strong mixing. The crystals that separated were collected on a filter under nitrogen, washed with a 1:1 water–methanol mixture, and then with methanol. The solid material was redissolved in a small amount of ice-cold, deaerated water, and the solution was filtered rapidly and treated with methanol (*ca.* 30 vol. %). The crystals were collected on a filter, washed with a 1:1 methanol–water mixture, then with methanol and subsequently with ether, and dried for 8 hr. *in vacuo* over P_2O_5 at 100°.

Anal. Calcd. for $K_6[(CN)_5Co\cdot SO_2\cdot Co(CN)_5]\cdot 4H_2O$: C, 16.10; H, 1.07; S, 4.28; N, 18.7. Found: C, 16.3; H, 1.25; S, 4.15; N, 18.65.

To 70 ml. of an aqueous deaerated solution of 1.19 g. of $CoCl_2\cdot 6H_2O$ and 1.7 g. of KCN was slowly added 30 ml. of methanol containing 0.57 g. of $SnCl_2\cdot 2H_2O$ with vigorous mixing and in an N_2 atmosphere at 0°. The color changed from green to pale brown and then to dark brown. Finally, a dark brown solid started to separate. Its separation was completed by the addition of about 30 ml. of deaerated methanol. The crystalline product was collected on a filter and washed with a 1:1 methanol–water mixture and then with methanol. The dark brown solid was dissolved in a small amount of ice-cold, deaerated water and precipitated very rapidly with methanol. After filtration and washing with a methanol–water mixture followed by methanol, the solid was dried over P_2O_5 *in vacuo*.

Anal. Calcd. for $K_6[(CN)_5Co\cdot SnCl_2\cdot Co(CN)_5]$: C, 14.83; N, 17.46; Cl, 8.88. Found: Sample 1: C, 14.2; N, 16.8; Cl, 9.05. Sample 2: C, 13.4; N, 15.4; Cl, 10.3.

Spectra.—A Cary Model 14 spectrophotometer was used. The solutions were prepared in an N_2 atmosphere and transferred to the cell under nitrogen (the details will be described later[6]). Infrared spectra were taken on a Perkin-Elmer grating infrared Model 337 spectrophotometer in Nujol mull. An ordinary Beckman Model 9 potentiometer was used for potentiometric titrations with a bright platinum electrode combined with a commercial saturated calomel electrode.

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The Reaction of Boron Trifluoride with Sodium Nitrate and Sodium Nitrite

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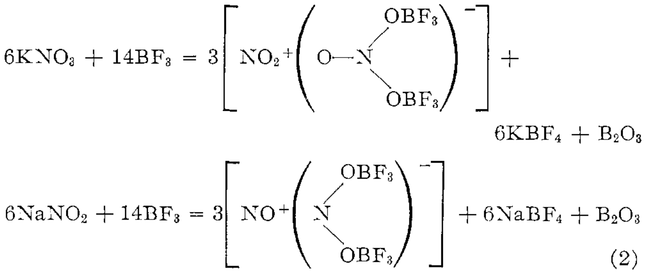
The interaction of nitrate[1,2] and nitrite[2] salts with boron trifluoride has been studied previously. Baumgarten proposed reaction 1 for potassium nitrate and boron trifluoride at 400–500°.

$$6KNO_3 + 9BF_3 = 6KBF_4 + (BOF)_3 + 3N_2O_3\,(2NO_2 + {}^1/_2O_2) \quad (1)$$

Sprague, *et al.*, studied the interaction of boron trifluoride with potassium nitrate and sodium nitrite by passing a stream of boron trifluoride over the salt in a Pyrex tube. The reaction was initiated by flaming the material with a torch. They proposed the reaction shown below.

We have recently reinvestigated these reactions at lower temperatures and under more controlled conditions.



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

$$6NaNO_2 + 14BF_3 = 3\left[NO^+\left(N\begin{matrix}OBF_3\\ \\ OBF_3\end{matrix}\right)^-\right] + 6NaBF_4 + B_2O_3 \quad (2)$$

Experimental Section

Materials.—Reagent grade sodium nitrite and sodium nitrate were purchased from the Allied Chemical Co.

Purification of Boron Trifluoride.—Matheson 99% pure material was fractionated through a −126° bath. The vapor pressure at −111.6° was 301.4 mm., in good agreement with the value of 301 mm. given by Brown.[3] The infrared spectrum agrees with that of Baily, *et al.*,[4] and Vanderryn.[5]

Reaction of Boron Trifluoride and Sodium Nitrate.—In a typical reaction 0.0395 g. (0.464 mmole) of sodium nitrate and 1.35 mmoles of boron trifluoride were sealed in a Pyrex tube fitted with a break-seal. The lower three-fourths of the tube was placed in a furnace which was maintained at 180° for 48 hr. Gaseous products were then admitted to the vacuum line, condensables were collected at −196°, and noncondensables were collected by means of a Toepler pump. After *PVT* measurement of these fractions, condensables were characterized by an infrared spectrum and noncondensables by a mass spectrum. The reaction vessel was filled with dry nitrogen and transferred to a nitrogen-flushed drybag, where X-ray capillaries were loaded and mulls for infrared spectra were prepared. There was no evidence of etching in any of the reaction tubes.

Raman Spectra.—The Brandmuller technique[6] was employed on samples of the solid which had sublimed to the cold ends of the reaction tubes. The 4358-Å. Hg line was used for excitation, and a Gaertner two-prism spectrograph was employed (*f* 3.5; dispersion, *ca.* 150 cm.$^{-1}$/mm. in the region of interest). Considerable fluorescence was evident in all spectra.

Reaction of Boron Trifluoride and Sodium Nitrite.—The procedures were the same as those for sodium nitrate. In addition, the reaction of BF_3 with a suspension of $NaNO_2$ in *sym*-tetrachloroethane was followed on the vacuum line at −23 and 0°.[7]

Results

Sodium Nitrate.—When sodium nitrate and boron trifluoride were heated in a tube furnace as previously described, a white solid sublimed to the top of the reaction tube, leaving behind a white residue. X-Ray powder diffraction data for $NaBF_4$ and for nitrosyl tetrafluoroborate[8] were compared with products of the reaction, and it was found that the powder pattern of the sublimate matched quite well that of nitrosyl tetrafluoroborate, while the powder pattern of the residue matched the most intense lines of sodium tetrafluoroborate.

The mass spectrum of the noncondensable gas produced in this reaction contained only two sets of peaks

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(1) P. Baumgarten and W. Bruns, *Ber.*, **72**, 1753 (1939).

(2) R. W. Sprague, A. B. Garett, and H. H. Sisler, *J. Am. Chem. Soc.*, **82**, 1059 (1960).

(3) H. C. Brown and R. B. Johannsen, *ibid.*, **72**, 2937 (1950).

(4) C. R. Baily, J. B. Hale, and J. W. Thompson, *Proc. Roy. Soc.* (London), **161**, 107 (1937).

(5) J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959).

(6) J. Brandmuller, *Z. angew. Phys.*, **5**, 95 (1953).

(7) This experiment was performed by John J. Rupp. In view of the explosive nature of dinitrogen tetroxide in the presence of chloronated solvents [*Chem. Eng. News*, **42**, No. 47, 53 (1964)] there may be some danger of explosion associated with this reaction.

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

having significant intensities. These occurred at mass to charge ratios of 14, 16, 28, and 32 and correspond to the unipositive ions of atomic and molecular nitrogen and oxygen. The ratio of the intensity of the O_2^+ peak to that of the N_2^+ peak was 12:1. Thus, the major gaseous product of the reaction is oxygen. *PVT* measurement of this gas revealed that 0.294 mole of O_2 was produced per mole of $NaNO_3$.

An infrared spectrum of the condensable gas showed that it was boron trifluoride, and *PVT* measurement indicated that the ratio of BF_3 consumed per $NaNO_3$ is 2.72.

A balanced chemical equation consistent with all of the previous data with the exception of the quantity of oxygen recovered is

$$3NaNO_3 + 8BF_3 = 3NaBF_4 + 3NOBF_4 + {}^3/_2O_2 + B_2O_3 \quad (3)$$

The theoretical ratios are: BF_3 consumed/$NaNO_3$ = 2.67 and O_2 produced/$NaNO_3$ = 0.500. The high ratio observed for BF_3 consumed per $NaNO_3$ may be explained by a slight but ill-defined reaction of BF_3 with B_2O_3. The literature contains conflicting reports on the stability of boron–oxygen–fluorine containing materials at room temperature.[9,10] Therefore, the interaction of B_2O_3 and BF_3 was investigated under conditions used in the reaction of BF_3 with $NaNO_3$ and with $NaNO_2$. Boric oxide (1.32 mmoles) and boron trifluoride (2.84 mmoles) were allowed to react in a heated sealed tube, and 0.22 mole of BF_3 was absorbed per mole of B_2O_3. On this basis, an approximate correction may be applied to yield a ratio of 2.62 for BF_3 consumed per $NaNO_3$ exclusive of the BF_3–B_2O_3 reaction. The low experimental value for the oxygen evolved suggests that perhaps some other oxygen containing compound such as nitryl tetrafluoroborate might also be formed in the reaction. However, no evidence for NO_2BF_4 could be found in either the X-ray powder patterns or the infrared and Raman spectra of the solid reaction products. An infrared spectrum of a Fluorolube mull on Irtran plates had a band at 2340 cm.$^{-1}$ (NO^+ stretch) but no absorption at 2380 cm.$^{-1}$, the region of NO_2^+ absorption. To ensure that NO_2BF_4 would not be lost during sample preparation, Raman spectra were obtained on the sublimate in unopened reaction tubes. All major vibrations associated with BF_4^- and NO^+ were evident in the spectra, but the 1400 cm.$^{-1}$ vibration of NO_2^+ was not detected. Several repetitions of the reaction have resulted in varying quantities of oxygen while the nature of the solid products appears to be unchanged. From the relative intensities of the published X-ray powder patterns and spectra we estimate that the percentage of nitryl tetrafluoroborate in the sublimate necessary to explain the low oxygen would have been easily detected in our X-ray, infrared, or Raman experiments.

When the entire length of the unopened reaction tube was heated in the furnace, it became filled with an intensely colored brown gas (no doubt NO_2). Upon cooling to room temperature, the brown color disappeared. This result indicates that the BF_3 adducts of the nitrogen oxides dissociate at elevated temperatures, and therefore the reaction proposed by Baumgarten is correct for the temperature range in which he was working. However, the reaction proposed by Sprague, *et al.*, appears incorrect.

Sodium Nitrite. (A) Reaction with Less Than a Stoichiometric Quantity of Boron Trifluoride.—Sodium nitrite (1.94 mmoles) and boron trifluoride (2.43 mmoles) were heated in a sealed tube at 190° for 5 weeks. There was no sublimate formed in this reaction. *PVT* measurements made in a calibrated portion of the vacuum line showed that 0.548 mmole of gaseous products was formed. A mass spectrum of the gas showed that it was nitric oxide and that there was no unreacted boron trifluoride.

X-Ray powder data for the nonvolatile solid products and for authentic samples of sodium nitrate and sodium tetrafluoroborate indicate that the white residue is a mixture of sodium tetrafluoroborate and sodium nitrate. An infrared spectrum of a perchlorobutadiene mull of the residue confirmed the presence of nitrate (band at 1367 cm.$^{-1}$) and tetrafluoroborate (broad band at 1000–1100 cm.$^{-1}$). There was no evidence for the presence of unreacted nitrite. A reaction scheme consistent with these observations is

$$9NaNO_2 + 8BF_3 = 6NO + 3NaNO_3 + 6NaBF_4 + B_2O_3$$

This scheme involves a Lewis acid induced disproportionation of nitrite which is analogous to the proton-induced disproportionation in aqueous solution

$$3HNO_2 = 2NO + HNO_3 + B_2O_3$$

(B) Reaction with Excess Boron Trifluoride.—Sodium nitrite (0.597 mmole) and excess boron trifluoride (5.49 mmoles) were heated in a sealed tube equipped with a break-seal at 190° for 1 week. As in the case of the reaction of sodium nitrate, a white solid sublimed to the cool end of the reaction tube leaving a white residue behind. The powder pattern of the residue matches quite well that of sodium tetrafluoroborate while that of the sublimate matches the pattern of nitrosyl tetrafluoroborate.

The noncondensable gaseous products (0.0254 mmole) were pumped into a calibrated portion of the Toepler pump. Nitric oxide was found to be the major constituent by a mass spectrum.

A mass spectrum of the condensable gas showed it to be a mixture of boron trifluoride and nitric oxide with boron trifluoride as the major component. It is thus apparent from these data that the major gaseous product of the reaction is nitric oxide.

From the previous results it is clear that in the presence of excess boron trifluoride, the sodium nitrate which is formed in the initial reaction reacts further with boron trifluoride according to eq. 3. The reaction as written in eq. 3 involves the formation of molecular oxygen which would be expected to react with the nitric oxide formed in the first step to give dinitrogen tetroxide. Evans, *et al.*,[8] have shown that boron tri-

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

[10] E. M. Magee, *J. Inorg. Nucl. Chem.*, **22**, 155 (1961).

fluoride reacts with dinitrogen tetroxide to form nitrosyl tetrafluoroborate, nitryl tetrafluoroborate, and boric oxide as shown in eq. 4.

$$3N_2O_4 + 8BF_3 = 3NO_2BF_4 + 3NOBF_4 + B_2O_3 \qquad (4)$$

As in the case of the reaction of sodium nitrate, there was no evidence for the presence of nitryl tetrafluoroborate among the products. Evans reports that the ratio of nitrosyl to nitryl tetrafluoroborate in the product was a function of the reaction conditions. In view of the identification of NO, $NOBF_4$, and $NaBF_4$ among the ultimate products of the reaction of sodium nitrite with boron trifluoride eq. 5 is implied. However, we did not detect NO_2BF_4 among the products, and one possible explanation is that in addition to eq. 5 some reaction took place *via* eq. 6 which would reduce the quantity of NO_2BF_4 produced and render its detection difficult. In any case, reaction 2 proposed by Sprague, *et al.*, for the interaction of $NaNO_2$ with BF_3, appears incorrect since it does not account for NO and $NOBF_4$ production. Furthermore, the instability of $NaNO_2$ in the presence of BF_3 at low temperature indicates that their product, formulated as $[NO^+][NO_2 \cdot 2BF_3^-]$, is unlikely.

$$18NaNO_2 + 40BF_3 = 6NO + 18NaBF_4 + 5B_2O_3 + 9NOBF_4 + 3NO_2BF_4 \qquad (5)$$

$$3NaNO_2 + 8BF_3 = 3NaBF_4 + B_2O_3 + 3NOBF_4 \qquad (6)$$

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Mode of Attachment of Amides in $B_{10}H_{12} \cdot$2amide Complexes

BY W. R. HERTLER AND E. L. MUETTERTIES

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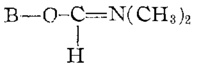
Earlier work in two laboratories[1,2] described the reaction of decaborane(14) with dimethylformamide (DMF) to give $B_{10}H_{12} \cdot 2DMF$. Pace, *et al.*, proposed that the amide in $B_{10}H_{12} \cdot 2DMF$ was bonded to boron through oxygen on the basis of infrared spectral data.[2] In subsequent work, it was found[3] that $B_{10}H_{10}^{2-}$ reacted with dimethylformamide in the presence of strong acid to give $2\text{-}B_{10}H_9 \cdot DMF^-$. The structure $2\text{-}B_{10}H_9\text{-}OCH{=}N(CH_3)_2^-$ was proposed for this product because the proton magnetic resonance spectrum showed the presence of two nonequivalent methyl groups at τ 6.9 (doublet, J = 0.8 c.p.s.) and 7.1 (doublet, J = 1.2 c.p.s.), corresponding, respectively, to the methyl groups *cis* and *trans* to the "formyl" hydrogen atom. Absorption in the infrared spectrum of the product at 1680 cm.$^{-1}$ was noted. Similarly, the presence of two methyl resonances (doublets, J = 0.8 and 1.3 c.p.s.) in the n.m.r. spectrum of $BCl_3 \cdot DMF$ led to the assignment of B–O rather than B–N bonding.[4]

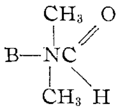
Recently Fein, *et al.*,[5] reinvestigated the reaction of decaborane(14) with dimethylformamide and other amides. They assigned an infrared absorption at 1675 cm.$^{-1}$ to C=O stretching and proposed that $B_{10}H_{12} \cdot 2DMF$ has the structure $B_{10}H_{12}[N(CH_3)_2CHO]_2$.

In order to resolve the conflicting structural assignments (*i.e.*, to determine whether the bonding is of type A or B), an n.m.r. study was undertaken and is the subject of this note.



$$\mathrm{B{-}O{-}\underset{\underset{\textstyle H}{|}}{C}{=}N(CH_3)_2}$$

A



B

The 60-Mc. proton n.m.r. spectrum of $B_{10}H_{12} \cdot 2DMF$[5] in DMF-d_7 at 29° shows a multiplet of intensity 1 centered at τ 2.0, a doublet at τ 6.95 (J = 0.6 c.p.s.) of intensity 3, and a doublet at τ 7.25 (J = 1 c.p.s.) of intensity 3. If bonding is of type A, then the doublets at τ 6.95 and 7.25 can be assigned, respectively, to methyl groups *cis* and *trans* to the "formyl" hydrogen atom (τ 2.0). These results and their interpretation are similar to those reported earlier[3] for $2\text{-}B_{10}H_9OCH{=}N(CH_3)_2^-$. In order to rationalize the spectral data in terms of a type-B structure, it is necessary to invoke a barrier to rotation about the C–$N(CH_3)_2$ bond so that the two methyl groups are nonequivalent and unequally coupled to the formyl hydrogen atom. The barrier to rotation about the C–N bond in DMF has been attributed to C=N character resulting from overlap of the p orbitals of nitrogen and carbonyl carbon.[6] In the case of structure B, there is no possibility for such delocalization, and any barrier to rotation would have to be due to steric hindrance. Such a barrier should be small, and the two methyl groups should become equivalent at elevated temperatures. At 50°, the two methyl resonances of $B_{10}H_{12} \cdot 2DMF$ are unchanged in position, but the intensity of the peaks gradually diminishes as new peaks appear at the same positions as the peaks of free DMF, namely τ 2.28, 7.36 (doublet, J = 0.7 c.p.s.), and 7.51 (doublet, J = 1.3 c.p.s.). Apparently at 50°, ligand exchange occurs as

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