Preparation of N,N′-Diarylsilaimidazolidines.—Equimolar amounts of the N,N′-diarylethylenediamine and dimethylbis(diethylamino)silane are heated together with stirring in the presence of a small amount (<0.1 g) of ammonium sulfate. A temperature sufficient to melt the diamine is generally necessary. Liberated diethylamine is removed from the reaction vessel by a stream of nitrogen and can be collected in a cold trap if desired. After perhaps 5 hr of reaction time, the material is allowed to cool and then, after solidification, is recrystallized from benzene or benzene–hexane. Because the starting diamine and the product imidazolidine have similar solubilities, purification is difficult. Sublimation was attempted in several cases but did not markedly improve the purity. Yields after recrystallization were in the 20–50% range. Compounds were characterized by their nmr spectra and analytical data. Physical properties and analytical data are listed in Table IV.

Acknowledgments.—This investigation was supported by National Science Foundation Grant GP-5025. We are indebted to the National Science Foundation for a predoctoral fellowship to C. H. Y.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE
UNIVERSITY OF CALIFORNIA AND THE INORGANIC MATERIALS RESEARCH DIVISION OF THE LAWRENCE
RADIATION LABORATORY, BERKELEY, CALIFORNIA 94720

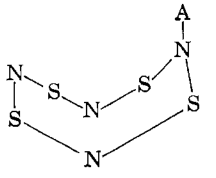
Adducts of Sulfur Nitride with Boron Trihalides and Antimony Pentachloride

BY KENNETH J. WYNNE AND WILLIAM L. JOLLY

Received July 13, 1966

Sulfur nitride in methylene chloride reacts with BF_3 to form burgundy-colored crystals of $S_4N_4 \cdot BF_3$ and with BCl_3 to form red-orange needles of $S_4N_4 \cdot BCl_3$. The BF_3 adduct decomposes reversibly to S_4N_4 and BF_3 when heated, whereas the BCl_3 adduct sublimes with slight decomposition. The properties of the adducts are consistent with structures in which the Lewis acid is coordinated to a nitrogen atom of an S_4N_4 ring, as in $S_4N_4 \cdot SbCl_5$. The boron trifluoride in $S_4N_4 \cdot BF_3$ may be displaced by BCl_3 or $SbCl_5$. In an attempt to displace BCl_3 from $S_4N_4 \cdot BCl_3$ with $SbCl_5$, the adduct $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ formed. This reaction was unexpected because no diadducts were found in the reaction of S_4N_4 with either excess BCl_3 or $SbCl_5$. The conversion of $S_4N_4 \cdot BCl_3$ to $S_4N_4 \cdot SbCl_5$ may be effected by treating $S_4N_4 \cdot BCl_3$ with $SbCl_5$ to give $S_4N_4 \cdot BCl_3 \cdot SbCl_5$, followed by heating this substance *in vacuo* at 90° to form $S_4N_4 \cdot SbCl_5$ and BCl_3.

The following adducts of S_4N_4 with Lewis acids have been prepared: $S_4N_4 \cdot SbCl_5$,[1,2] $2S_4N_4 \cdot SnCl_4$,[1,2] $S_4N_4 \cdot TiCl_4$,[1,2] $S_4N_4 \cdot 2SO_3$,[3] $S_4N_4 \cdot 4SO_3$,[3] $S_4N_4 \cdot TeBr_4$,[4] $S_4N_4 \cdot 4SbF_5$,[5] and $4S_4N_4 \cdot BF_3$.[6] Only for $S_4N_4 \cdot SbCl_5$ is definite structural information available. An X-ray study[7] has shown this adduct to have a structure of type I where A represents the coordinated Lewis acid.



I

The unusual stoichiometry reported for the BF_3 adduct, and the lack of information regarding the other boron trihalide adducts, led us to a systematic study of the reaction of S_4N_4 with the boron trihalides.

Experimental Section

General.—Moisture-sensitive materials were handled in a nitrogen-filled polyethylene glove bag or a standard vacuum line. Analyses were performed in the microanalytical laboratory of this department by V. Tashinian and F. Balistreri.

Infrared spectra were recorded in the 700–4000-cm^{-1} range with a Perkin-Elmer Infracord Model 137B, in the 400–700-cm^{-1} range with a Perkin-Elmer Infracord Model 137 equipped with a KBr prism, and in the 33–400-cm^{-1} range with a Beckman IR-11 grating spectrophotometer. Samples were generally prepared in a nitrogen atmosphere as Nujol mulls and then pressed between either KBr or polyethylene plates. Methylene chloride solution spectra were run in a 0.1-mm KBr cavity cell.

Methylene chloride was refluxed for 3–4 hr over P_2O_5, distilled, and stored in a nitrogen atmosphere. Sulfur nitride was prepared and purified according to the method described by Villena-Blanco and Jolly.[8]

Sulfur Nitride–Boron Trifluoride Adduct.—A slurry of 8.45 g of sulfur nitride and 135 ml of CH_2Cl_2 was prepared in a flask equipped with a gas inlet tube and an outlet protected with a $CaSO_4$ drying tube. While stirring with a magnetic stirrer, BF_3 was bubbled at *ca.* 4–6 bubbles/sec. The solution, initially red-orange, immediately turned dark burgundy. The BF_3 flow was terminated after 40 min, the gas bubbler was removed, and the slurry was filtered, yielding 7.89 g of dark burgundy-colored $S_4N_4 \cdot BF_3$. A further yield of 3.07 g of relatively large crystals (*ca.* 3 × 1 × 1 mm) was obtained by cooling the filtrate to −15°; the total yield was 95%. On heating, the product became continually lighter in color above 90° until melting occurred at 145–147°.

Anal. Calcd for $S_4N_4 \cdot BF_3$: S, 50.88; N, 22.23; formula weight, 252.1. Found: S, 50.22; N, 22.21; molecular weight, 259 (in $CHCl_3$, with vapor pressure osmometer).

The Nujol-mull infrared spectrum showed the following peaks[9]

---

[1] O. C. M. Davis, *J. Chem. Soc.*, **89**, 1575 (1906).

[2] H. Wölbling, *Z. Anorg. Allgem. Chem.*, **57**, 281 (1908).

[3] M. Goehring, H. Hohenschutz, and R. Appel, *Z. Naturforsch.*, **9b**, 678 (1954).

[4] E. E. Aynsley and W. A. Campbell, *J. Chem. Soc.*, 832 (1957).

[5] B. Cohen, T. R. Hopper, D. Hugell, and R. D. Peacock, *Nature*, **207**, 748 (1965).

[6] O. Glemser and H. Ludemann, *Angew. Chem.*, **70**, 190 (1958).

[7] D. Neubauer and J. Weiss, *Z. Anorg. Allgem. Chem.*, **303**, 28 (1960).

[8] M. Villena-Blanco and W. L. Jolly, UCRL Report No. 11294, Jan. 1964.

[9] Values enclosed in brackets refer to peaks in a broad envelope.

[1171 m, 1138 ms, 1117 s, 1070 s, 1040 vs, 1014 m, 949 s, 908 m, 888 s, 840 mw], 724 vw, 697 vw, 682 vw, 658 ms, 623 ms, 567 w, 552 w, 527 s, 502 m, 490 w, sh, 420 ms cm^{-1}. In CH_2Cl_2 solution absorptions were at 1121 m, 1058 ms, 964 m, 933 m, 882 s, 658 sh on solvent, 623 m, 569, w, and 527 s cm^{-1}.

The adduct turns yellow upon exposure to air after approximately 10 min. The infrared spectrum of a sample exposed for 4 hr indicated the presence of S_4N_4 and BF_3 hydrolysis products. The solubility of the adduct in CH_2Cl_2 at 25° is approximately 2.7 g/100 ml, in contrast to S_4N_4 which is soluble to the extent of *ca.* 1 g/100 ml. The density of $S_4N_4\cdot BF_3$ was determined by flotation in CCl_4–CBr_4 to be 2.0 g/cc. The sulfur nitride–boron trifluoride adduct (1.61 mmoles) was decomposed at 140° in a sealed tube for 11 hr. Nitrogen (3.02 mmoles) and BF_3 (1.53 mmoles) were the only volatile products isolated, while the yellow residue consisted of 6.34 mmoles of S.

Reaction of $S_4N_4\cdot BF_3$ with BCl_3 and $SbCl_5$.—Boron trichloride was bubbled through 3.09 mmoles of $S_4N_4\cdot BF_3$ in 100 ml of CH_2Cl_2. After 2 hr, the solution was cooled, filtered, and evaporated to *ca.* 5 ml, yielding a total of 1.62 mmoles of $S_4N_4\cdot BCl_3$ (54%). Upon evaporation of the filtrate to dryness, 0.373 g of a mixture of $S_4N_4\cdot BCl_3$ and its hydrolysis products was isolated.

Antimony pentachloride (31.3 mmoles) was added to 6.75 mmoles of $S_4N_4\cdot BF_3$ in 140 ml of CH_2Cl_2. The solution was filtered, giving 4.22 mmoles of $S_4N_4\cdot SbCl_5$ (62%).

Sulfur Nitride–Boron Trichloride Adduct.—This compound was prepared by mixing CH_2Cl_2 solutions of the reactants and cooling the resulting solution to −15°. The red-orange crystals that separated melted at 137–138°. Large quantities of the adduct were more conveniently prepared by bubbling BCl_3 through a slurry of S_4N_4 in CH_2Cl_2 cooled to 0°; yields were 60% or greater in both methods.

Anal. Calcd for $S_4N_4\cdot BCl_3$: S, 42.69; N, 18.59; Cl, 35.28; formula weight, 301.5. Found: S, 42.78; N, 18.29; Cl, 35.96, molecular weight, 285 (in $CHCl_3$, with vapor pressure osmometer).

Little decomposition was found in crystalline $S_4N_4\cdot BCl_3$ after exposure to air for 24 hr, whereas the powder is more reactive. This low reactivity is rather unusual for BCl_3 adducts, which are usually quite moisture sensitive. The infrared spectrum indicates S_4N_4 and $B(OH)_3$ are the major products of material exposed to the atmosphere.

The solubility of $S_4N_4\cdot BCl_3$ in CH_2Cl_2 is *ca.* 0.8 g/100 ml. The infrared spectrum of a filtered solution of $S_4N_4\cdot BCl_3$ which was protected from the atmosphere to prevent hydrolysis showed no measurable change after 9 days at 23°. During this time, only about 0.5% of the adduct decomposed to molecular nitrogen.

Although S_4N_4 reacts with Cl_2 rapidly to give high yields of $S_3N_3Cl_3$ in a matter of minutes, $S_4N_4\cdot BCl_3$ was found to be relatively unreactive to Cl_2. Most of the starting material was recovered after 10-hr exposure to a rapid stream of Cl_2 in CH_2Cl_2.

The infrared spectrum showed the following peaks:[9] [1064 s, 1042 m], [982 s, 958 s], 864 m, [736 m, 720 m], [695 m, 678 m, 660 m], 625 m, 614 mw, sh, 552 mw, 518 m, 430 m cm^{-1}. In CH_2Cl_2 solution absorptions were at 1061 m, 961 w, sh, 945 m, 859 w, 558 vw, and 524 mw cm^{-1}.

Sulfur Nitride–Antimony Pentachloride Adduct.—The preparative method was similar to that reported,[7] except CH_2Cl_2 was the solvent. The melting point was 160–162°, compared to the literature[7] value of 144°.

Anal. Calcd for $S_4N_4\cdot SbCl_5$: S, 26.54; N, 11.59; Cl, 36.68. Found: S, 26.70; N, 11.56; Cl, 36.68.

The infrared spectrum showed the following peaks:[9] 1060 s, 978 ms, 808 m, 821 ms, 705 w, 625 m, 513 ms, 413 m, [371 s, 364 s, 345.5 s, 309 w, sh], 275.5 m, 246.5 m, 238 w, sh, 211 w, [177.5 s, 164 m], 140 w cm^{-1}.

Sulfur Nitride–Boron Trichloride–Antimony Pentachloride Adduct.—Antimony pentachloride (1.0 ml, 7.84 mmoles) in 35 ml of CH_2Cl_2 was added in small portions to a solution of $S_4N_4\cdot BCl_3$ (0.851 g, 2.82 mmoles) in 130 ml of CH_2Cl_2. On addition of 4 ml of $SbCl_5$ solution the resulting mixture remained the same red-orange color for *ca.* 30 sec and then became cloudy owing to the formation of a yellow precipitate. Addition of $SbCl_5$ was continued; more precipitate formed, but the solution lightened in color appreciably when an amount of solution containing 2.7 mmoles of $SbCl_5$ had been added. The rest of the $SbCl_5$ solution was added to ensure an excess. After filtering, 1.40 g of $S_4N_4\cdot BCl_3\cdot SbCl_5$ was isolated. On heating, the material darkened from 120 to 127° and melted at 127–128°. The same substance could be prepared by bubbling BCl_3 through a suspension of $S_4N_4\cdot SbCl_5$ in CH_2Cl_2. This substance turns orange in a few seconds on exposure to the atmosphere. It is insoluble in CH_2Cl_2 and CCl_4. When $S_4N_4\cdot BCl_3\cdot SbCl_5$ was heated to 85–93°, with constant removal of volatiles in a −196° trap, $S_4N_4\cdot SbCl_5$ and BCl_3 were formed.

Anal. Calcd for $S_4N_4\cdot BCl_3\cdot SbCl_5$: S, 21.36; N, 9.33; Cl, 47.2. Found: S, 21.47; N, 9.58; Cl, 46.8.

The infrared spectrum showed the following peaks:[9] 1317 vw, 1059 vw, 1018 vs, 932 s, 900 vs, 875 w, 840 vs, 811 m, 788 vs, 748 m, 703 mw, 691 ms, 677 s, [552 s, 517 m], 461 m, [419 m, 407 ms], 359 vs, 320 s, 294 ms, 269 ms, 241.5 m, 208 s, 181 vs, 78 w, 52 w cm^{-1}.

Attempts to Prepare Diadducts.—Boron trichloride, in tenfold excess, was heated in a sealed tube with $S_4N_4\cdot BCl_3$ in CH_2Cl_2 at 34° for 57 hr in an attempt to form a diadduct. Pressure was released upon opening the flask, presumably owing to nitrogen, and S_2Cl_2 was found among the products. A small amount of light yellow solid was produced in the reaction, but was not investigated further. Antimony pentachloride (27.2 mmoles) was distilled into $S_4N_4\cdot SbCl_5$ (2.04 mmoles). The mixture turned from red to yellow in 2 hr and remained unchanged in color for an additional 9 hr. In addition to $SbCl_5$, a white, slightly volatile solid, assumed to be $SbCl_3$, was observed while distilling volatiles from the reaction mixture. The nonvolatile residue weighed 0.82 g more than the original $S_4N_4\cdot SbCl_5$. This compares with a calculated weight increase of 0.76 g, based on the equation

$$S_4N_4\cdot SbCl_5 + 2SbCl_5 \longrightarrow S_4N_4Sb_2Cl_{12} + SbCl_3$$

When the volatile materials were treated with chlorine, an uptake of 2.1 mmoles of Cl_2 was observed (calcd 2.04, based on the above equation and the conversion of $SbCl_3$ to $SbCl_5$).

Anal. Calcd for $S_4N_4Sb_2Cl_{12}$: N, 6.57; Cl, 49.86. Found: N, 6.2; Cl, 50.2.

The product (mp 128–129°) exhibited infrared absorptions[9] (in cm^{-1}) at 1060 ms, 1016 s, 619 w, and [455 m, 426 m]. It was insoluble in CH_2Cl_2 and was not investigated further.

Sulfur Nitride–Boron Tribromide.—A solution of 3 ml (31.7 mmoles) of BBr_3 in 25 ml of CH_2Cl_2 was added slowly to a solution of S_4N_4 (2.35 g, 12.75 mmoles) in 150 ml of CH_2Cl_2. The solution turned a dark burgundy color, with the separation of a precipitate. Filtration yielded a gooey, orange-brown mass. It was washed with 10 ml of CH_2Cl_2 and held *in vacuo* for 15 hr, yielding 4.2 g of brown solid. When flushing the glove bag, a distinct odor of bromine was detected. The material imparted a faint orange-yellow coloration when mixed with CH_2Cl_2.

Anal. Calcd for $S_4N_4\cdot BBr_3$: S, 29.49; N, 12.89; Br, 55.13. Found: S, 27.1; N, 12.75; Br, 57.7.

The infrared spectrum showed the following peaks[9] (in cm^{-1}): [1310 s, 1000 ms, 820 m, 670 w]. Inasmuch as $S_4N_4\cdot BBr_3$ was found to be finely divided, moisture sensitive, and insoluble in CH_2Cl_2, it was not investigated further.

Results and Discussion

$S_4N_4\cdot BF_3$.—Whereas we found that bubbling BF_3 into a suspension of S_4N_4 in CH_2Cl_2 gives an almost quantitative yield of a material of composition $S_4N_4\cdot BF_3$, Glemser and Ludemann[6] found that a material of over-all composition $4S_4N_4\cdot BF_3$ formed in a direct reaction of BF_3 gas with solid S_4N_4 at room temperature. Perhaps incomplete reaction was responsible for the unusual stoichiometry observed by these investigators.

The lability of the adduct is shown by the fact that passage of nitrogen through a CH_2Cl_2 solution for 12–14 hr or evaporation of solvent *in vacuo* or heating the solid *in vacuo* causes loss of BF_3 and formation of S_4N_4. The dissociation pressure of the adduct was measured in an immersible tensimeter over the temperature range 30–70°. The combined data for two runs are presented in Table I, where the observed pressures may be compared with those calculated from the equation $\log P_{\mathrm{mm}} = 10.82 - 3270/T$. From this equation we calculate the values $\Delta H° = 15.0$ kcal mole^{-1} and $\Delta S° = 31$ eu for the reaction

$$S_4N_4 \cdot BF_3(s) \longrightarrow S_4N_4(s) + BF_3(g)$$

In the absence of the heats of sublimation for S_4N_4 and $S_4N_4 \cdot BF_3$, we cannot compare the base strength of S_4N_4 with that of any other Lewis base.

TABLE I

DISSOCIATION PRESSURE DATA FOR THE REACTION $S_4N_4 \cdot BF_3(s) \longrightarrow S_4N_4(s) + BF_3(g)$

	Pressure, mm	
T, °K	Obsd	Calcd
305.90	1.15	1.35
307.97	1.65	1.59
309.90	2.00	1.86
313.10	2.45	2.40
320.75	4.10	4.21
321.35	4.30	4.37
322.0	4.65	4.57
327.30	6.85	6.76
327.36	6.75	6.76
332.35	9.55	9.77
333.13	10.00	10.00
337.65	13.70	13.62
339.91	16.00	15.85
342.35	18.60	18.62
348.20	25.65	26.92
348.65	27.50	27.55

In CH_2Cl_2 solution, BF_3 in the adduct may be replaced by BCl_3 or $SbCl_5$ as shown by the equations

$$S_4N_4 \cdot BF_3 + BCl_3 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot BCl_3 + BF_3$$

$$S_4N_4 \cdot BF_3 + SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot SbCl_5 + BF_3$$

$S_4N_4 \cdot BF_3$ decomposes at 140° in a sealed tube as follows

$$S_4N_4 \cdot BF_3 \longrightarrow 4S + 2N_2 + BF_3$$

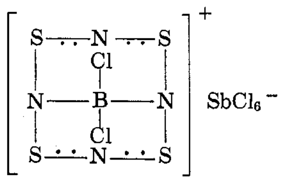
By analogy with the structure of $S_4N_4 \cdot SbCl_5$,[7] $S_4N_4 \cdot BF_3$ is believed to have a structure of type I, with a B–N bond.

$S_4N_4 \cdot BCl_3$.—By analogy with $S_4N_4 \cdot SbCl_5$, the structure of $S_4N_4 \cdot BCl_3$ is believed to be of type I. The infrared spectrum and general physical properties are consistent with this view. The absorption envelope with maxima at 736 and 720 cm^{-1} lies in the usual region assigned to "BCl_3" modes[10] in donor–BCl_3 adducts. The strong absorptions at 695, 678, and 660 cm^{-1} lie in the region where sulfur–nitrogen compounds usually have strong absorptions. S_4N_4, for example, has strong absorptions at 727 and 698 cm^{-1}. It seems likely that the absorptions in the entire region between 660 and 736 cm^{-1} may be due to combinations of S–N and BCl_3 modes, rather than simple group absorptions. The infrared spectrum in CH_2Cl_2 solution is very similar to that in Nujol mull. However, as in the $S_4N_4 \cdot BF_3$ case, the absorptions are shifted significantly, especially the 982- and 958-cm^{-1} absorptions in the solid which occur at 961 and 945 cm^{-1} in solution. The similarity of the solid and solution spectra and the absence of BCl_3 bands in the solution spectrum are consistent with a predominantly undissociated species in solution.

$S_4N_4 \cdot BCl_3$ is a moderately stable substance, subliming at 115° *in vacuo* with only slight decomposition. This is in contrast to the ready dissociation of $S_4N_4 \cdot BF_3$ and may be explained by the fact that BCl_3 is a much stronger Lewis acid than BF_3. However, in a sealed tube during 6 hr at 140°, a sample of $S_4N_4 \cdot BCl_3$ decomposed to nitrogen, S_2Cl_2, a small amount of BCl_3, and a tan nonvolatile residue of empirical formula $BN_{1.3}S_{1.6}Cl_{0.2}$. This residue was moisture sensitive and insoluble in CCl_4 and CH_2Cl_2. It decomposed in a sealed tube at 245° to a white solid which did not melt below 350°. The infrared spectrum of $BN_{1.3}S_{1.6}Cl_{0.2}$ shows only two absorptions above 400 cm^{-1} (at 1400 s and 800 m cm^{-1}) corresponding to no species known to us. We speculate that the structure may be polymeric and involve an [–N=B—S–] type of system.

$S_4N_4 \cdot BCl_3 \cdot SbCl_5$.—In an attempt to displace the BCl_3 from $S_4N_4 \cdot BCl_3$ with $SbCl_5$ in CH_2Cl_2, a yellow precipitate of $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ formed.

Three possible structural formulations were considered for the diadduct: A, $[S_4N_4 \cdot SbCl_4]^+[BCl_4]^-$; B, $[S_4N_4BCl_2]^+[SbCl_6]^-$; and C, $Cl_3B–S_4N_4–SbCl_5$ (B–N and Sb–N bonds). For B one can conceive of the BCl_2 group being bound to one nitrogen atom, as in structure I, or bound to two nitrogen atoms, as in structure II



II

Formulation A may be eliminated on the basis that the characteristic BCl_4^- absorption envelope[10,11] is not observed in the infrared spectrum.

The far-infrared spectra of $KSbCl_6$ and $S_4N_4 \cdot SbCl_5$ were obtained to determine if significant differences in Sb–Cl frequencies would be found, corresponding to the different coordination around antimony. Potassium hexachloroantimonate(V) was prepared by stirring KCl and $SbCl_5$ in CH_2Cl_2 for 47 hr. The infrared spectrum, not previously reported, showed absorptions at 349, 181, and 72 cm^{-1}. By analogy with the spectra of other octahedral species,[12] and from a knowledge of the Raman spectrum[13] of the $SbCl_6^-$ ion, these bands

---

[10] K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, **87**, 4750 (1965).

[11] W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1772 (1960).

[12] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[13] Landolt-Börnstein, "Physikalisch-Chemische Tabellen," I. Band, 2. Teil, Springer-Verlag, Berlin, 1951, p 281.

are assigned to ν_3, ν_4, and a lattice vibration, respectively. The $S_4N_4 \cdot SbCl_5$ adduct showed absorptions at 345.5 and 177.5 cm^{-1}, and $S_4N_4 \cdot BCl_3 \cdot SbCl_5$ showed absorptions at 357 and 181 cm^{-1}. The small differences in the respective Sb–Cl frequencies in all three cases does not allow a choice between formulations B and C for the diadduct. Absorptions in the B–Cl and B–N region slightly favor formulation B, with structure II. Nöth and Lukas[14] have reported B–Cl frequencies at 849 and 842 cm^{-1} and a B–N absorption at 925 cm^{-1}, for $\{[(CH_3)_2NH]_2BCl_2\}Cl$. Possibly the peaks at 840 and 932 cm^{-1} of the diadduct correspond to the B–Cl and B–N frequencies, respectively, expected for tetravalent boron.

The formation of the mixed adduct was surprising because diadducts of BCl_3 and $SbCl_5$ were not formed even though excess BCl_3 and $SbCl_5$ were present in the preparation of the corresponding monoadducts. Our attempts to form diadducts with BCl_3 and $SbCl_5$ indicated that, if the diadducts formed at all, they were unstable under the reaction conditions.

Although we were unable to convert $S_4N_4 \cdot BCl_3$ into $S_4N_4 \cdot SbCl_5$ directly by treatment with $SbCl_5$, this conversion can be effected by the following successive reactions.

$$S_4N_4 \cdot BCl_3 + SbCl_5 \xrightarrow{CH_2Cl_2} S_4N_4 \cdot BCl_3 \cdot SbCl_5$$

$$S_4N_4 \cdot BCl_3 \cdot SbCl_5 \xrightarrow{85\text{–}90^\circ} S_4N_4 \cdot SbCl_5 + BCl_3$$

Acknowledgment.—This work was supported by the United States Atomic Energy Commission.

[14] H. Nöth and S. Lukas, *Chem. Ber.*, **95**, 1505 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING,
RESEARCH DIVISION, NEW YORK UNIVERSITY, NEW YORK, NEW YORK

Reactions of Boron Trifluoride with Oxides of Nitrogen

BY ASIM B. RAY

Received June 6, 1966

A quantitative study of the reactions between BF_3 and the oxides of nitrogen (N_2O_3, N_2O_4, and N_2O_5) was carried out in the absence of solvents. The final products were mixtures of B_2O_3 and $NOBF_4$ in the case of N_2O_3, and $NOBF_4$ and O_2 with N_2O_4 and NO_2BF_4 in the case of N_2O_5. In the detailed study of the N_2O_4–BF_3 system some of the postulated intermediates were isolated. A mechanism capable of explaining the observations of different authors under divergent conditions is suggested.

The reactions between boron trifluoride and oxides of nitrogen have been the subject of a number of papers.[1–4] Most of these reactions were carried out in the presence of a solvent and below room temperature. The various solid products obtained in these reactions were formulated as NO^+ or NO_2^+ salts of complex boron-containing anions;[1–4] the solids $BF_3 \cdot N_2O_3$, $BF_3 \cdot N_2O_4$, and $BF_3 \cdot N_2O_5$ were regarded,[1–3] respectively, as $NO^+(BF_3NO_2)^-$, $NO_2^+(BF_3NO_2)^-$, and $NO_2^+(BF_3ONO_2)^-$. Recently[5] it has been shown that the above formulations are erroneous and in reality they are, respectively, mixtures of B_2O_3 and $NOBF_4$, B_2O_3 and various proportions of $NOBF_4$ and NO_2BF_4 (depending upon reaction conditions), and B_2O_3 and NO_2BF_4.

Other allied interesting reactions[4,6,7] are those of alkali metal nitrate and nitrite with boron trifluoride in the higher temperature range. Sprague, *et al.*,[4] have carried out the reactions between oxides of nitrogen and BF_3 under various conditions: (a) in the presence of solvents at low temperatures and (b) in the gaseous phase. They also studied the reactions of KNO_3 and $NaNO_2$ with BF_3 at elevated temperatures. In all of the above reactions where the same reactants were used they claimed to have obtained identical compounds, *i.e.*, NO^+ or NO_2^+ salts of complex boron-containing species. However, Scott and Shriver[7] have shown (at 180°) that with $NaNO_3$ the only products obtained were $NaBF_4$, $NOBF_4$, B_2O_3, and O_2, while with nitrite the products depending upon reaction conditions were nitric oxide, nitrate, B_2O_3, $NaBF_4$, and $NOBF_4$. In no case were the compounds claimed by Sprague, *et al.*, obtained.

It is also interesting to note that in the methods of preparation of $NOBF_4$ both N_2O_3[8,9] and N_2O_4[10] have been recommended.

We studied the reactions between BF_3 and oxides of nitrogen at room temperature and in the absence of any solvent. Particular attention was given to N_2O_4. In order to obtain stoichiometry of the reactions, various proportions of the reactants were employed.

The main purpose of this paper is to correlate the

[1] G. B. Bachman and J. Hokama, *J. Am. Chem. Soc.*, **79**, 4370 (1957).

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

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

[4] R. W. Sprague, A. B. Garett, and H. H. Sisler, *ibid.*, **82**, 1059 (1960).

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

[6] P. Baumgarten and W. Burns, *Ber.*, **72**, 1753 (1939).

[7] R. N. Scott and D. F. Shriver, *Inorg. Chem.*, **3**, 857 (1964).

[8] E. Wilke-Dörfurt and G. Balz, *Z. Anorg. Allgem. Chem.*, **159**, 197 (1927).

[9] E. Wilke-Dörfurt, *Angew. Chem.*, **37**, 712 (1924).

[10] S. A. Voznesenskii and P. P. Kurski, *J. Gen. Chem. USSR*, **8**, 524 (1938).