Matrix Isolation–Mass Spectroscopy Study of the Reaction of Boron Trifluoride with Trimethylamine–Alane and Trimethylamine–Gallane

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The gas-phase reactions of BF_3 with $(CH_3)_3N\cdot AlH_3$ and $(CH_3)_3N\cdot GaH_3$ were studied with a combination matrix isolation–infrared spectrometer–mass spectrometer apparatus. The initial reaction products were BF_2H and $N(CH_3)_3$; no AlH_3 or GaH_3 was detected. The reaction is a halide–hydride exchange and not a Lewis acid displacement reaction. The previously reported reaction of BF_3 with $(CH_3)_3N\cdot GaH_3$ to produce uncoordinated gallium hydride in both the gas and condensed phases was not observed. A reaction mechanism is proposed to account for the reactions in both phases.

Introduction

Little structural and spectroscopic information is available on the monomeric trihydrides of the boron-group elements. These electron-deficient molecules are more stable as hydride-bridged oligomers and polymers such as B_2H_6 and the higher boranes and the solid $(AlH_3)_x$. These polymers apparently do not readily dissociate to give identifiable yields of monomeric MH_3. The few studies that have been reported on these monomeric trihydrides have generated these species with use of specialized techniques.

The preparation of what was reported to be an unstable liquid and gaseous uncoordinated gallium hydride (GaH_3) has been published.[1] Liquid gallium hydride was generated by a Lewis acid displacement reaction at −15 °C:

$$BF_3(g) + (CH_3)_3N\cdot GaH_3(s) \rightarrow$$
$$(CH_3)_3N\cdot BF_3(s) + GaH_3(l) \quad (1)$$
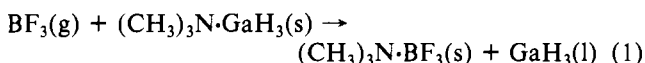
GaH_3 was reported to be an oil, apparently associated, that decomposed above −15 °C to Ga and H_2. When this reaction was performed in the gas phase at room temperature in an infrared gas cell, a sharp absorption at 2000 cm^{-1} was reported to appear before diminishing in intensity a few minutes later. This transient species was attributed to an unstable gaseous gallium hydride.

Kaldor and Porter reported the isolation of a monomeric BH_3 in 1971.[2] The pyrolysis products of BH_3CO were trapped in an argon matrix, and three new absorptions in the infrared spectrum were assigned to a monomeric planar D_{3h} BH_3 molecule.

A gaseous AlH_3 and its dimer Al_2H_6 have been detected in a time-of-flight mass spectrometer by Breisacher and Siegel.[3] Al was heated in a low-pressure hydrogen atmosphere, and ion peaks due to $AlH_3{}^+$ and $Al_2H_6{}^+$ were observed. Using the same technique, they found much smaller amounts of $GaH_3{}^+$ and $InH_3{}^+$ but no dimers as in the Al study. The relative abundances of the hydrides formed in these reactions were used as a measure of the hydride stability, which was given as $AlH_3 > GaH_3 > InH_3$.[4] Attempts to trap AlH_3 in a matrix using the Al + H atom reaction were unsuccessful.[5]

Following ref 1, we decided to study reactions of BF_3 with trimethylamine adducts of metal trihydrides as a possible source of GaH_3 and perhaps the other group 3A hydrides. We hoped to trap these unstable molecules in an inert-gas or N_2 matrix immediately after their formation.

We first studied the reaction of $(CH_3)_3N\cdot AlH_3$ since AlH_3 was expected to be more stable than GaH_3. Our matrix iso-

lation apparatus was designed so a flow reactor could be used as the gas deposition system and a mass spectrometer, which was attached behind the 18 K sample substrate, could be used to sample the deposition beam and monitor the reaction. This system would allow us to vary the reaction conditions and to study the mechanism of the reaction in detail.

We found that the reaction between BF_3 and $(CH_3)_3N\cdot AlH_3$ did not proceed as given in ref 1 but rather as a halide–hydride exchange reaction. The combination of a flow reactor with a matrix isolation apparatus and a mass spectrometer proved to be a powerful combination for studying the detailed mechanism of this reaction.

When our studies indicated that in the gas phase a halide–hydride exchange occurred, we also tried to prepare the uncoordinated liquid gallane following the published procedure.[1] We observed an initial product of this reaction different from that previously reported. This result can be interpreted with a reaction mechanism that is consistent with our gas-phase results but inconsistent with the formation of uncoordinated GaH_3.
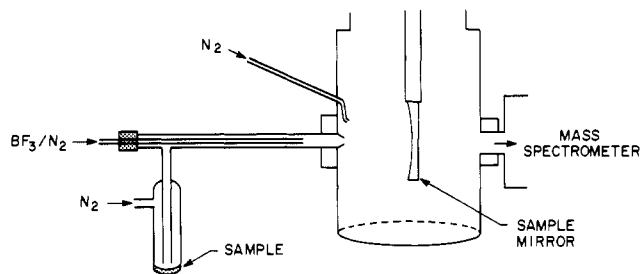
Experimental Section

Three types of experiments were done in this study. Initially the gas-phase reactions of BF_3 with $(CH_3)_3N\cdot AlH_3$ and $(CH_3)_3N\cdot GaH_3$ were studied mass spectrometrically in a flow reactor to determine the experimental conditions necessary to effect a reaction and to identify the predominant reaction products. The flow reactor was then adapted for matrix isolation depositions, and the reaction products were trapped at 17–18 K and their infrared spectra studied. The mass spectrometer was also used to monitor the progress of the matrix depositions. Additionally, the bulk reactions between BF_3 and solid trimethylamine–alane and trimethylamine–gallane were studied using standard vacuum line techniques.

Flow Reactor. A simple flow reactor shown in Figure 1 was used to study the gas-phase reactions. It consisted of two gas entry ports to introduce the volatile $(CH_3)_3N\cdot MH_3$ (M = Al or Ga) and BF_3 in a carrier gas (Ar or N_2) separately into the reaction zone. The BF_3 inlet tube was equipped with a sliding seal so that the reaction distance could be varied by a factor of about 100. The flow rates were not known so we could only measure the relative reaction times. The reaction products were analyzed either by mass spectrometry or by infrared spectroscopy using the matrix isolation technique.

$(CH_3)_3N\cdot MH_3$ (M = Al, Ga) was sublimed into the trap prior to an experiment to ensure a pure sample, and during the experiment the solid was kept in a constant-temperature bath. For $(CH_3)_3N\cdot AlH_3$, the bath was at −35 °C for the mass spectrometric work and at −50 °C for the matrix isolation studies. The more volatile $(CH_3)_3N\cdot GaH_3$ was kept at lower temperatures of −47 and −65 °C for the mass spectrometric and matrix experiments, respectively. The hydride was swept into the reaction zone by a stream of Ar or N_2 gas. The vapor pressure of these complexes is not known at these temperatures, but we estimate that in the reaction zone the $Ar(N_2)$/hydride ratio was 200 in the mass spectrometric experiments and 500–1000 in the matrix experiments. The ratio of $N_2(Ar)/BF_3$ used was ~75.

Equipment. Initially the products of the reaction were analyzed by sampling the reaction products in the flow reactor through a small

(1) Greenwood, N. N.; Wallbridge, M. G. H. *J. Chem. Soc.* **1963**, 3912.
(2) Kaldor, A.; Porter, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 2140.
(3) Breisacher, P.; Siegel, B. *J. Am. Chem. Soc.* **1964**, *86*, 5053.
(4) Breisacher, P.; Siegel, B. *J. Am. Chem. Soc.* **1965**, *87*, 4255.
(5) Nibler, J.; Lesiecki, M., private communication.

Figure 1. Experimental apparatus for matrix isolation–mass spectrometry. The initial mass spectrometric experiments were performed with the gas entry nozzles entering directly into the mass spectrometer; the matrix isolation apparatus was not present.

hole into the ionization region of a small time-of-flight mass spectrometer (Bendix Model RGA-1). The mass spectrometer was pumped by a trapped 4-in. diffusion pump. The pressures in the mass spectrometer chamber were typically 5×10^{-6} torr or lower during an experiment. This mass spectrometer gave unit resolution at $m/e \sim 75$ and could scan to $m/e \sim 750$.

For the matrix isolation–infrared studies, the gaseous reaction products generated in the flow reactor were deposited on a concave brass mirror cooled by a CTI Model 20 closed-cycle refrigerator to a temperature of 17–18 K as measured by a Cu vs. Au–0.07 atom % Fe thermocouple embedded in the back of the mirror. Another orifice situated above the flow reactor nozzle allowed the codeposition of a separate gas as needed (Figure 1). Deposition rates of 1.5–2 mmol/h were used. Often an additional pump was used on the flow reactor so that only a fraction of the product gases was sampled. This allowed fast flow rates and hence short reaction times while maintaining the slow deposition rate necessary for good matrices.

Warm-up experiments were done by turning off the refrigerator and allowing the mirror and the sample to warm to 40 K. The refrigerator was then turned on again and the sample recooled to 18 K. Warm-up of the sample occurred in 2–4 min, and cool-down to 18 K took less than 1 min.

Infrared spectra were obtained by a reflection technique. CsI was used as the outer window of the vacuum chamber. A purged Beckman IR12 spectrometer, which scans from 4000 to 200 cm^{-1}, was used to record the spectra. The frequency accuracy was estimated to be about ±1 cm^{-1}.

In some experiments the mass spectrometer, independently pumped by either a trapped 4-in. diffusion pump or a Perkin-Elmer Ultek TNB ion pump, was placed behind the 18 K mirror (Figure 1). A segment of the circular brass mirror was cut out to allow a portion of the sample beam from the flow reactor to pass through the deposition target and enter the mass spectrometer chamber. The mass spectrometer was used to adjust flow rates in the matrix experiments as well as allow mass spectral analysis of the products being deposited. The detection limit of the mass spectrometer when used in this configuration was set by the background pressure. With a diffusion pump the background pressure in the mass spectrometer chamber was 5×10^{-8} torr. The matrix isolation chamber pressure during a deposit was 10^{-7}–10^{-6} torr. Since the reactants were diluted with matrix gas to a partial pressure of about 5×10^{-8} torr, the ion peaks due to the species of interest were often at the level of the background peaks. The ion pump lowered the background pressure in the mass spectrometer chamber to below 1×10^{-9} torr, and it was used in most experiments. However, the ion pump did not pump Ar efficiently over extended periods.

A Varian CH7 mass spectrometer was used for the analysis of gaseous products from the bulk reactions.

Materials and Preparation of Samples. Ar (UHP, Matheson) or N$_2$ (PP, Matheson) was used as the matrix gas as well as the carrier gas in the mass spectrometric studies; for the matrix work it was purified by passing it over Linde 4A sieves at 1.5 atm immediately before deposition.

(CH$_3$)$_3$N·AlH$_3$ was synthesized by the reaction of LiAlH$_4$ (Metal Hydrides) and (CH$_3$)$_3$NHCl (Matheson Coleman and Bell) in diethyl ether[6] and purified by vacuum sublimation. (CH$_3$)$_3$NHCl was first purified by recrystallization from CHCl$_3$ (treated with 2,2-dimethoxypropane to remove H$_2$O) and dried by pumping under a vacuum.

(CH$_3$)$_3$N·AlD$_3$ was prepared in the same manner with (CH$_3$)$_3$NDCl and LiAlD$_4$ (Merck Sharp and Dohme, Canada, 99 atom % D). (CH$_3$)$_3$NDCl was made by reacting N(CH$_3$)$_3$ with DCl; DCl was in turn prepared by the reaction of C$_6$H$_5$COCl with D$_2$O.[7]

(CH$_3$)$_3$N·GaH$_3$ was synthesized by the reaction of LiGaH$_4$ with (CH$_3$)$_3$NHCl.[8] The LiGaH$_4$ was prepared from the reaction of finely powdered LiH (Matheson Coleman and Bell) and GaCl$_3$ (Research Organic/Inorganic) in diethyl ether.[9] It was not isolated.

Solid-Phase–Gas-Phase (Bulk) Reactions. Reactions of solid (CH$_3$)$_3$N·MH$_3$ with BF$_3$ were studied in a high-vacuum glass manifold. (CH$_3$)$_3$N·AlH$_3$ (0.3 mmol, 12.7 mg) was sublimed into a Pyrex tube equipped with a high-vacuum Teflon-in-glass valve, and an equimolar amount of BF$_3$ was condensed into the tube at –196 °C. A reaction occurred when the tube was warmed to –78 °C as observed by the formation of a white solid with the appearance of fine needles. No further reaction occurred by warming the reaction contents to room temperature. The products were separated according to volatilities and analyzed. The 5.5 mg of volatiles at –78 °C was mainly BF$_3$ with some BF$_2$H and B$_2$H$_6$ as identified by their mass and infrared spectra. A white sublimable solid, 30.5 mg, was identified by its mass and IR spectra as (CH$_3$)$_3$N·BH$_3$ with traces of (CH$_3$)$_3$N·AlH$_3$. A nonvolatile residue, 0.11 mg, had an IR absorption at 984 cm^{-1} (Nujol mull) and effervesced slightly in H$_2$O.

In a similar reaction using 0.10 mmol each of (CH$_3$)$_3$N·GaH$_3$ (13.2 mg) and BF$_3$, a reaction occurred upon warming the tube above –78 °C but below 0 °C. A viscous, clear liquid formed, which upon warming to room temperature led to the evolution of a gas and precipitation of white and gray solids. Volatiles at –78 °C, 1.0 mg, contained B$_2$H$_6$ from IR and mass spectra. A sublimable white solid, 12.7 mg, was identified as (CH$_3$)$_3$N·BF$_3$ from mass and IR spectra. A gray nonvolatile residue (Ga) was found to weigh 7.3 mg.

Results

Mass Spectrometric Studies. Preliminary studies of the reactions of (CH$_3$)$_3$N·AlH$_3$ with BF$_3$ were monitored on the time-of-flight mass spectrometer. Initially, mass spectra were obtained for the reactants, N(CH$_3$)$_3$ and (CH$_3$)$_3$NBF$_3$, to establish the fragmentation patterns of each molecule. At an ionizing energy of 70 eV, the major ion fragments of (CH$_3$)$_3$N·AlH$_3$ were at m/e 88, 72, 59 (sh), 58, 43, 42, 41, 29, and 15 and of (CH$_3$)$_3$N·BF$_3$ at m/e 108, 92, 59 (sh), 58, 42, 30, and 15. The fragmentation pattern of BF$_3$ and N(CH$_3$)$_3$ agreed with standard data.

The reaction of BF$_3$ with (CH$_3$)$_3$N·AlH$_3$ in the flow reactor was then studied. Figure 2 shows a partial mass spectrum of this reaction. The reaction distance and the Ar–(CH$_3$)$_3$N·AlH$_3$ flow rate were held constant. The reaction was then studied as a function of BF$_3$ flow rate and hence the concentration of BF$_3$. Initially Ar was passed over (CH$_3$)$_3$N·AlH$_3$ at –35 °C with no BF$_3$ flow; Figure 2a shows its ion fragment C$_3$H$_9$NAlH$_2$$^+$ at m/e 88. The introduction of BF$_3$ into the reactor led to a decrease in this ion peak and the appearance of ion fragments associated with (CH$_3$)$_3$NBF$_3$ at m/e 108 (C$_3$H$_9$NBF$_2$$^+$) (Figure 2b). Increasing the flow rate of BF$_3$ led to a further diminishing of the (CH$_3$)$_3$N·AlH$_3$ peaks and to the formation of more (CH$_3$)$_3$N·BF$_3$ (Figure 2c). However, fragments due to N(CH$_3$)$_3$ itself appeared, and the formation of (CH$_3$)$_3$N·BF$_3$ lagged behind the disappearance of (CH$_3$)$_3$N·AlH$_3$. Note that in Figure 2d the full intensity of the ion peaks of (CH$_3$)$_3$N·BF$_3$ at m/e 108 and 92 is not attained until after the m/e 88 ion peak has disappeared, indicating that (CH$_3$)$_3$N·BF$_3$ is not an initial reaction product. The N(CH$_3$)$_3$ was identified as a product; its ion peaks were sufficiently intense that its presence could be confirmed after subtraction of contributions from the fragmentation of the trimethylamine adducts. It was not clear from the mass

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(7) Shoemaker, D. P.; Garland, C. W.; Steinfeld, J. I.; Nibler, J. W. "Experiments in Physical Chemistry", 4th ed.; McGraw-Hill: New York, 1981; p 444.

(8) Shriver, D. F.; Shirk, A. E. *Inorg. Synth.* **1977**, *17*, 42.

(9) Shirk, A. E.; Shriver, D. F. *Inorg. Synth.* **1977**, *17*, 45.
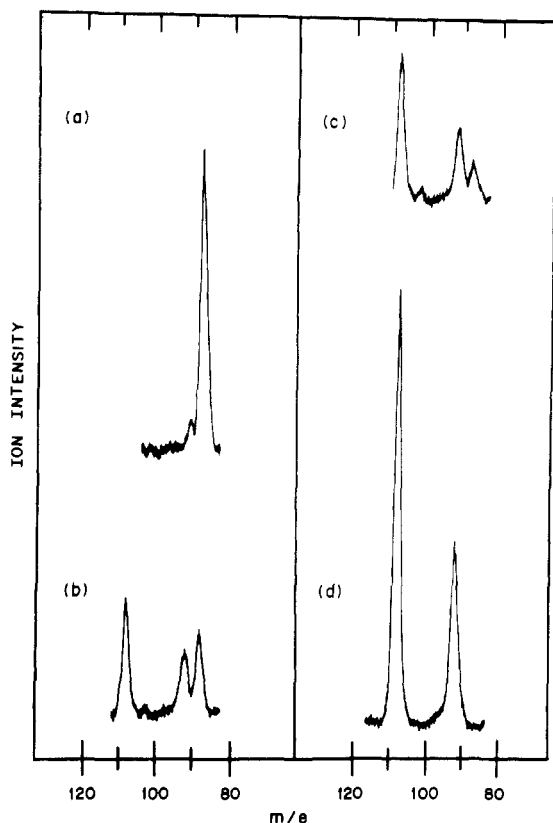
Figure 2. Mass spectra of the BF_3 + $(CH_3)_3N \cdot AlH_3$ gas-phase reaction: (a) $(CH_3)_3N \cdot AlH_3$–Ar; (b) BF_3–Ar flow introduced into (a); (c, d) BF_3–Ar flow progressively increased over that in (b).
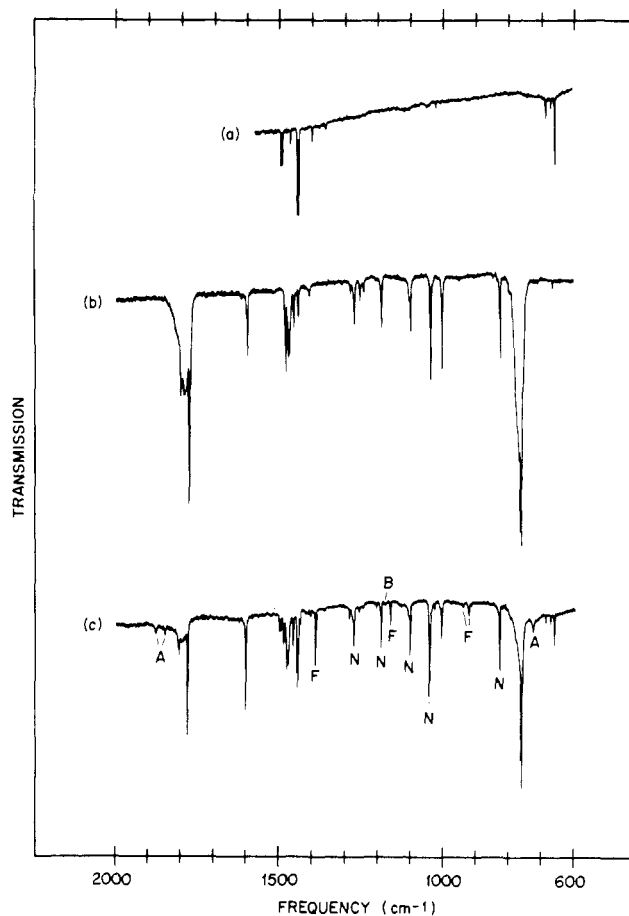
spectrometric experiments if AlH_3 was formed or not. While ion peaks at m/e 29 and 30 were present, BF^+ and $N(CH_3)_3$ fragments also appear there.

The mass spectrometric studies indicated that the gas-phase reaction of $(CH_3)_3N \cdot AlH_3$ with BF_3 proceeded rapidly. The reagent spectra disappeared, and new ion peaks due to products appeared. The observed products of the reaction that could be easily and clearly identified were $N(CH_3)_3$ and $(CH_3)_3$-$N \cdot BF_3$. The $(CH_3)_3N \cdot BF_3$ was likely due to the secondary reaction of excess BF_3 with $N(CH_3)_3$, which is a primary product of the reaction.

The reaction of BF_3 with $(CH_3)_3N \cdot GaH_3$ proceeded more slowly. Under the flow reactor conditions used for the alane reactions only BF_3 and $(CH_3)_3N \cdot GaH_3$ ion peaks were observed. When much lower flow rates and reaction distances 3 times as long (225 mm) were used, the m/e 130 ion peak of $(CH_3)_3N \cdot GaH_3$ was observed to decrease in intensity. Ion peaks due to $(CH_3)_3N \cdot BF_3$ were observed to appear.

Matrix Isolation–Infrared Studies. The matrix isolation–IR technique provided more rigorous and sensitive identification of the reaction products, particularly since many of the species have similar ion fragments in their mass spectra. Also, the practical sensitivity to transient species is higher than in the mass spectral experiments because of the much larger sample undergoing analysis.

(1) $(CH_3)_3N \cdot AlH_3$ + BF_3. Figure 3a is a spectrum of BF_3 isolated in N_2; its spectrum agrees with that reported.[10] Figure 3b shows the IR spectrum of $(CH_3)_3N \cdot AlH_3$ isolated in the N_2 matrix. Its absorptions are in good agreement with the gas-phase values.[11] Table I lists the observed frequencies; the vibrations of the trimethylamine portion of the complex are not included.
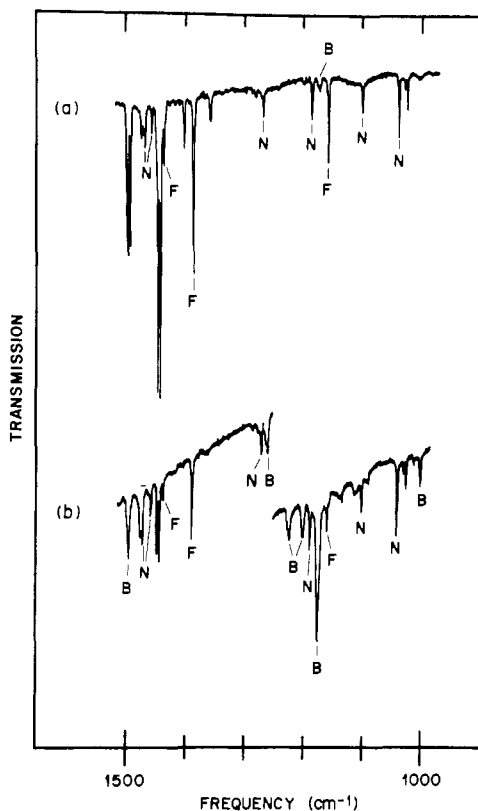
(10) Shimanouchi, T. *J. Phys. Chem. Ref. Data* **1972**, *1*, 189.
(11) Fraser, G. W.; Greenwood, N. N.; Straughan, B. P. *J. Chem. Soc.* **1963**, 3742.

Figure 3. Infrared spectra at 18 K: (a) BF_3–N_2; (b) $(CH_3)_3N \cdot AlH_3$–N_2; (c) BF_3–N_2 + $(CH_3)_3N \cdot AlH_3$–N_2 (5 mm reaction distance). The labeled bands are discussed in the text.

Table I. Infrared Absorptions of $(CH_3)_3N \cdot AlH_3$ and $(CH_3)_3N \cdot AlD_3$,[a] (cm^{-1})

$(CH_3)_3N \cdot AlH_3$		$(CH_3)_3N \cdot AlD_3$	
N_2 matrix	gas phase[b]	N_2	gas phase[b]
507 vw	533	504.7 w	~540
561 vw			
758.8 vs	768	555.8 m	562
761.4 s	773	561.6 s	567
1772.5 s	1792	1287.9 w	1304
1788.5 w, br		1295.6 s	
1798.2 w		1305 w, br	
		1316 sh, w	
		1325 sh, vw	

[a] Does not include absorptions due to the $-N(CH_3)_3$ portion.
[b] Reference 11.

Figure 3c is a spectrum of the reaction mixture of the two at a reaction distance of 5 mm. Free trimethylamine (absorptions labeled N) is one of the principal products present, as observed in the mass spectrometric studies. Very little $(CH_3)_3N \cdot BF_3$ is present; its most intense absorption is at 1176 cm^{-1}, which is the weak feature labeled B in Figure 3c. $(CH_3)_3N \cdot BF_3$ was produced in sizable quantities only when the reaction distance was greater than 25 mm, as is discussed below.

The absorptions labeled A in Figure 3c at 724, 1843, and 1872 cm^{-1} are in the Al–H bending (also Al–F stretching) and the Al–H stretching regions. They were occasionally observed with short reaction distances ($\sim$5 mm) but not at all when the reaction distance was lengthened. They never appeared with an intensity >0.02 ODU. We tentatively assign these absorptions to AlH_2F, as is discussed later.

Table II. Observed Vibrational Frequencies of HBF_2 and DBF_2 $(cm^{-1})^a$

	HBF$_2$		DBF$_2$	
	N$_2$ matrix	gas phase[b]	N$_2$ matrix	gas phase[b]
$\nu_1(A_1)$	2644	2620	1980	1965
$\nu_2(A_1)$	1156	1165	1121.3	1127
			(1142.1)	
$\nu_3(A_1)$	542	540		540
$\nu_4(B_1)$	1385.1	1401.5	1374.5	1392.5
	(1433.7)	(1451)	(1423.0)	
$\nu_5(B_1)$				
$\nu_6(B_2)$	918	925	772.7	785
	(936)	(942)	(793)	(805)

^{a} Values in parentheses for the ^{10}B molecule. ^{b} Reference 12.

Table III. Infrared Absorptions of $(CH_3)_3N\cdot GaH_3$ $(cm^{-1})^a$

N$_2$ matrix	gas phase[b]	soln[c]
481 w	475 m ⎫	
	482 m ⎬ PQR	
	488 m ⎭	
539 w	523 m	
737.2 s	715 w	726
745.6 ms	758 vs	745
750.4 m		
757.7 w		
1828.9 vs	1853 vs	1832
1850.9 w		1852

^{a} Does not include absorptions due to the $N(CH_3)_3$ portion.
^{b} Reference 14b. ^{c} Reference 14a.

Figure 4. Infrared spectra at 18 K of the BF_3–N_2 + $(CH_3)_3N\cdot AlH_3$ reaction: (a) 10 mm reaction distance; (b) 150 mm reaction distance. The labeled bands are discussed in the text.

The absorptions in Figure 3c labeled F, the most intense of which is the 1386-cm^{-1} band, were assigned to the known molecule BF_2H. Reaction of $(CH_3)_3N\cdot AlD_3$ with BF_3 produced the appropriate infrared absorptions for BF_2D as well as for $N(CH_3)_3$. Absorptions due to ^{10}B and ^{11}B were observed for some of the vibrations. Table II lists our observed frequencies for BF_2H and BF_2D with reported gas-phase values.[13] A small matrix shift (1.2% or less) in the frequencies is apparent, but it is no larger than that observed for BF_3 in N_2. The agreement between our observed values and the reported gas-phase values is good; undeniably BF_2H is a reaction product.

The mass spectrometric studies indicated that $(CH_3)_3N\cdot BF_3$ was a major product of secondary reactions. This was substantiated in the infrared studies; Figure 4 shows portions of the infrared spectra of deposits obtained at reaction distances of 10 and 150 mm, respectively. At short reaction times (Figure 4a) there is very little evidence for $(CH_3)_3N\cdot BF_3$, which has a strong absorption at 1176 cm^{-1}. However, at long

reaction times, when secondary reactions are likely, an absorption due to $(CH_3)_3N\cdot BF_3$ (labeled B) is the most intense band in the spectrum. In contrast, BF_2H (labeled F) and $N(CH_3)_3$ (N) are observed in both spectra.

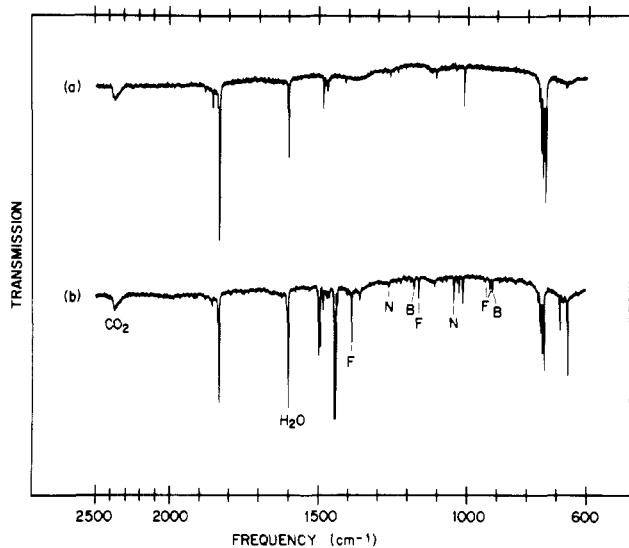One can conclude that the primary products of the reaction of BF_3 with $(CH_3)_3N\cdot AlH_3$ are $N(CH_3)_3$ and BF_2H. No evidence for AlH_3 was found in the IR spectrum. The formation of $(CH_3)_3N\cdot BF_3$ certainly results from the reaction of excess BF_3 with the free $N(CH_3)$. The gas-phase reaction of BF_3 with $N(CH_3)_3$ is reported to be fast;[13] therefore it is not surprising that it forms readily in these experiments.

The matrix isolation–infrared studies are consistent with the mass spectral results except that BF_2H was not observed in our mass spectra. Porter has reported the mass spectrum of BF_2H; the parent is weak but the fragment HBF^+ appeared.[12] We searched for the $H^{11}BF^+$ fragment at m/e 31 but could not reliably detect it above the noise. The identification of this molecule, which has intense IR absorptions, as a primary product was firm in the matrix–IR studies. It is reasonable to observe BF_2H in the matrix but not the mass spectrometer. The sample size in the IR–matrix studies is many orders of magnitude larger than that entering the mass spectrometer; thus the matrix experiment is more sensitive to small concentrations of transients. Probably the concentration of BF_2H was simply smaller than could be detected by the mass spectrometer. The existence of BF_2H as a primary reaction product is clear.

In the depositions monitored mass spectrometrically, fragments due to the parent compounds, trimethylamine, and the matrix gas were detected. The mass spectrometer was useful to the matrix depositions because it enabled us to monitor the reaction conditions.

In an attempt to isolate a reaction intermediate, BF_3–N_2 and $(CH_3)_3N\cdot AlH_3$–N_2 were codeposited from separate nozzles onto the cold mirror. With codeposition no reaction will occur, and as expected, the IR spectrum showed only absorptions due to the two reactants. A reaction between the trapped reagents can be induced by annealing the matrix above the temperature where diffusion of the trapped species can occur. When the sample was annealed to 40 K and recooled to 18 K, three weak but reproducible absorptions each for the reactions BF_3 + $(CH_3)_3N\cdot AlH_3$ and BF_3 + $(CH_3)_3N\cdot AlD_3$ were observed. These were at 714, 1893, and 1914 cm^{-1} for the hydride and at 546, 1232, and 1392 cm^{-1} for the deuteride. We attribute these bands to an intermediate complex which, in the gas phase, further decomposes to the observed products.

In order to show that none of the observed absorptions in any of these experiments were due to the bis(amine) complex, we prepared $2(CH_3)_3N\cdot AlH_3$ by codepositing $N(CH_3)_3$ and $(CH_3)_3N\cdot AlH_3$–Ar mixtures from separate nozzles and an-

(12) Porter, R. F.; Wason, S. K. *J. Phys. Chem.* **1965**, *69*, 2208.

(13) Bauer, S. H.; Martinez, J. V.; Price, D.; Jones, W. D. In "Boron-Nitrogen Chemistry"; American Chemical Society: Washington, DC, 1964; Adv. Chem. Ser. No. 42, p 35.

Figure 5. Infrared spectra at 18 K: (a) $(CH_3)_3N\cdot GaH_3-N_2$; (b) $(CH_3)_3N\cdot GaH_3-N_2 + BF_3-N_2$ (reaction distance 165 mm). The broad absorption at 2350 cm^{-1} is due to gas-phase CO_2 present in the purge gas of the IR-12. The labeled bands are discussed in the text.

nealing the matrix. Small amounts of $2(CH_3)_3N\cdot AlH_3$ formed upon annealing and recooling the matrix. The observed matrix spectrum agreed with the reported spectrum of this complex.[11] These experiments demonstrated that none of the IR absorptions observed in the flow reactor studies were due to matrix-isolated $2(CH_3)_3N\cdot AlH_3$.

(2) $(CH_3)_3N\cdot GaH_3 + BF_3$. Figure 5a shows the infrared spectrum of $(CH_3)_3N\cdot GaH_3$ isolated in N_2. Its observed frequencies are listed in Table III and compared with reported frequencies.[14] Figure 5b shows the spectrum of the reaction of $(CH_3)_3N\cdot GaH_3$ with BF_3. This reaction proceeded much more slowly. Long reaction distances ($\sim$165 mm) and approximately double the concentration of reactants in the flow reactor were necessary to observe a reaction. For sufficient dilution to ensure isolation of the reaction products, a separate flow of pure matrix gas was deposited simultaneously with the sample from the flow reactor. Figure 5b shows that in addition to unreacted parent absorptions, the three species present are BF_2H (labeled F), free trimethylamine (N), and a small amount of $(CH_3)_3N\cdot BF_3$ (B). No additional absorptions such as one at 2000 cm^{-1}, which was previously assigned to GaH$_3$[1] in the gas phase, were found. It is concluded that the reaction of BF_3 with $(CH_3)_3N\cdot GaH_3$ proceeds through a halide–hydride exchange as does the gas-phase reaction of $(CH_3)_3N\cdot AlH_3$ with BF_3.

Solid-Phase–Gas-Phase Reactions. In the light of the conclusion that the gas-phase reaction of trimethylamine–gallane with BF_3 was not a Lewis acid displacement reaction, we examined the reaction of solid $(CH_3)_3N\cdot GaH_3$ with BF_3, which was reported to yield solid $(CH_3)_3N\cdot BF_3$ and a viscous, clear liquid, GaH$_3$.[1] When equimolar amounts of BF_3 and $(CH_3)_3N\cdot GaH_3$ were reacted, the initial low-temperature product was a single-phase, clear viscous liquid. A white solid did not appear until the sample was warmed to near room temperature, and it was accompanied by the evolution of a gas and coprecipitation of a gray solid as well. The white solid was analyzed as $(CH_3)_3N\cdot BF_3$ from both its mass and its infrared spectra; its formation was essentially quantitative. The other two products were H_2 gas and Ga metal as reported in ref 1. These decomposition products are the same as had been

reported for this reaction; however, it was observed here that $(CH_3)_3N\cdot BF_3$ formed upon decomposition of, and not simultaneously with, the clear liquid.

The reaction of solid $(CH_3)_3N\cdot AlH_3$ with BF_3 was also studied; this reaction was complete upon warming the reaction tube from −196 to −78 °C. The major products were a volatile white solid, $(CH_3)_3N\cdot BH_3$, and a nonvolatile white residue, which is probably polymeric AlF_3 containing a small amount of hydride. Traces of BF_2H and B_2H_6 and unreacted BF_3 and $(CH_3)_3N\cdot AlH_3$ were also detected.

Discussion

The reactions of BF_3 with $(CH_3)_3N\cdot AlH_3$ and $(CH_3)_3N\cdot GaH_3$ in the gas phase proceeded via a hydride–halide exchange and not through a Lewis acid displacement reaction. The initial products were identified as BF_2H and $N(CH_3)_3$. No evidence for AlH_3 or GaH_3 as reaction products was found. $(CH_3)_3N\cdot BF_3$ was a secondary reaction product formed from excess BF_3 reacting with $N(CH_3)_3$. In the reactions of BF_3 with solid $(CH_3)_3N\cdot AlH_3$ and $(CH_3)_3N\cdot GaH_3$, the major products were $(CH_3)_3N\cdot BH_3$ and AlF_3 and $(CH_3)_3N\cdot BF_3$, Ga, and H_2, respectively. Some questions remain concerning (1) the nature of the AlH- and GaH-containing product of the gas-phase reactions and (2) the qualitative differences in the observed products when BF_3 reacts with solid $(CH_3)_3N\cdot AlH_3$ as compared with solid $(CH_3)_3N\cdot GaH_3$.

The first question is simple to answer. Since we have identified BF_2H and $N(CH_3)_3$ as products of the gas-phase reactions, the logical remaining products are AlH_2F and GaH_2F. As noted, we observed weak absorptions in the regions of AlH and AlF vibrations, which we tentatively assign to an unstable AlH_2F. Since these absorptions appeared only early in the reaction and never in large concentrations, we propose that MH_2F (M = Al, Ga) is unstable and decomposes to MF and H_2. An alternative mode of decomposition of MH_2F to MH and HF is less likely thermodynamically, and no HF absorption was observed in the IR spectra.

Thus in the gas phase we believe the overall reaction is

$$BF_3 + (CH_3)_3N\cdot MH_3 \rightarrow BF_2H + N(CH_3)_3 + MF + H_2 \tag{2}$$
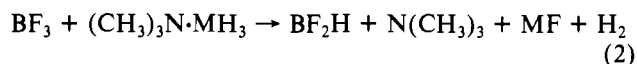
It is possible to estimate the equilibrium constant for this reaction from standard thermodynamic data[12,16] and to estimate the ΔH_f and the absolute entropy of $(CH_3)_3N\cdot MH_3$ from those known for the $(CH_3)_3N\cdot BH_3$ adduct.[15] We estimate that

$$K_c \simeq 10^{-10}[P \text{ (atm)}]^2$$

at the low pressure used for the matrix depositions (10^{-7}–10^{-6} atm in reactants) and the reaction should proceed.

It is unlikely that such a complicated reaction would occur in a single step. We propose that the reaction proceeds via the formation of $(CH_3)_3N\cdot MH_3BF_3$, in which halide–hydride exchange occurs:

$$BF_3 + (CH_3)_3N\cdot MH_3 \rightarrow (CH_3)_3N\cdot MH_3BF_3$$

$$(CH_3)_3N\cdot MH_3BF_3 \rightarrow BF_2H + MH_2F + N(CH_3)_3$$
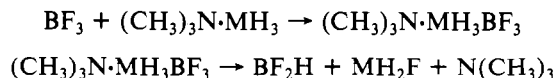
MH_2F can further decompose to MF + H_2. To account for the gas-phase reactions, we need only require that the intermediate be a transition state although there is some evidence that it is more likely to be a true complex. The intermediate, $(CH_3)_3N\cdot MH_3BF_3$, is similar to known complexes of B, Al, and Ga.[17,18] For example, the known compound $(CH_3)_3$-

(14) (a) Shriver, D. F.; Amster, R. L.; Taylor, R. C. *J. Am. Chem. Soc.* **1962**, *84*, 1321. (b) Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorg. Chem.* **1963**, *2*, 1036.

(15) Stone, F. G. A. *Chem. Rev.* **1958**, *58*, 101.
(16) (a) Wagman, D. D., et al. *NBS Tech. Note (U.S.)* **1968**, *No. 270–3*. (b) Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *NSRDS-NBS-37*.
(17) Ruff, J. K. *Inorg. Chem.* **1963**, *2*, 515.

$N \cdot AlH_2BH_4$ is stable and is thought to have a structure consisting of the amine bonded to the Al and one or two hydrogen bridges between the Al and B atoms from its NMR and IR spectra.[17]

As described above, attempts were made to isolate the proposed intermediate complex by codepositing BF_3 and $(CH_3)_3N \cdot AlH_3$ directly onto the cold window from separate nozzles, annealing the sample at 40 K, and then recooling to 18 K. Three new absorptions appeared in the IR spectrum in the regions where AlH and AlF stretching and AlH bending vibrations usually occur. The spectrum was consistent with that expected of the complex $(CH_3)_3N \cdot AlH_3BF_3$. This strongly suggests that the complex exists; however, such evidence is not conclusive.

The reactions of gaseous BF_3 with solid $(CH_3)_3N \cdot AlH_3$ and $(CH_3)_3N \cdot GaH_3$ yielded products not only differing from the gas-phase reactions but differing from each other as well. The aluminum hydride reaction yielded $(CH_3)_3N \cdot BH_3$ and AlF_3; the gallium hydride reaction gave $(CH_3)_3N \cdot BF_3$, Ga, and H_2. However, it is possible to understand the different course of these reactions using the mechanism we have proposed; i.e., an unstable complex $(CH_3)_3N \cdot MH_3BF_3$ initially forms and then decomposes via the most favorable route for that particular complex. At low pressures, in the gas phase the reaction is kinetically controlled and reaction 2 is the most likely path. At higher concentrations, e.g., in the cold liquid, the complex has time to exchange further; the reaction then will be thermodynamically controlled and the complex will decompose along one of two pathways to give the thermodynamically most stable products:

$$(CH_3)_3N \cdot BH_3 + MF_3 \leftarrow (CH_3)_3N \cdot MH_3BF_3 \rightarrow$$
$$\text{I}$$

$$(CH_3)_3N \cdot BF_3 + M + H_2$$
$$\text{II}$$
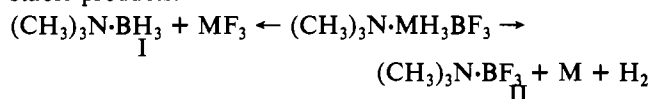
Using available thermochemical data,[15,16] we can estimate that the products I are more stable by 68 kcal/mol than products II for the Al reaction whereas the products II are more stable by 13 kcal/mol for the gallium reaction, which is consistent with our results.

As discussed earlier, the reaction of solid $(CH_3)_3N \cdot GaH_3$ with BF_3 in our hands proceeded in a slightly different manner than previously reported.[1] The initial product was a clear single-phase liquid; the precipitation of the solid $(CH_3)_3N \cdot BF_3$ occurred only upon decomposition of this clear liquid. The liquid was more likely to be an unstable complex than uncoordinated gallium hydride. Our final products gave the same analysis as reported previously,[1] i.e., $(CH_3)_3N \cdot BF_3$, Ga, and H_2.

A transient absorption near 2000 cm^{-1} observed in an infrared gas cell experiment[1] had been assigned to an unstable, gaseous gallium hydride. This absorption was not found in our studies. The gas-phase reactions as studied here were done in the presence of a buffer gas and a much lower pressure of reactants (we estimate it to be a factor of 10^3 or 10^4 lower). It is unlikely that these differences would substantially alter the reaction mechanism, and thus we doubt that the transient absorption was in fact uncoordinated GaH_3.

Conclusion

The gas-phase reactions of BF_3 with $(CH_3)_3N \cdot AlH_3$ and $(CH_3)_3N \cdot GaH_3$ proceed via a halide–hydride exchange and not a Lewis acid displacement reaction. BF_2H and $N(CH_3)_3$ were the principal reaction products observed. A reaction mechanism for these gas-phase reactions consisting of the initial formation of the complex $(CH_3)_3N \cdot MH_3BF_3$ has been proposed to account for both the gas-phase and the solid-phase–gas-phase reaction products.

In particular, no evidence was found for the formation of uncoordinated GaH_3 or AlH_3 from reaction of either $(CH_3)_3N \cdot AlH_3$ or $(CH_3)_3N \cdot GaH_3$ with BF_3.

We also showed that a mass spectrometer–matrix isolation–infrared spectrometer apparatus is useful in determining the mechanism of a complex reaction.

(18) Greenwood, N. N.; Storr, A. *J. Chem. Soc.* **1965**, 3426.