[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Reactions of Some Oxides of Nitrogen with Boron Trifluoride

BY ROBERT W. SPRAGUE,[1] ALFRED B. GARRETT AND HARRY H. SISLER

RECEIVED JULY 6, 1959

The reactions of BF_3 with the oxides of nitrogen, N_2O_3, N_2O_4 and N_2O_5 have been studied. In addition, the reactions of BF_3 with N_2O_4 in the presence of ozone, and with solid KNO_3 and $NaNO_2$, have been investigated. Chemical analysis, X-ray powder patterns, infrared spectra, magnetic susceptibilities and electrical conductivities show that the products of these reactions may be reasonably formulated as nitrosyl and nitryl mono- and difluoroboro nitrites and nitrates. A plausible mechanism for these reactions is outlined. Criteria for the identification of nitrosyl and nitryl ions by infrared spectra are presented.

The acidic nature of the oxides of nitrogen is well known, and numerous investigators have studied their reactions with such Lewis bases as amines, ethers, esters and olefins.[2-6] However, only relatively little attention[7,8] has been given their behavior toward the stronger Lewis acids.

This is a report of a study of the reactions of oxides of nitrogen with boron trifluoride. It has been known for some time that N_2O_4 (in this study the term N_2O_4 will be used to refer to the equilibrium mixture of NO_2 and N_2O_4) reacts with boron trifluoride to form a stable, white, solid compound, with the reported composition $N_2O_4 \cdot 2BF_3$.[9,10] More recently, Bachman and co-workers reported the formation of a compound of the composition $N_2O_4 \cdot BF_3$ by the reaction between N_2O_4 and BF_3 in nitromethane solution and the formation of a compound of the composition $N_2O_3 \cdot BF_3$ by the reaction of N_2O_3 and BF_3 in nitromethane solution.[11,12] Schmeisser[13] first reported the compound $N_2O_5 \cdot BF_3$, and very recently Bachman and co-workers reported using this compound as a nitrating agent.[14] It also has been reported that NO and BF_3 react at low temperatures to form a red compound, which decomposes above $-111°$.[15]

Experimental

A summary of the experimental work is presented below; detailed descriptions of the procedures and results are available.[16]

Reactions of BF_3 with N_2O_3 and N_2O_4, respectively, were carried out in the gas phase in a specially constructed Pyrex glass reactor, provided with separate inlet tubes for the two reacting species and a third inlet for dry nitrogen. The solid reaction products settled out at the bottom of the reactor as the gas flow reversed direction to the reactor outlet. BF_3 was present in excess at all times during the reaction. The reaction of BF_3 and N_2O_4 was also carried out with ozonized oxygen replacing the flow of dry nitrogen. All of the products were finely divided, extremely hygroscopic, white solids. All handling of the products was done in an atmosphere of dry nitrogen, and the products were stored in a desiccator over anhydrous calcium sulfate. All of the products sublimed (without evidence of melting) below 100° in vacuum. Some of the product from the gas phase reaction of BF_3 and N_2O_4 was recrystallized from concentrated H_2SO_4.

The reaction of BF_3 and N_2O_4 was also carried out in liquid SO_2 at $-80°$ and in 100% HNO_3 at 0° by bubbling a mixture of BF_3 and dry nitrogen through solutions of N_2O_4 in these solvents.

The reaction of BF_3 with N_2O_5 was carried out in carbon tetrachloride solution by bubbling a mixture of BF_3 and dry nitrogen through the N_2O_5 solution.

The reaction of BF_3 with KNO_3 or $NaNO_2$ was carried out by passing a stream of BF_3 gas over the powdered salt contained in a bent 8 mm. Pyrex glass tube. The reaction was initiated by warming the tube with a torch. As the reaction progressed, a white solid sublimed out of the reaction zone; at the end of the reaction, there was still a white solid left in the reaction zone.

$NOBF_4$ was prepared by essentially the same method as that used by Wilke-Dorfurt.[17] NO_2BF_4 was prepared by subliming $NOBF_4$ in a stream of ozonized oxygen. $(NO)_2SnCl_6$ and $NOSbCl_6$ were prepared by the reaction of nitrosyl chloride with $SnCl_4$ and $SbCl_5$, respectively, in liquid SO_2.

All physical handling of the materials for sampling, for X-ray powder work, and for preparation of mulls for infrared spectra was carried out in a cut off erlenmeyer flask, arranged so that a flow of dry nitrogen was maintained over the sample at all times. On occasion, the products were kept under these conditions for as long as 3 hr. with no sign of hydrolysis (which occurred in a few minutes if they were left exposed to air).

Analysis of the products was carried out by hydrolyzing the product in excess standard NaOH, diluting to a measured volume and analyzing for the individual elements on separate aliquots. Fluorine was determined as CaF_2; boron was determined by mannitol titration to the phenolphthalein end-point on the filtrate from the fluorine determination; nitrogen was determined by the Kjeldahl method, using DeVarda's alloy to reduce the nitrogen species to NH_3. The analytical method was tested on "standard samples" consisting of mixtures of NH_4BF_4, $NaNO_3$, $NaNO_2$, H_3BO_3 and NH_4HF_2. The products of the reactions of BF_3 with KNO_3 and $NaNO_2$ were analyzed by a commercial laboratory.

The equivalent weight for hydrolysis was determined from the total amount of base used in the initial hydrolysis and subsequent hydrolysis of BF_4^- during the precipitation of CaF_2. The oxidation-reduction equivalent weights were determined by hydrolyzing a sample in an excess of standard

---

[1] Rocketdyne, Dept. 596-92, 6633 Canoga Ave., Canoga Park, Calif.

[2] E. Scaife, *et al.*, *J. Chem. Soc.*, 2627 (1949); *ibid.*, 1093 (1943); *ibid.*, 52 (1946).

[3] H. H. Sisler, *et al.*, THIS JOURNAL, **75**, 5188 (1953); *ibid.*, **75**, 5191 (1953); *ibid.*, **74**, 877 (1952).

[4] C. C. Addison, *et al.*, *J. Chem. Soc.*, 1338 (1953); *ibid.*, 1390 (1952); *ibid.*, 1298 (1951); *ibid.*, 1303 (1951); *Quart. Rev.*, **9**, 115 (1953).

[5] G. E. Carlson, *et al.*, THIS JOURNAL, **59**, 843 (1937); *J. Org. Chem.*, **5**, 1 (1940).

[6] H. Wieland, *et al.*, *Ann.*, **424**, 71 (1921); *ibid.*, **424**, 75 (1921); *ibid.*, **424**, 100 (1951).

[7] E. E. Aynsley, G. Hetherington and P. L. Robinson, *Chem. & Ind.* (*London*), 1117 (1951).

[8] E. E. Aynsley, R. Nichols and P. L. Robinson, *J. Chem. Soc.*, 623 (1953).

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

[10] H. H. Batey and H. H. Sisler, THIS JOURNAL, **74**, 3408 (1952).

[11] G. B. Bachman, H. Feuer, B. R. Bluestein and C. M. Vogt, *ibid.*, **77**, 6188 (1955).

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

[13] M. Schmeisser, *Angew. Chem.*, **64**, 616 (1952).

[14] G. B. Bachman and J. L. Dever, THIS JOURNAL, **80**, 5871 (1958).

[15] G. R. Finley, *J. Chem. Ed.*, **24**, 149 (1947).

[16] Dissertation, Robert W. Sprague, presented in partial fulfillment of the requirements for the degree Doctor of Philosophy in the Graduate School of the Ohio State University: University Microfilms, Ann Arbor, Michigan, Dissertation Abstracts, **18**, 785 (1958). L. C. Card No. Mic. 58-570, 197 pp., $2.60.

[17] Wilke-Dorfurt, *Angew. Chem.* **37**, 712 (1924).

TABLE I

ANALYSIS OF BF_3–NITROGEN OXIDE REACTION PRODUCTS

Reaction	Found				Formula assigned	Calculated			
	%N	%B	%F	%O		%N	%B	%F	%O
$N_2O_3 + BF_3$ (gas)	11.26	10.84	59.09	18.81	$N_2O_3 \cdot 2BF_3$	13.23	10.22	53.85	22.68
$N_2O_4 + BF_3$ (gas)	12.06	9.53	49.56	28.85	$N_2O_4 \cdot 2BF_3$	12.30	9.50	50.07	28.11
$N_2O_4 + BF_3 + O_3$ (gas)	10.57	8.47	43.66	37.30	$N_2O_6 \cdot 2BF_3$	10.79	8.23	43.90	36.97
$N_2O_5 + BF_3$ (CCl_4)	14.91	6.90	35.24	42.95	$N_2O_5 \cdot BF_3$	15.93	6.15	32.41	45.50
$N_2O_4 + BF_3$ (SO_2)	11.58	8.87	48.45	31.10	$N_2O_4 \cdot 2BF_3$	12.30	9.50	50.07	28.11
$N_2O_4 + BF_3$ (HNO_3)	11.61	8.93	65.53	13.93	$NOBF_4$	11.99	9.26	65.05	13.69
$N_2O_4 + BF_3$ (recryst. H_2SO_4)	10.27	8.55	60.21	20.79	$NOBF_4 + NO_2BF_4$	...	...	...	...

ceric sulfate solution and determining the excess ceric sulfate with standard ferrous sulfate solution.

The electrical conductivity of a saturated solution of the BF_3–N_2O_4 reaction product in liquid sulfur dioxide was determined with an Industrial Instrument, Inc., Model RC 16B conductivity bridge, using 60 cycle alternating current. This conductivity was compared with the conductivity of a saturated solution of KF in liquid SO_2.

The magnetic susceptibilities of the solid products were determined by the Gouy method. All measurements were made at constant field strength and at room temperature. The sample tube was calibrated with water at the same volumes as the sample volumes.

All of the products were crystalline solids, and X-ray powder patterns of the products sealed in Lindemann glass capillary tubes of 0.5 or 0.3 mm. diameter were obtained, using CuKα radiation. The particle size of the products as obtained was sufficiently small that no further grinding was necessary. Complete tabulations of θ, $d_{h,k,l}$ and relative intensities are available.[16]

The infrared spectra of the materials were obtained from mulls of the solids in Nujol and Fluorolube-S. The spectra were taken on NaCl, sapphire and silicon windows using a Perkin-Elmer, Model 21, double-beam spectrophotometer, with NaCl optics. The silicon windows were prepared by polishing slabs of single crystal silicon, furnished by the Pigments Department, E. I. du Pont de Nemours & Company, to a finished thickness of 1.1 mm.; at this thickness the windows showed approximately 50% transmission, compared to air, from 2.5 to 15 microns. The mulls were prepared and placed between windows without exposure to moisture by use of the cut off erlenmeyer flask described above. Complete tabulations of the observed absorptions, corrected for instrument calibrations, and figures showing the spectra are available.[16]

Results, Discussion and Conclusions

A summary of the analytical results and most probable formulas is presented in Table I. A comparison of experimental and theoretical equivalent weights is presented in Table II; the theoretical equivalent weights are based on the most probable formulas shown in Table I. Although in some cases the analytical results differ significantly from theoretical, these results, taken in conjunction with the other experimental data, adequately serve to characterize the nature of the materials. The deviations from theoretical analyses probably are due to three main sources: first the difficulty commonly encountered in obtaining accurate results for boron and fluorine analyses (particularly when these elements are present together), second, sampling difficulties, consequent upon the extremely hygroscopic nature of the materials, and third, the possibility of not obtaining exact stoichiometry under the reaction conditions.

A comparison of experimental and theoretical magnetic susceptibilities is presented in Table III. For purposes of calculating the theoretical mole susceptibilities, the values of Pascal constants given by Selwood[18] were modified so that they would sum to the values of ionic susceptibilities for NO_3^-, NO_2^- and BF_4^- shown by this author. The modified Pascal constants are: $N^{+5} = -6.17 \times 10^{-6}$; $N^{+3} = -0.78 \times 10^{-6}$; $B^{+3} = -7.0 \times 10^{-6}$; $F^{-1} = -8.0 \times 10^{-6}$; $O^{-2} = -4.61 \times 10^{-6}$.

TABLE II

HYDROLYSIS AND OXIDATION-REDUCTION EQUIVALENT WEIGHTS

Compound	Hydrolysis		Oxid.-Red.	
	Expt.	Theory	Expt.	Theory
$N_2O_3 \cdot 2BF_3$	26.74	26.45	...	...
$N_2O_4 \cdot 2BF_3$	28.39	28.46	128.7	113.8
$N_2O_5 \cdot BF_5$	33.64	35.18	0.0	0.0
$N_2O_6 \cdot 2BF_3$	...	..	144.0	129.83

TABLE III

MAGNETIC SUSCEPTIBILITIES

Compound 666	Experimental		Theor.
	Gram suscept. × 10^6	Mole suscept. × 10^6	Mole suscept. × 10^6
$N_2O_3 \cdot 2BF_3$[a]	−0.58	−12.3	−77.39
$N_2O_4 \cdot 2BF_3$	−3.53	−80.4	−87.39
$N_2O_5 \cdot BF_3$	−3.37	−82.1	−66.39
$N_2O_6 \cdot 2BF_3$	−2.92	−75.8	−102.0

[a] Values for this material are subject to large error due to the small sample size available. ΔW was 0.0002 g.—about the probable weighing error.

Experimental values for specific and equivalent electrical conductivities of saturated solutions of $N_2O_4 \cdot 2BF_3$ and KF in liquid SO_2 at its boiling point are: specific conductivities: $N_2O_4 \cdot 2BF_3 = 5.4 \times 10^{-5}$; $KF = 1.8 \times 10^{-5}$; equivalent conductivities: $N_2O_4 \cdot 2BF_3 = 27.3$; $KF = 37.8$.

The above experimental data show that the reactions of oxides of nitrogen under the conditions of this investigation result in the addition of two moles of BF_3 per mole of nitrogen oxide, except for the case of N_2O_5, where one mole of BF_3 added under the experimental conditions. The equivalent weights for oxidation–reduction indicate there is no change in average oxidation state for the nitrogen oxides as a result of this reaction, except possibly in the case where the reaction with N_2O_4 was run in the presence of ozone. The observation of one equivalent of reducing power toward ceric sulfate in this case indicates the presence of a peroxy group, which hydrolyzes to hydrogen peroxide, rather than a change in the oxidation state of nitrogen. The electrical conductivity of the $N_2O_4 \cdot 2BF_3$, taken in conjunction with the physical properties—failure to melt at temperatures up to 250°, insolubility in non-polar solvents—suggests that the materials should be formulated as ionic compounds. The observed diamagnetism of all these compounds is compatible with either ionic structures or structures involving

---

(18) Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956.

addition compounds of the molecules but is not compatible with a structure containing NO_2 radicals.

The X-ray powder patterns and infrared spectra of these compounds provide the most help in arriving at reasonable structures. The most striking feature of the X-ray powder patterns is the close agreement of the most intense lines among the different products. This agreement immediately suggests the presence of some common grouping, which largely controls the structures of these materials; variations in the structures would result from less important distortions of the parent structure due to accommodation of different additional groups within the unit cell. It is believed that the common structural unit involved is the BF_3O group.

Fig. 1 shows a comparison of the X-ray powder patterns for several products. It is apparent that the more intense lines of the reaction products and the fluoroborates, $NOBF_4$ and NO_2BF_4, are in rather good agreement. The agreement is best where the compositions approximate the substitution of an oxygen atom for a fluorine and deviate more where there are several additional atoms to be accommodated, as in the case of $N_2O_5 \cdot BF_3$. Since oxygen and fluorine look very nearly alike to X-rays, it is reasonable to assume that the BF_4 and BF_3O groupings should look much the same, provided their spatial orientations are similar.

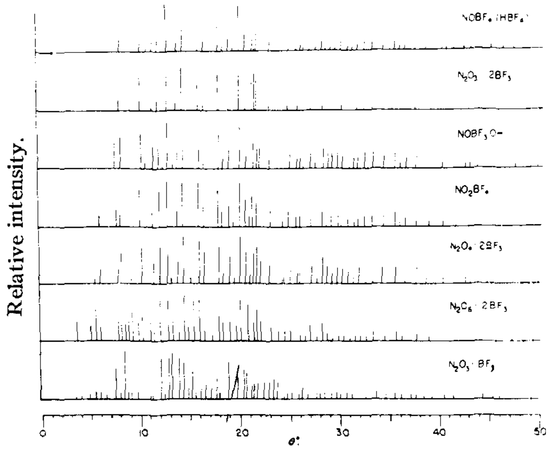


Fig. 1.

Fig. 2 shows a comparison of the X-ray powder patterns of $N_2O_3 \cdot 2BF_3$, $N_2O_4 \cdot 2BF_3$ and the sublimate from the reaction of BF_3 and $NaNO_2$. It is clear that the sublimate from the BF_3–$NaNO_2$ reaction is $N_2O_3 \cdot 2BF_3$; this conclusion is substantiated by comparison of the infrared spectra of these materials, which are found to be identical.

Fig. 3 shows a comparison of the powder patterns of $N_2O_4 \cdot 2BF_3$, $N_2O_6 \cdot 2BF_3$ and the sublimate from the reaction of KNO_3 and BF_3. Although these patterns are similar, they are by no means identical. This similarity, plus the infrared data, leads to the conclusion that the product of the KNO_3–BF_3 reaction is $N_2O_5 \cdot 2BF_3$.

Figs. 4 and 5 compare the powder patterns of the residues from the reactions of BF_3 with $NaNO_2$ and KNO_3, respectively, with $NaBF_4$ and B_2O_3, and KBF_4 and B_2O_3. It is clear that these residues are mainly mixtures of the appropriate fluoroborates and B_2O_3.

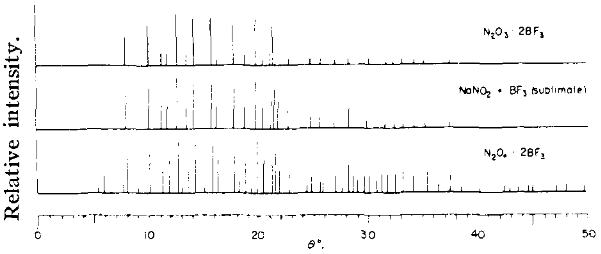


Fig. 2.

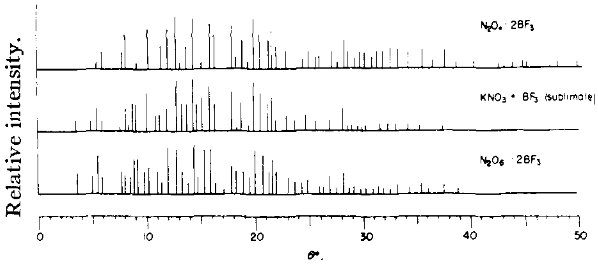


Fig. 3.

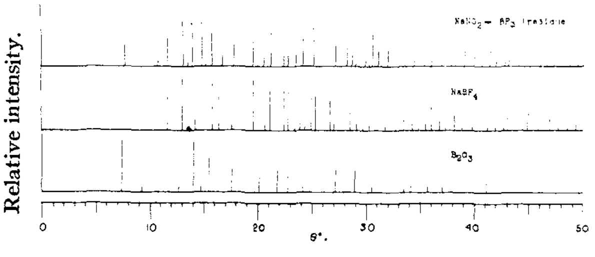


Fig. 4.

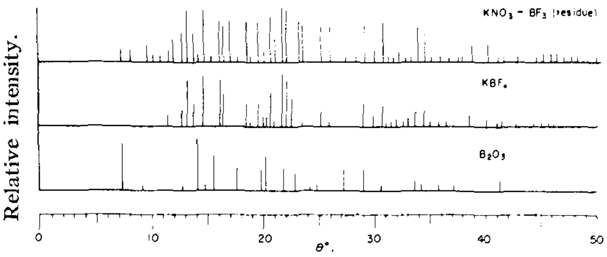


Fig. 5.

In the course of this research, a reliable criterion for identification of the NO^+ ion from infrared spectra was developed. It was observed that compounds containing the NO^+ ion showed a strong absorption at 1808–1820 cm.$^{-1}$ when the spectra were obtained on NaCl windows, but this absorption was missing when the spectra were obtained on sapphire or silicon windows. Since the strongest absorption in the spectrum of NOCl is in this region, these observations are readily accounted for by a reaction of NO^+ with Cl^- of the NaCl windows to form NOCl. This phenomenon was observed for the established nitrosyl salts $NOBF_4$, $NOBF_3OH$, $NOSbCl_6$ and $(NO)_2SnCl_6$. Additional evidence for the presence of NO^+ lies in bands at 2100–2350 cm.$^{-1}$ (previously reported by Millen and Watson)[19] and by a band in the region 1602–1640 cm.$^{-1}$.

---

(19) D. Millen and D. Watson, *J. Chem. Soc.*, 1369 (1957).

TABLE IV

PRINCIPAL BANDS IN INFRARED ABSORPTION SPECTRA OF BF_3–NITROGEN OXIDE REACTION PRODUCTS (NUJOL MULLS ON NaCl WINDOWS)

$NOBF_4$	$NOBF_3OH$	NO_2BF_4	$N_2O_3 \cdot 2BF_3$	$N_2O_4 \cdot 2BF_3$	$N_2O_5 \cdot BF_3$	$N_2O_6 \cdot 2BF_3$
					3770-m	
3575-m	3570-m		3570-ms			3412-m
		3348-m		3349-ms	3348-m	
3205-ms	3215-m		3238-s			
		2384-ms		2384-ms	2384-s	2372-ms
2341-w	2330-mw		2337-mw	2340-m		
2234-w	2256-mw		2256-mw	2234-w		
			2223-w			
2117-w	2117-w					
	1905-mw		1916-vw	1832-w		
1817-s[a]	1810-ms[a]		1811-s[a]	1805-vw[a]		1808-vw[a]
						1777-vw
	1675-m	1675-ms		1675-s	1675-s	1663-s
1638-w			1633-mw			
		1602-ms	1592-mw	1596-ms	1596-s	1592-ms
1337-ms	1333-s				1354-vs	1407-s
1306-ms	1302-s	1307-vs	1307-ms	1307-vs	1308-vs	1335-vs
		1260-vs		1256-vs	1256-vs	1255-vs
1020–1100-vs	1020–1100-vs	1020–1100-vs	1020–1100-vs	1020–1100-vs	1020–1100-vs	1020–1100-vs
	885-m		885-m		903-s	930-ms
		839-ms		845-s	845-ms	833-ms
		819-m			818-m	815-m
		786-ms		786-s	786-s	782-s
770-mw		769-mw	769-m	769-s		
724-mw	724-w	726-ms	724-m	729-s	730-ms	738-s
668-mw	674-w		673-mw		678-m	668-mw

[a] An NOCl band does not appear when sapphire or silicon windows are used.

The work of Teranishi and Decius[20] on the infrared spectrum of N_2O_5 solid affords the main literature on the absorptions of the NO_2^+ ion. Bands which are common to the spectra of solid N_2O_5 and NO_2BF_4 are found in the regions 2384–2395, 1675–1680, 1308, 819 and 769–772 cm.$^{-1}$. Of these absorptions, the band at 2384–2395 cm.$^{-1}$ seems definitely attributable to NO_2^+, and probably those at 1675–1680, 1308, 1256–1260 and 819 cm.$^{-1}$ also result from NO_2^+. Since NO_2^+ is a strong Lewis acid, it is possible that some of these absorptions are due to some covalent character in the bonding situation of NO_2^+. Dodd, Rolfe and Woodward[21] give a critical comparison of the fundamental frequencies in NO_2F, NO_2Cl and NO_2OH (HNO_3); N–O antisymmetric stretching frequencies occur in these molecules in the region 1675–1793 cm.$^{-1}$, N–O symmetric stretching frequencies in the region 1293–1320 cm.$^{-1}$ and bending frequencies in the region 794–925 cm.$^{-1}$. The NO_2^+ ion is involved in primarily covalent bonding in all these molecules. For purposes of establishing the presence of the NO_2^+ ion in this research, primary reliance was placed on the absorption in the region 2384–2395 cm.$^{-1}$, with the absorptions in the regions 1675–1680, 1256–1260 and 819 cm.$^{-1}$ taken as supporting evidence. There does not appear to be any reaction with NaCl windows in the case of nitryl salts to assist in the identification.

The most characteristic feature of the infrared spectra of fluoroborates is a wide, strong band in the region 1020–1100 cm.$^{-1}$. This band was observed for KBF_4, $RbBF_4$, $NOBF_4$, NO_2BF_4 and $NOBF_3OH$. Apparently substitution of one fluorine of the fluoroborate by OH does not affect the position of this band, which may be attributed to tetrahedral boron bonded predominantly to fluorine; this band does not appear in the spectra of BF_3, H_3BO_3 or B_2O_3, where the boron bonds lie in a trigonal plane. Accordingly, the presence of a wide, strong band at 1020–1100 cm.$^{-1}$ was taken to indicate the presence of a BF_4 or BF_3O grouping.

The positions or the infrared absorptions are tabulated in Table IV. The spectrum of $N_2O_3 \cdot 2BF_3$ clearly shows the presence of NO^+ (on comparison of the spectra on NaCl and sapphire windows), while the spectra of $N_2O_4 \cdot 2BF_3$, $N_2O_5 \cdot BF_3$, and $N_2O_6 \cdot 2BF_3$ all show the presence of NO_2^+. The spectra of all these materials show the presence of tetrahedral boron as BF_3O by the wide, strong band at 1020–1100 cm.$^{-1}$.

The spectrum of the sublimate from the reaction of $NaNO_2$ and BF_3 was identical with that of $N_2O_3 \cdot 2BF_3$. The spectrum of the residue from this reaction shows the presence of BF_4 or BF_3O and indicates the presence of B_2O_3. The spectrum of the sublimate from the reaction of KNO_3 and BF_3 shows the presence of NO_2^+ and BF_3O groups; the spectrum of the residue from this reaction shows the presence of BF_4 or BF_3O and indicates the presence of B_2O_3.

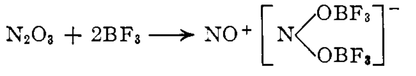
In formulating the products of all these reactions from the experimental evidence, we may start with the compound in which nitrogen has the lowest oxidation state, *viz.*, $N_2O_3 \cdot 2BF_3$. The infrared spectrum shows the presence of a nitrosyl ion; re-

---

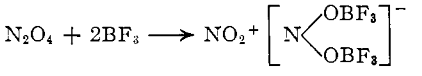
(20) R. Teranishi and J. Decius, *J. Chem. Phys.*, **21**, 1116 (1953).

(21) R. E. Dodd, J. A. Rolfe and L. A. Woodward, *Trans. Faraday Soc.*, **52**, 145 (1956).

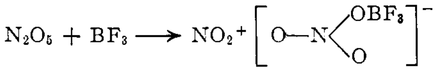
moval of NO^+ from $N_2O_3{\cdot}2BF_3$ leaves a remainder of $NO_2{\cdot}2BF_3$ and this remainder is most reasonably formulated as a nitrite ion, with a BF_3 group attached to each oxygen. This formulation accounts for both the NO^+ and the BF_3O absorptions in the infrared spectrum. Similar reasoning leads to formulations of the other products as nitrosyl and nitryl mono- and difluoroboro nitrites and nitrates. The reactions postulated are



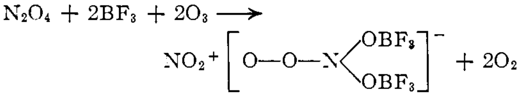
$$N_2O_3 + 2BF_3 \longrightarrow NO^+\left[N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^- \quad (1)$$



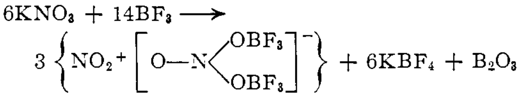
$$N_2O_4 + 2BF_3 \longrightarrow NO_2^+\left[N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^- \quad (2)$$



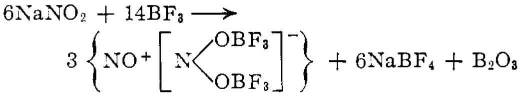
$$N_2O_5 + BF_3 \longrightarrow NO_2^+\left[O{-}N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right]^- \quad (3)$$



$$N_2O_4 + 2BF_3 + 2O_3 \longrightarrow NO_2^+\left[O{-}O{-}N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^- + 2O_2 \quad (4)$$



$$6KNO_3 + 14BF_3 \longrightarrow 3\left\{NO_2^+\left[O{-}N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^-\right\} + 6KBF_4 + B_2O_3 \quad (5)$$



$$6NaNO_2 + 14BF_3 \longrightarrow 3\left\{NO^+\left[N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^-\right\} + 6NaBF_4 + B_2O_3 \quad (6)$$

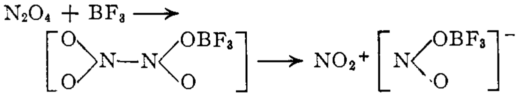
$$N_2O_4 + BF_3 \xrightarrow{(HNO_3)} NOBF_4{}^{22} + \text{(other boron species)} \quad (7)$$

$$N_2O_4{\cdot}2BF_3 \xrightarrow{(H_2SO_4)} NOBF_4{}^{23} + NO_2BF_4{}^{23} + \text{(other boron species)} \quad (8)$$

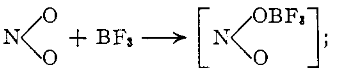
The formulation of the compound $N_2O_6{\cdot}2BF_3$ as a difluoroboroperoxy nitrate takes into account the reducing power toward ceric sulfate.

Although the above formulations are consistent with the infrared spectra of these materials, the X-ray data should be re-examined in the light of these formulations. The point in question is whether the fluoroboro nitrite and nitrate ions can be accommodated in the parent fluoroborate structures without undue distortion of the structure or placing impossible requirements upon the dimensions of these ions. The structures of $NOBF_4$ and $BF_3{\cdot}H_2O$ have been investigated by Klinkenberg and Ketelaar[24,25] and those of NH_4BF_4 and $RbBF_4$ by Hoard and Blair.[26] All these structures are orthorhombic and contain four moles per unit cell. In order to accommodate the fluoroboro nitrites and nitrates in the fluoroborate structures, we must substitute an oxygen for one fluorine in each BF_4 unit and connect the resulting tetrahedra in pairs to nitrogen atoms. The minimum fluorine–fluorine distances between tetrahedra in ammonium and rubidium fluoroborates are 3.01 and 3.17 Å., respectively. If we take a somewhat smaller value, say 2.78 Å., as the O–O distance between BF_3O groups (on the basis of the smaller unit cell size of $NOBF_4$), we may see what sort of N–O bond lengths and O–N–O bond angles would be required. The minimum N–O bond distance would, of course, result from an O–N–O bond angle of 180° and would be 1.39 Å. Reducing the O–N–O bond angle requires an increase in N–O bond length. The O–N–O bond angle in the nitrite ion is about 130°.[27] It is reasonable to expect this bond angle to be opened up somewhat by repulsions of the unshared electron densities on the BF_3O groups. Wells[27] estimates the normal N–O single bond length as about 1.43 Å.; if this figure is used, the required O–N–O bond angle is 153°. If, as another example, the O–N–O bond angle is reduced to 144°, an N–O bond length of 1.45 Å. is required. The above figures indicate that it should be possible to incorporate the fluoroboro nitrate and nitrite ions into the original fluoroborate structure without requiring impossible dimensions for the group. Accordingly, the above formulations of the products are plausible in terms of the X-ray data and account for the similarities in the powder patterns as observed.

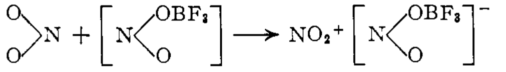
The mechanism of these reactions should initially involve uncharged species, rather than ionic, since the reactions were carried out in the gas phase or in solvents of low dielectric constant. When the N_2O_4–BF_3 reaction was carried out in HNO_3, a different product was observed. The mechanism should also account for the fact that previous work on the reactions of N_2O_3, N_2O_4 and N_2O_5 by Bachman and co-workers[11,12,14] indicates the addition of only one mole of BF_3 per mole of oxide, as was found in this research for the reaction of N_2O_5. The mechanism fulfilling these conditions is



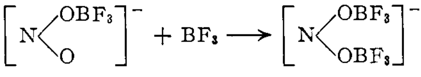
$$N_2O_4 + BF_3 \longrightarrow \left[\begin{smallmatrix}O\\O\end{smallmatrix}N{-}N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right] \longrightarrow NO_2^+\left[N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right]^- \quad (9)$$



$$N\begin{smallmatrix}O\\O\end{smallmatrix} + BF_3 \longrightarrow \left[N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right];$$



$$\begin{smallmatrix}O\\O\end{smallmatrix}N + \left[N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right] \longrightarrow NO_2^+\left[N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right]^- \quad (9a)$$



$$\left[N\begin{smallmatrix}OBF_3\\O\end{smallmatrix}\right]^- + BF_3 \longrightarrow \left[N\begin{smallmatrix}OBF_3\\OBF_3\end{smallmatrix}\right]^- \quad (10)$$

If the reaction is carried out in an excess of BF_3, reaction 10 producing a difluoroboro salt is expected. If the reaction is carried out in a nonpolar solvent, precipitation of the monofluoroboro salt from the reaction zone may well occur in preference to reaction 10. This latter situation applies to the case of the N_2O_5 reaction in this research (CCl_4 solvent) and to the work of Bachman *et al.*[11,12,14] (nitromethane solvent).

The fact that the reaction of N_2O_4 and BF_3 in HNO_3 as solvent leads to $NOBF_4$ indicates that this reaction probably proceeds by ionization of N_2O_4 to nitrosyl and nitrate ions, solvolysis of BF_3 to fluoroboric and hydroxyfluoroboric acids and finally precipitation of $NOBF_4$ when its solubility is exceeded. A mixture of NO_2BF_4 and $NOBF_4$ was obtained

---

[22] The infrared spectrum, X-ray powder pattern and chemical analysis of the product of the reaction of N_2O_4 and BF_3 in HNO_3 solvent identify this material as $NOBF_4$.

[23] Similarly, the product obtained upon recrystallizing $N_2O_4{\cdot}2BF_3$ from concentrated H_2SO_4 was identified as a mixture of $NOBF_4$ and NO_2BF_4.

[24] L. J. Klinkenberg, *Rec. Trav. Chim.*, **56**, 749 (1937).

[25] L. J. Klinkenberg and J. A. A. Ketelaar, *ibid.*, **54**, 959 (1935).

[26] J. L. Hoard and V. Blair, THIS JOURNAL, **57**, 1985 (1935).

[27] A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., Oxford University Press, London, 1950.

from H_2SO_4 solution, because in concentrated H_2SO_4 the nitrate ion is converted to NO_2^+.

Acknowledgments.—The authors wish to take this opportunity to acknowledge the support of this work by the U. S. Naval Ordnance Test Station, China Lake, California, through a research contract with the Research Foundation of the Ohio State University and to thank these organizations for permission to publish this research.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

The Heat Capacity and Thermodynamic Functions of β-Uranium Deuteride from 5 to 350°K.[1,2]

BY BERNARD M. ABRAHAM, DARRELL W. OSBORNE, HOWARD E. FLOTOW AND ROBERT B. MARCUS

RECEIVED JULY 20, 1959

The heat capacity of UD_3 has been measured in an adiabatic calorimeter from 5 to 350°K. The enthalpy and entropy at 298.15°K. calculated from the data are 2577 ± 5 cal. mole^{-1} and 17.20 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, respectively. The entropy and free energy of formation for UD_3 at 298.15°K. as well as the heat of formation at the absolute zero were calculated from these data and the previously reported heat of formation and have the values −46.76 cal. deg.$^{-1}$ mole^{-1}, −17,080 cal. mole^{-1} and −29,000 cal. mole^{-1}. It was found that the calculated and observed dissociation pressures are not in agreement. A similar discrepancy was found for UH_3 and it was suggested that the source might be a particle size effect in the dissociation pressure measurements or the heat of transition of the α-form of UH_3 to the β-form. These heat capacity data were combined with the reported values for UH_3 to calculate the hydrogen and deuterium vibration frequencies in the compounds. An anomaly in the heat capacity was observed which arises from the transition from the ferromagnetic state to the paramagnetic state. The maximum in the heat capacity is 11.72 cal. deg.$^{-1}$ mole^{-1} and occurs at 167.6 ± 0.5°K. It was estimated that 1.19 cal. deg.$^{-1}$ mole^{-1} is the entropy change in the transition which is less than the expected value, $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1}, from the Heisenberg theory of ferromagnetism. Measurements of the magnetization of UD_3 do not appear to be in accord with the thermal measurements.

Introduction

Measurements of the heat capacity of β-UH_3 from 5 to 350°K. previously have been reported from this Laboratory.[3] In order to observe the effect of isotopic substitution on the thermodynamic properties as well as on the ferromagnetic transition similar measurements have been made on β-UD_3. We report here the heat capacity measurements on β-UD_3, the thermodynamic functions derived from the measurements and an analysis of the data from which the vibrational frequencies of H and D in the hydride molecule were calculated and also some conclusions regarding recently reported magnetic measurements on β-UD_3.

The structure of β-UD_3 is identical to that of β-UH_3. The unit cell has cubic symmetry and contains eight uranium atoms arranged as in α-tungsten, *i.e.*, $2U_I$ at $(0,0,0)$ and $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and $6U_{II}$ at $\pm(\frac{1}{4},0,\frac{1}{2})$.[4] The lattice constant a_0 is equal to 6.62 kX units; all of the U–D distances are equal to 2.32 Å. as in β-UH_3. The density of β-UD_3 is equal to 11.11 g./cc. which is to be compared to 10.92 g./cc. for the density of β-UH_3.

The deuteride has been shown to be ferromagnetic but with a saturation moment of 0.98 Bohr magnetons per atom at 1.3°K. compared with 1.18 Bohr magnetons for UH_3.[5] Although the data are not presented by Henry, the statement was made: "The absolute moment of uranium deuteride seems to be less, for all equal conditions of temperature and magnetic field, than that of the hydride." Karchevskii, *et al.*,[6,7] have reported the Curie temperature of UH_3 as 182.0°K. and of UD_3 as 178.4°K., the former in close agreement with the value 181°K. given by Lin and Kaufmann.[8] Karchevskii[7] has in addition determined the magneto-caloric effect for both compounds and finds that the effect is 1.6 times greater for UH_3 at the Curie temperature than for UD_3. One might expect therefore to observe some difference between the heat capacity of β-UH_3 and β-UD_3 at low temperatures as a result of the smaller magnetic moment and smaller magneto-caloric effect for UD_3.

Experimental

The UD_3 sample was prepared from high purity uranium in the form of rods 3 mm. in diameter, made by the Metallurgy Division of this Laboratory.[9] Spectroscopic analysis of the uranium showed the presence of these various elements in p.p.m.: Al, 5; Cr, 1; Cu, 1; Fe, 2; Mg, 0.5; and Si, 10; all other elements were below the limits of spectroscopic detection. Chemical analysis showed 24 p.p.m. of carbon and less than 10 p.p.m. of nitrogen. After removal of a small amount of surface oxide with nitric acid, the uranium metal was placed in a reaction vessel attached to a vacuum line. It was converted to UD_3 by reaction at 190 to 200° with deuterium gas liberated from the thermal decomposition of another sample of UD_3. Under these conditions the β-phase is formed.

The operation of transferring the sample from the reaction vessel to the calorimeter and soldering it shut was performed in a dry-box under an atmosphere of purified helium. Two 1-gram portions were taken for analysis at the time the calorimeter was loaded. These were assayed by thermally decomposing the samples on a vacuum line and volumetrically determining the total gas evolved. The amount of gas collected corresponded to 99.65% of the theoretical for UD_3. The isotopic composition of the gas, determined mass spec-

---

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented in part at the 133rd meeting of the Am. Chem. Soc., San Francisco, April 13–18, 1958.

(3) H. E. Flotow, H. R. Lohr, B. M. Abraham and D. W. Osborne, THIS JOURNAL, **81**, 3529 (1959).

(4) R. E. Rundle, *ibid.*, **73**, 4172 (1951).

(5) W. Henry, *Phys. Rev.*, **109**, 1976 (1958).

(6) A. I. Karchevskii, E. V. Artyushkov and L. I. Kikoin, *Zhur. Eksptl. i Teoret. Fiz.*, **36**, 636 (1959).

(7) A. I. Karchevskii, *ibid.*, **36**, 638 (1959).

(8) S. T. Lin and A. R. Kaufmann, *Phys. Rev.*, **102**, 640 (1956).

(9) B. Blumenthal and R. A. Noland, "Progress in Nuclear Energy," Vol. I, Pergamon Press, London and New York, 1956, Series V, pp. 62-80.