those given by Sharp and Thorley[7] for $NOBF_4$. The discrepancy in the X-ray data has been resolved, Sharp and Thorley's published values being misprinted,[15] but we have no explanation for the 47 cm.$^{-1}$ discrepancy between our and Sharp and Thorley's infrared values. It is not due to the mulling agent since both Nujol and Fluorolube mulls give 2340 cm.$^{-1}$ with no indication of sample decomposition in either case; furthermore, the Raman spectra were obtained using the dry powdered products, and the value obtained, 2340 cm.$^{-1}$, agrees with our infrared value, rather than with Sharp and Thorley's value of 2387 cm.$^{-1}$.[16]

Table I

Raman and Infrared Data for the N_2O_3–BF_3 Reaction Product[a] (cm.$^{-1}$)

Raman	Infrared	Assignment
2340 s[b]	2340 m	$\nu(N{\equiv}O)^-$
	~1050 vs, b	$\nu_3(BF_4)^-$
768 m	769 m	$\nu_1(BF_4)^-$
	528 s	$\nu_4(BF)_4^-$
	517 s	
361 w		$\nu_2(BF)_4^-$

[a] This material and the other products of reaction between BF_3 and the nitrogen oxides, when examined as thick mulls in the infrared, showed additional weak bands assignable to the BF_4^- ion[14]; these were near 1300 (sharp), 1830 (broad), 2020 (broad), and 2180 (broad) cm.$^{-1}$ [b] vs, very strong; s, strong; m, medium; w, weak; b, broad.

The assignments of the BF_4^- bands quoted in Table I are based on published data.[17-19] We may write a reasonable over-all reaction scheme

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

Sprague, *et al.*,[2] quote elemental analyses for the gas-phase reaction product which are in accord with this scheme. According to the scheme the product contains approximately 9% B_2O_3 which was not detected spectroscopically. However, this is not surprising in view of the lack of prominent, sharp bands in either infrared[20] or Raman[21] spectra of polymeric boric oxide. Boric oxide is not readily obtainable in a crystalline form so that its nondetection in the X-ray powder pattern is not surprising either. However, a sample which was exposed to atmospheric moisture prior to the recording of its X-ray powder pattern, gave, in addition to the $NOBF_4$ pattern, the strongest lines of boric acid; the concentration of boric acid was visually estimated to be in the 5–10% range.

Attempts were made to isolate the B_2O_3 from the reaction products but neither vacuum sublimation nor solvent extraction yielded significant residues. This may be due to secondary reactions during sublimation[22] and to the solubility of the boric oxide in the

---

[11] E. Wilke-Dörfurt and G. Balz, *Z. anorg. allgem. Chem.*, **159**, 219 (1927); G. Balz and E. Mailänder, *ibid.*, **217**, 161 (1934).

[12] D. Cook, S. J. Kuhn, and G. A. Olah, *J. Chem. Phys.*, **33**, 1609 (1960).

[13] J. Brandmuller, *Z. angew. Physik*, **5**, 95 (1953).

[14] L. W. Herscher, *Spectrochim. Acta*, **11**, 901 (1959).

[15] D. W. A. Sharp, private communication.

[16] A referee has kindly informed us that he has, in unpublished work, prepared $NOBF_4$ by allowing BF_3 to react with NOF and has found X-ray diffraction and infrared absorption data in agreement with ours; *i.e.*, $\nu(NO^+)$ at 2340 ± 2 cm.$^{-1}$.

[17] G. L. Coté and H. W. Thompson, *Proc. Roy. Soc.* (London), **A210**, 217 (1951).

[18] J. O. Edwards, G. C. Morrison, V. F. Rose, and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 266 (1955).

[19] J. Goubeau and W. Bues, *Z. anorg. Chem.*, **268**, 221 (1952).

[20] E. G. Brame, J. L. Margrave, and V. W. Meloche, *J. Inorg. Nucl. Chem.*, **5**, 48 (1957).

[21] M. Harrand, *Ann. Phys.*, **13**, 309 (1957).

[22] R. F. Porter, D. R. Bidinosti, and K. F. Watterson, *J. Chem. Phys.*, **36**, 2104 (1962).

TABLE II

X-RAY POWDER DATA FOR $NOBF_4$[a]

d (obsd.), Å.	d (calcd.),[b] Å.	I/I_1 (obsd.)	*hkl*	d (obsd.), Å.	d (calcd.), Å.	I/I_1 (obsd.)	*hkl*
5.50	5.497	24	110		1.833		330
	4.456		020	1.83	1.826	5	103
4.41	4.404	40	101		1.789		113
3.96	3.948	8	111	1.78	1.783	5	241
3.76	3.757	12	120		1.770		232
3.51	3.505	100	021	1.76	1.765	5	312
	3.492		200		1.753		042
3.25	3.251	12	210		1.746		400
3.13	3.133	80	121		1.744		331
	2.838		002		1.742		023
2.82	2.821	60	211		1.728		150
2.75	2.749	12	220		1.714		410
	2.733		130	1.70	1.700	3	142
2.52	2.521	40	112		1.690		123
	2.474		221		1.669		322
2.46	2.463	3	131		1.652		151
2.39	2.394	8	022		1.641		411
2.26	2.265	60	122	1.63	1.636	8	213
	2.263		230		1.626		420
	2.253		310	1.61	1.610	5	340
2.23	2.229	8	040	1.585	1.588	2	250
2.20	2.202	12	202		1.566		242
	2.154		301	1.56	1.563	3	421
2.14	2.139	8	212		1.559		223
2.12	2.123	12	140	1.555	1.556	3	133
	2.102		231		1.549		341
2.10	2.094	40	311		1.540		332
	2.074		041	1.535	1.529	3	251
2.07	2.063	12	320	1.500		2	
1.98	1.988	5	141	1.465		2	
	1.975		222	1.436		3	
	1.969		132	1.406		2	
	1.939		321	1.370		2	
	1.879		240	1.330		3	

[a] See ref. 11 for sample preparation. [b] Calculated on the basis of $a = 6.983$, $b = 8.911$, $c = 5.675$ Å.; space group Pbnm. These lattice constants were determined from the observed d-values for the (120), (021), (121), (211), (200), (112), and (022) reflections. The data are in better agreement with these calculated d-values than with those calculated from the published lattice constants $a = 7.114$, $b = 8.808$, $c = 5.67$ Å. [L. J. Klinkenberg, *Rec. trav. chim.*, **56,** 749 (1937)].

solvents used to dissolve the tetrafluoroborate (see discussion of N_2O_4–BF_3 reaction product).

N_2O_5–BF_3.—Identification of the predominant product of the reaction between BF_3 and N_2O_5 as nitryl tetrafluoroborate is established by the spectrum drawn in Fig. 2 and the collected frequency data in Table III. The NO_2^+ ion is shown to be present by its strong Raman-active mode at 1400 cm.$^{-1}$ and by the two infrared-active modes, the bending mode near 600 cm.$^{-1}$ and the stretching mode near 2380 cm.$^{-1}$; the combination tone near 3750 cm.$^{-1}$ was also observed. The nature of the predominant anion present, BF_4^-, is also readily established.

TABLE III

RAMAN AND INFRARED DATA FOR THE N_2O_5–BF_3 REACTION PRODUCT[a] (CM.$^{-1}$)

Raman	Infrared	Assignment
	3750 w	[1399 + 2380], NO_2^+
	2380 m	NO_2^+, antisym. stretch
2341 w	2340 w, sh	$\nu(N\equiv O)^+$, impurity
1399 vs		NO_2^+, symm. stretch
	~1050 vs, vb	$\nu_3(BF_4)^-$
775 m	777 s	$\nu_1(BF_4)^-$ in NO_2BF_4
	769 m	$\nu_1(BF_4)^-$ in $NOBF_4$
	605 s	NO_2^+, bend
	590 s	
	532 s	$\nu_4(BF_4)^-$
	526 s	
	518 s	

[a] Splitting of $\nu_1(BF_4^-)$ occurs in $NaBF_4$[14]; such an effect may also contribute to the splitting observed here.

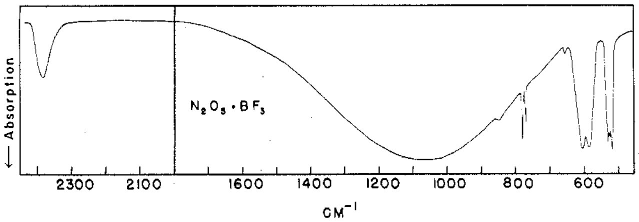


Fig. 2.—The infrared spectrum of the solid reaction product of N_2O_5 with BF_3. See Fig. 1 for sample handling details.

These spectra merit further discussion since the Raman spectrum has not been described previously while the published infrared studies were confined to the rock-salt prism range.[2,12] The present, more extensive data confirm the conclusion[12] that the compound is $NO_2^+ \cdot BF_4^-$. Particularly noteworthy is the bending mode of the nitryl which appears as a doublet, 605 and 590 cm.$^{-1}$.

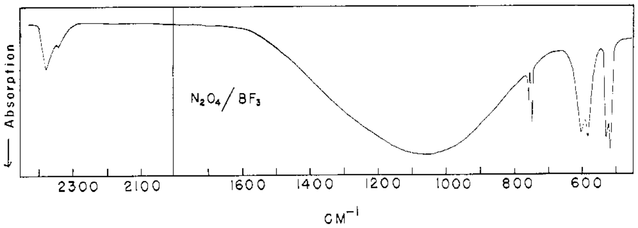


Fig. 3.—The infrared spectrum of a solid reaction product of N_2O_4 with BF_3. See Fig. 1 for sample handling details.

The 605 cm.$^{-1}$ component is also a doublet with separation of about 4 cm.$^{-1}$ in several of the samples examined. These splittings indicate that the site symmetry at the nitryl ion in the crystal is less than that of the isolated ion. Comparison with the spectra of the other two nitryl compounds for which this mode has been reported shows that the mode is surprisingly sensitive to the environment. In $NO_2^+ \cdot NO_3^-$ it appears[8] at 538 cm.$^{-1}$, while in $NO_2^+ClO_4^-$ it is reported[23] at 570 cm.$^{-1}$. This is especially surprising in view of the constancy of the two stretching modes of the nitryl ion in these and several other systems containing the ion.

That some $NOBF_4$ is also present in the product is indicated by the weak Raman band at 2340 cm.$^{-1}$ and by the doubling of the symmetrical stretching mode of the BF_4^- ion near 770 cm.$^{-1}$. This latter band is forbidden in the infrared for the isolated tetrahedral ion but appears because of the lowered symmetry in the crystal. Its frequency is somewhat sensitive to the nature of the cation; with NO_2^+ it appears at 777 cm.$^{-1}$ and with NO^+ at 769 cm.$^{-1}$. The appearance of some $NOBF_4$ is ascribed to the ease with which N_2O_5 decomposed to the lower oxides.

The over-all reaction scheme analogous to that discussed for the N_2O_3–BF_3 reaction is

$$3N_2O_5 + 8BF_3 \longrightarrow 6NO_2BF_4 + B_2O_3 \qquad (2)$$

Again, the B_2O_3 was not detected directly in either vibrational spectra or powder patterns. The X-ray patterns showed, by comparison with that of an authentic NO_2BF_4 sample, that the predominant component was NO_2BF_4 with some $NOBF_4$ present. In Table IV the X-ray powder data for NO_2BF_4 are given; these differ from the data reported previously[2,24] and show that the published data were obtained with a sample which was largely $NOBF_4$.

N_2O_4–BF_3.—It is now logical to expect the product of the reaction between N_2O_4 and BF_3 to be a mixture containing $NOBF_4$ and NO_2BF_4. The spectra confirm this; Fig. 3 and Table V. The X-ray patterns provide further confirmation. The ratio of nitryl to nitrosyl ions in the product varied with the reaction conditions, presumably because of different solubilities and reactions times. An over-all reaction scheme may be written

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

TABLE IV

X-RAY POWDER DATA FOR NO_2BF_4[a]

d, Å.	I/I_1
5.4	15
5.05	1
4.42	6
3.73	2
3.58	100
3.40	30
3.21	40
2.97	10
2.93	40
2.86	1
2.74	7
2.70	2
2.58	30
2.45	1
2.38	2
2.32	20
2.25	30
2.20	20
2.16	10
2.14	15
2.11	5
2.07	8
2.04	5
2.00	6
1.98	5
1.92	10
1.865	15
1.860	15
1.82	2
1.79	3
1.76	4
1.71	4
1.70	2
1.615	3
1.560	4
1.510	2
1.470	3
1.450	2
1.372	1
1.350	2
1.340	2
1.315	1
1.305	2

[a] See ref. 12 for sample preparation.

Here, as previously, the minor product, B_2O_3, was not detected spectroscopically.

A more extensive research for this minor constituent was made in this reaction product which, in its chemical properties, is the most interesting of the three studied; it has been shown to be both a good nitrating and a good nitrosating agent by Bachman, *et al.*,[25] and during the present studies. This is in accord with the present identification of the product as a mixture of NO_2^+ and NO^+ salts.

Using acetonitrile or tetramethylene sulfone as solvent it was possible to separate the product by repeated washings into two major components, $NOBF_4$, which is not appreciably soluble in these solvents, and NO_2BF_4, which is soluble. The separation was not complete and the presence or absence of B_2O_3 was not determined by this experiment.

---

(23) J. R. Soulen and W. F. Schwartz, *J. Phys. Chem.*, **66**, 2066 (1962).

(24) R. W. Sprague, Ph.D. Thesis, Ohio State University, 1958.

(25) G. B. Bachman, H. Fever, B. R. Bluestein, and C. M. Vogt, *J. Am. Chem. Soc.*, **77**, 6188 (1955).

TABLE V

RAMAN AND INFRARED DATA FOR THE N_2O_4–BF_3 REACTION PRODUCT (CM.$^{-1}$)

Raman	Infrared	Assignment
	3754 w	[2380 + 1399] NO_2^+
	2380 m	NO_2^+, antisym. stretch
2341 m	2340 w, sh	NO^+, fundamental
1399 s		NO_2^+, sym. stretch
	~1050 vs, b	$\nu_3(BF_4)^-$
776 m	777 m	$\nu_1(BF_4)^-$ in NO_2BF_4
768	769 m	$\nu_1(BF)_4^-$ in $NOBF_4$
	605 m	NO_2^+, bend
	590 m	
	531 m	$\nu_4(BF_4)^-$
528 vw	526 m	
	518 m	
354 w		$\nu_2(BF_4)^-$

Sublimation of the product left no residue but, when 3 g. of B_2O_3 was added to 50 g. of the product and the mixture was sublimed, there was again no residue. The B_2O_3 had presumably reacted with one or both of the major constituents.

The mother liquor, from a preparation in which 0.25 mole of N_2O_4 and 0.68 mole of BF_3 were allowed to react in 250 g. of nitromethane to yield 56 g. of solid product, was evaporated to dryness under vacuum. Strong heating was required near the end of the drying process. About 7 g. of residue was obtained; this was washed with acetonitrile. The infrared spectrum showed the residue to be a mixture of B_2O_3 and H_2BO_3 with the former predominating; exposure to atmospheric moisture increased the boric acid content and the X-ray powder diffraction pattern confirmed the identification.

This result shows that at least some of the B_2O_3 or its precursor is held in solution in the mother liquor after separation of the major reaction products. A possible explanation for this may be the formation of trifluoroboroxine as a reaction product.

$$3N_2O_4 + 9BF_3 \longrightarrow 3NOBF_4 + 3NO_2BF_4 + (BOF)_3$$

This presumably cyclic molecule dissociates

$$(BOF)_3 \longrightarrow B_2O_3 + BF_3$$

giving an over-all reaction as written previously. It is not clear from the literature what the stability of $(BOF)_3$ might be in the present situation. The molecule has been detected mass spectrometrically at high temperature,[22,26] whereas in another investigation of the solid it was concluded that decomposition occurred above −135°.[27] A further investigation suggested stability of the solid to 80° at which temperature it decomposed to B_2O_3 and BF_3.[28]

Trifluoroboroxine is probably considerably more soluble than boric oxide in all the solvents used in these preparations and so its presence would account for the retention of B_2O_3 in the mother liquor. However, if it does occur as a reaction product, its stability in the solid product is such that it decomposes rather rapidly; there was no indication in the infrared spectra of any of the products of the bands ascribed by Fisher, *et al.*,[27] to trifluoroboroxine.

Conclusion

No evidence for the existence, in the final products of reaction, of complex anions such as $[NO\cdot OBF_3]^-$ was obtained during this study. The predominant reaction products of BF_3 with the nitrogen oxides, N_2O_3, N_2O_5, and N_2O_4, were satisfactorily shown to be the ionic compounds $NOBF_4$, NO_2BF_4, and mixtures of these. Of course, the reaction mechanisms are undoubtedly complicated and anions of the type postulated in the literature may exist as reaction intermediates.

Acknowledgment.—We are grateful to Miss Y. S. Lo for experimental assistance.

---

(26) D. L. Hildenbrand, L. P. Theard, and A. M. Saul, *J. Chem. Phys.*, **39**, 1973 (1963).

(27) H. D. Fisher, W. J. Lehmann, and I. Shapiro, *J. Phys. Chem.*, **65**, 1166 (1961).

(28) E. M. Magee, *J. Inorg. Nucl. Chem.*, **22**, 155 (1961).