(6) H. Noth and H. Beyer, *Chem. Ber.*, **93**, 2251 (1960).
(7) O. T. Beachley, Jr., and J. D. Bernstein, *Inorg. Chem.*, **12**, 183 (1973).
(8) H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Amer. Chem. Soc.*, **61**, 1080 (1939).
(9) A. B. Burg and J. Boone, *J. Amer. Chem. Soc.*, **78**, 1521 (1956).
(10) S. S. Uppal and H. C. Kelly, *Chem. Commun.*, 1619 (1970).
(11) T. Durkin, L. DeHayes, and J. Glore, *J. Chem. Educ.*, **48**, 452 (1971).
(12) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).
(13) G. A. Anderson and J. J. Lagowski, *Inorg. Chem.*, **10**, 1910 (1971).
(14) J. W. Wiggins and G. E. Ryschkewitsch, *Inorg. Chim. Acta*, **4**, 33 (1970).
(15) A. W. Laubengayer and O. T. Beachley, Jr., *Inorg. Chem.*, **4**, 578 (1965).
(16) R. Hoffman, *J. Chem. Phys.*, **40**, 2474 (1964).
(17) P. M. Kuznesof and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 1683 (1968).

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Gas-Phase Calorimetry of Trimethyl Group Va Bases with Boron Lewis Acids[1]

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The reaction between the group Va Lewis bases trimethylphosphine, trimethylarsine, and trimethylstibine and the boron Lewis acids boron trifluoride, boron trichloride, boron tribromide, diborane, and trimethylborane has been studied using gas-phase calorimetry. The heat of reaction, ΔH_{rxn}, at 25°, is reported for the reactions $(CH_3)_3M(g) + BX_3(g) \rightarrow (CH_3)_3M \cdot BX_3(s)$ for 11 of the 15 possible adducts. Trimethylborane underwent no reaction with either trimethylarsine or trimethylstibine, and trimethylstibine reacted anomalously with diborane and boron trifluoride. In general, the relative base strengths were in the order trimethylphosphine > trimethylarsine > trimethylstibine and the relative acid strengths were in the order boron tribromide > boron trichloride ≈ borane > boron trifluoride > trimethylborane.

Introduction

It is a generally accepted tenet that the Lewis basicity of trivalent group Va compounds decreases with the heavier congeners. Numerous studies have been concerned with the Lewis base interaction of amines and phosphines with boron Lewis acids;[2,3] however, few data are available for the arsines and stibines. We have used gas-phase calorimetry to evaluate the magnitude of the interaction between a set of boron Lewis acids and trimethylarsine and trimethylstibine. As a reference point, we have also examined by the same technique the adducts of trimethylphosphine.

Experimental Section

Preparations. (a) Trimethylphosphine. Trimethylphosphine[4] was prepared by the dropwise addition of 13.75 g (0.1 mol) of phosphorus trichloride to an ethereal solution containing a slight excess of methylmagnesium iodide under inert atmosphere. The trimethylphosphine and ether were distilled onto an aqueous solution containing 47.0 g (0.2 mol) of silver iodide, and the trimethylphosphine was isolated as the trimethylphosphine–silver iodide complex.[5] The complex was decomposed by mild heating under vacuum and the trimethylphosphine was purified *via* trap-to-trap distillation using an ethyl acetate (−83.6°) slush bath to trap the trimethylphosphine. The purity of the trimethylphosphine was confirmed by its vapor pressure[6] and gas-phase ir[7] and ^{1}H nmr[8] spectra.

(b) Trimethylarsine. Trimethylarsine[9] was prepared by the dropwise addition of a solution of 18.15 g (0.1 mol) of arsenic trichloride in 125 ml of xylene to a solution containing a slight excess of methylmagnesium iodide in *n*-butyl ether under an inert atmosphere. The temperature of the reaction was kept well below 50°. The trimethylarsine was distilled into a three-necked flask fitted with suitable stopcocks to allow direct transfer to a high-vacuum system. The trimethylarsine was purified using standard trap-to-trap distillation procedures with an ethyl acetate (−83.6°) slush bath used to trap the purified product. The purity of the product was verified by its vapor pressure[6] and gas-phase ir[10] and ^{1}H nmr spectra.[8]

(c) Trimethylstibine. Trimethylstibine[11] was prepared by the dropwise addition of an ethereal solution of 22.8 g (0.1 mol) of antimony trichloride to a solution containing excess methylmagnesium iodide in diethyl ether under inert atmosphere. The ether and trimethylstibine were distilled into a three-necked flask with maintenance of the inert atmosphere. The trimethylstibine was converted to trimethylantimony dibromide[12] by the addition of a solution of elemental bromine in carbon tetrachloride to the ethereal solution of trimethylstibine until the brown color of the bromine solution persisted. The trimethylantimony dibromide which resulted was air stable and was readily purified by filtration. The trimethylantimony dibromide was reduced by the action of granular zinc and water to yield trimethylstibine which was collected on a vacuum line and purified by trap-to-trap distillation. A chloroform slush bath (−63°) was used to collect the trimethylstibine. Vapor pressure measurements[6] and gas-phase ir[13] and ^{1}H nmr[8] spectra were used to verify the purity of the trimethylstibine.

(d) Trimethylborane. Trimethylborane[14] was prepared by the slow dropwise addition of a solution of 26 ml (0.1 mol) of BF_3 etherate in 200 ml of ether to excess methylmagnesium iodide in ether at 0°. The trimethylborane was collected in a trap at liquid nitrogen temperature (−196°) using a dry nitrogen carrier gas system. A Dry Ice–acetone slush bath (−78°) was used to trap out the diethyl ether in the product stream. The trimethylborane was transferred to a high-vacuum system and purified by conventional trap-to-trap distillation techniques, using a carbon disulfide slush bath (−112°) to trap the trimethylborane. Purity of the trimethylborane was confirmed by vapor pressure measurements.[15]

(e) Diborane. Diborane[16] was produced by the action of 1.6 g (0.029 mol) of potassium borohydride on 30 ml of 85% phosphoric acid (orthophosphoric acid) in an apparatus attached to a high-vacuum system. Diborane was trapped in a liquid nitrogen trap (−196°) and was purified by repeated passage through a trap held at −112° (carbon disulfide slush) to remove any less volatile materials. Purity of the diborane was verified *via* gas-phase ir spectroscopy[17] and vapor pressure measurements.[16]

(f) Boron Tribromide. Boron tribromide was obtained commercially (Alfa) and was purified on a high-vacuum system by trap-to-trap distillation using a chlorobenzene (−45°) slush bath to trap the boron tribromide. The purity of the boron tribromide was confirmed by vapor pressure measurements[18] and gas-phase ir spectroscopy.[19]

(g) Boron Trichloride. Boron trichloride was obtained commercially (Matheson Gas Products) and purified on a high-vacuum system by trap-to-trap distillation using a carbon disulfide (−112°) slush bath to trap the pure boron trichloride. The purity of the boron trichloride was checked by vapor pressure measurements[20] and ir spectroscopy.[21]

(h) Boron Trifluoride. Boron trifluoride was obtained commercially (Matheson Gas Products) and purified on a high-vacuum system by trap-to-trap distillation using a trap at liquid nitrogen (−196°) temperature to hold the purified boron trifluoride. The purity of the boron trifluoride was confirmed by vapor pressure measurements[22] and gas-phase ir spectroscopy.[23]

Calorimetry. (a) Calorimeter. The calorimeter used in these experiments was of the constant-temperature environment type.[24] All reactions were run at 25.00°. The temperature of the bath surrounding

Figure 1. Gas-phase calorimetry cell.

the calorimeter was maintained at 24.95° using a Tronac PTC-1000 precision temperature controller. The calorimeter was electrically calibrated by passing a 96-mA constant current from an E. H. Sargent coulometric current source, Model IV, through an 83-ohm heater for a time measured by the timer in the current source. An Eppley cell and an NBS standard resistor were used as primary electrical standards. The temperature in the calorimeter was monitored *via* a Wheatstone bridge using a 10 K thermistor with the bridge unbalance recorded on a Sargent recorder, Model SR, and driving an attached Kiethly Instruments 150B microvolt ammeter. The bridge was operated with 0.01° full scale, or $\pm 5 \times 10^{-5}$° sensitivity. The calorimeter vessel was a 400-ml vacuum glass dewar containing the sample cell, heater, thermistor probe, magnet, stirrer, and the calorimetric fluid, which was water in all experiments.

(b) Calorimetry Cell. The calorimetry cell (Figure 1) was constructed of 18-mm Pyrex glass and measured 70 mm in length when sealed. The cell was connected to a high-vacuum system for loading by standard taper joints attached to each end of the cell. Following connection to the high-vacuum line, the cell was evacuated to a pressure of 1×10^{-4} Torr or less. The sample of gas to undergo reaction was then measured using a calibrated portion of the high-vacuum line in conjunction with a mercury manometer and a cathetometer. The vacuum line calibrations were made assuming ideal gas behavior with manometer volume taken into account. (The standard quantity of reactant used in each experiment was 0.100 mmol except in those systems involving boron tribromide, where low volatility forced a reduction to 0.029-mmol quantities.) The measured amount of reactant gas was condensed into the cell using liquid nitrogen, and the cell was sealed at the constriction. The cell was then carefully turned over, the other end was connected to the vacuum line, and the loading procedure for the other reactant was repeated.

(c) Calorimetry Procedure. Once filled, the calorimetry cell was placed in the calorimeter with the stainless steel ball held securely in place by an Alnico IV magnet, and the system was brought to 24.98° and allowed to equilibrate. An electrical calibration was done using an amount of heat estimated to be the same as the chemical heat. After thermal equilibrium was reestablished, the magnet was moved allowing the stainless steel ball to drop, breaking the break-seal with resultant mixing and reaction of the gases. A second electrical calibration was done after reestablishing thermal equilibrium. All temperature rises were estimated by the method of Wadso.[24b] The smallest experimental heats observed were on the order of 1 cal, which produced a temperature rise of 0.0025°, with an uncertainty due to temperature measurement of 2%. The data presented in Table I represent average values of at least four experiments. The greatest source of error in our procedure was encountered in the measurement of the small quantities (0.1 mmol) of gaseous reactants used in each experiment. The experimental values fall within a 5% error range.

Instrumentation. Proton nmr spectra were run on a Varian Associates nmr spectrometer, Model XL-100-15, or on a Varian Associates A-60 nmr spectrometer. Ir spectra were recorded on a Perkin-Elmer Model 457 grating spectrophotometer using a gas-phase ir cell fitted with CsI windows. All purification and manipulation of compounds were carried out on a Pyrex-glass high-vacuum system of the type described by Shriver.[25] The tensimeter[26] used to determine the K_p for the trimethylarsine–boron trifluoride system was constructed of Pyrex glass using greaseless Teflon stopcocks and couplings. Pressure was measured using a capillary tube mercury manometer in conjunction with a cathetometer.

Table I. Measured Enthalpies,[a] ΔH_{rxn} (kcal/mol)

Base	BF_3	BCl_3	BBr_3	BH_3	$B(CH_3)_3$
$(CH_3)_3P$	−45.5	−68.6	−122.3	−79.9[b]	−41.0
$(CH_3)_3As$	−20.4[c]	−46.2	−81.2	−49.6[b]	No reacn
$(CH_3)_3Sb$	−4.2[d]	−26.8	−19.8	−6.6[d]	No reacn

[a] For the reaction acid(g) + base(g) → adduct(s). [b] ΔH_{rxn} −17.75 kcal/mol. [c] Corrected for dissociation of adduct (see text). [d] Anomalous reaction; not simple adduct formation (see text).

Results

Trimethylphosphine in the gas phase reacted quantitatively at room temperature with boron trifluoride, boron trichloride, boron tribromide, trimethylborane, and diborane in the gas-phase to form the solid Lewis acid–Lewis base adducts of 1:1 stoichiometry as indicated by

$$Me_3P(g) + BX_3(g) \rightarrow Me_3P{\cdot}BX_3(s) \qquad (1)$$

where X = F, Cl, Br, H, or Me.

Trimethylarsine reacted completely in an analogous manner with boron trichloride, boron tribromide, and diborane and reacted incompletely with boron trifluoride (*vide infra*) at room temperature. No discernible reaction occurred at room temperature between trimethylborane and trimethylarsine.

Trimethylstibine formed 1:1 adducts with boron trichloride and boron tribromide and reacted anomalously with boron trifluoride and diborane. No reaction occurred between trimethylstibine and trimethylborane.

The heats of reaction, ΔH_{rxn}, observed for all of the boron acids, excluding diborane, involved the sum of the heats for eq 2 and 3, $\Delta H_{rxn} = \Delta H_{adduct} + \Delta H_{subl}$. The reactions where

$$\text{acid (g)} + \text{base (g)} \rightarrow \text{adduct (g)} \quad \Delta H_{adduct} \qquad (2)$$

$$\text{adduct (g)} \rightarrow \text{adduct (s)} \quad \Delta H_{subl} \qquad (3)$$

the acid was borane involved an additional step, that of symmetric cleavage of diborane into borane

$$^1/_2B_2H_6 \rightarrow BH_3 \quad \Delta H = 17.75 \text{ kcal/mol}^{27} \qquad (4)$$

The calorimetric data for reactions involving diborane have been corrected accordingly. The measured heats of reaction are summarized in Table I.

The adducts $Me_3P{\cdot}BF_3$, $Me_3P{\cdot}BCl_3$, $Me_3P{\cdot}BBr_3$, $Me_3P{\cdot}BH_3$, $Me_3P{\cdot}BMe_3$, $Me_3As{\cdot}BCl_3$, $Me_3As{\cdot}BBr_3$, $Me_3As{\cdot}BH_3$, $Me_3Sb{\cdot}BCl_3$, and $Me_3Sb{\cdot}BBr_3$ had small saturation vapor pressures at room temperature, indicating negligible dissociation of the adducts into their respective free acids and free bases, as well as negligible quantities of adduct in the vapor phase. As a typical example, the adduct $Me_3As{\cdot}BH_3$ had one of the highest pressures, 1.5 Torr at room temperature.[28] In the calorimetry cell this corresponded to less than 1% of the species being in the gas phase, which is well within our calorimetric accuracy. However, the adduct $Me_3As{\cdot}BF_3$ exhibited a considerable dissociation vapor pressure at room temperature. The ΔH_{rxn} for this system has been corrected for incomplete reaction in the ampoule. The correction in each experiment was calculated from the thermodynamic $K = 855$ (standard state is gas at 1 atm) obtained in a separate tensiometric experiment, where

$$K_p = \frac{a_{\text{solid adduct}}}{(a_{\text{gas-phase acid}})(a_{\text{gas-phase base}})} \approx \frac{1}{(P_{acid})(P_{base})} \qquad (5)$$

This equilibrium constant neglects any adduct in the gas phase, which, under the conditions of the experiment, is negligible.

Except as noted, all reactions were quantitative and of 1:1 stoichiometry. Under the conditions of the experiments no interaction or reaction other than simple Lewis acid–Lewis base adduct formation was observed. The reactions were monitored and the adducts characterized by ir–Raman and nmr spectroscopy, mass spectrometry, tensiometric titration, gas-phase displacement reactions, and melting points. The chemistry of these adducts and their characterization will be communicated separately.

Discussion

While there are numerous ways to evaluate the strength of a bond formed between a Lewis acid and a Lewis base, the most direct method is calorimetry. We have examined the reactions between the Lewis bases trimethylphosphine, trimethylarsine, and trimethylstibine with the Lewis acids boron trifluoride, boron trichloride, boron tribromide, trimethylborane, and diborane by gas-phase calorimetry.

The data in Table I represent the sum of the enthalpies for both the gas-phase acid–base reaction and the heat of sublimation of the adduct. In order to evaluate properly the relative strength of the methylated phosphine, arsine, and stibine Lewis bases toward the boron Lewis acids, it would be desirable to separate those two thermodynamic quantities. However, in a series of closely related compounds such as these, the heats of sublimation should not vary greatly and, in all probability, are related primarily to molecular weights. For the reactions of a particular boron Lewis acid with the series of bases, the variation between reaction enthalpies is at least 20 kcal/mol; therefore, small variations in heats of sublimation could not change the relative order of base strengths.

The method we employed allows at least a semiquantitative determination of acid–base interactions. It has the decided advantage that it requires an extremely simple, disposable calorimetry cell, and the data can be gathered rather quickly once the starting compounds are purified. Admittedly, the thermodynamic data are of relatively low accuracy (5%). The elegant thermodynamic data obtained by Brown and coworkers[29] by the use of gas-phase dissociation techniques yield highly accurate results (ΔH to ± 0.1 kcal/mol) and also gives the heat of formation of the adduct, ΔH_{adduct}, directly. The difference between the heats measured for a particular acid–base system by our gas-phase calorimetry and the heats calculated by gas-phase dissociation methods should be the heat of sublimation of the adduct. However, the gas-phase dissociation method is very tedious and, more importantly, is limited to the study of compounds that are appreciably, but not completely, dissociated in the range 0–160° and that are sufficiently volatile to provide significant pressure in the reaction vessel at temperatures for which the dissociation is not complete. This means that compounds which are highly dissociated (such as $Me_3As \cdot BF_3$)[30] and weakly dissociated (such as $Me_3As \cdot BCl_3$, $Me_3As \cdot BBr_3$, $Me_3P \cdot BCl_3$, and $Me_3P \cdot BBr_3$) cannot be studied by this technique. The gas-phase calorimetry also excludes all heats of solution. Solution calorimetry would be difficult to use on many of the systems studied because of high volatility and great reactivity of the free acids and bases and because of very limited solubility of the adducts.

In 1951 Hewitt and Holliday[31] made a study of the melting points of the borane adducts of trimethyl group Va bases: $Me_3P \cdot BH_3$, 100°; $Me_3N \cdot BH_3$, 94°; $Me_3As \cdot BH_3$, 72°; $Me_3Sb \cdot BH_3$, not formed at 25°. Using only melting points as a criterion for coordinate bond strength, they established that the order of decreasing basicity is $Me_3P > Me_3As > Me_3Sb$. Our calorimetric data support their conclusion, and, in fact, we find the same trend obtains for all of the boron acids used. Unlike Hewitt and Holliday, we found a reaction did occur between trimethylstibine and diborane; however, the reaction was not of simple adduct formation but appeared to be a condensation–polymerization reaction with the release of noncondensable gas.

The only trimethylborane adduct formed was $Me_3P \cdot BMe_3$. Brown and coworkers[32] previously found from gas-phase dissociation experiments a ΔH_{adduct} of −16.47 kcal/mol at 100°, while more recently Drago[33] reported a value of −16.24 kcal/mol at 25°. The difference between our ΔH_{rxn} value of −41.0 kcal/mol and their values yields a heat of sublimation of approximately −24.6 kcal/mol. Also recently the reaction between $Me_3P \cdot BMe_3$ and excess trimethylphosphine in toluene was studied by nmr spectroscopy.[34] The reaction was found to proceed by a dissociative mechanism, with a ΔH of −15 kcal/mol. A very weak interaction between trimethylborane and trimethylarsine has been reported[30] to occur at 0° ($K_p = 1.6$). Calorimetrically we found no reaction at 25°.

Brown[35] and Drago[33] both reported gas-phase ΔH_{adduct} values for $Me_3P \cdot BF_3$ of −18.9 kcal/mol. By subtraction from our ΔH_{rxn} of −45.5 kcal/mol, a heat of sublimation of −26.6 kcal/mol is obtained. The gas-phase dissociation method is unsuitable for study of the highly dissociated $Me_3As \cdot BF_3$ complex,[30] so we have no data with which to compare our value of −20.4 kcal/mol. The reaction of BF_3 with trimethylstibine was anomalous. A value of −4.2 kcal/mol was obtained in the calorimeter. Although this value was independent of stoichiometry, the products included both liquid- and gas-phase material, demonstrating that the measured ΔH_{rxn} does not correspond to simple adduct formation.

Relatively little information exists on the boron trichloride and boron tribromide adducts of these bases. Only two references to $Me_3As \cdot BCl_3$ appear in the literature,[31,36] with the only physical property given being the melting point. Apparently $Me_3Sb \cdot BCl_3$ has not previously been reported, and only a very recent reference[37] exists to $Me_3As \cdot BBr_3$ and $Me_3Sb \cdot BBr_3$. As can be seen in Table I, very strong adducts are formed between the methylated bases with boron tribromide and boron trichloride.

Several trends can be noted from the data in Table I. We find that, as expected, the base strength toward a particular boron acid generally decreases as the group Va base becomes heavier. The relative strengths of the boron acids toward each base are listed in order of decreasing strength: $BBr_3 > BCl_3 \approx BH_3 > BF_3 > BMe_3$. This trend is well established by the data and is consistent with the results previously found for the relative boron halide acid strengths toward pyridine and nitrobenzene[38] and with the previous results concerning the position of BH_3 as an electron acceptor with respect to boron halides.[39–41] While hard–soft–acid–base theory[42] can be used with reasonable success to predict the trends which were observed, some difficulty arises at several points. The most serious problem occurs with the adducts $Me_3Sb \cdot BCl_3$ and $Me_3Sb \cdot BBr_3$. The soft base Me_3Sb should form a stronger adduct with the softer acid BBr_3. In fact the stronger adduct is $Me_3Sb \cdot BCl_3$. Perhaps Drago's four-parameter method[33] using electrostatic (*E*) and covalent (*C*) terms would be useful. However, presently a lack of *C* and *E* values for the systems under investigation precludes such a comparison.

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Registry No. BF_3, 7637-07-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BH_3, 13283-31-3; BMe_3, 593-90-8; Me_3P, 594-09-2; Me_3As, 593-88-4; Me_3Sb, 594-10-5; $Me_3P \cdot BF_3$, 420-21-3; $Me_3As \cdot BF_3$, 52827-78-8; $Me_3Sb \cdot BF_3$, 52827-79-9; $Me_3P \cdot BCl_3$, 13292-83-6; $Me_3As \cdot BCl_3$, 52827-80-2; $Me_3Sb \cdot BCl_3$, 52827-81-3; $Me_3P \cdot BBr_3$, 13292-85-8; $Me_3As \cdot BBr_3$, 52827-82-4; $Me_3Sb \cdot BBr_3$, 52827-83-5; $Me_3P \cdot BH_3$, 1898-77-7; $Me_3As \cdot BH_3$, 2079-99-4; $Me_3Sb \cdot BH_3$, 52827-84-6; $MeP \cdot BMe_3$, 1558-34-5.

References and Notes

(1) Presented in part before the Inorganic Division, 167th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1974.

(2) K. Niedenzu and J. W. Dawson in "The Chemistry of Boron and Its Compounds," E. Muetterties, Ed., Wiley, New York, N. Y., 1967, pp 377–442; G. W. Parshall, *ibid.*, pp 617–667.
(3) T. D. Coyle and F. G. A. Stone in "Progress in Boron Chemistry," Vol. I, H. Steinberg and A. L. McCluskey, Ed., Macmillan, New York, N. Y., 1964, pp 83–160.
(4) H. Hibbert, *Ber. Deut. Chem. Ges.*, **39**, 160 (1906).
(5) F. G. Mann, A. F. Wells, and O. Purdie, *J. Chem. Soc.*, 1828 (1937); F. G. Mann and A. F. Wells, *ibid.*, 708 (1938).
(6) L. H. Long and J. F. Sackman, *Res. Corresp.*, **8**, 523 (1955).
(7) M. Halmann, *Spectrochim. Acta*, **16**, 407 (1960).
(8) R. G. Kostyanovskii, I. I. Chervin, V. V. Yakshin, and A. U. Stepanyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1629 (1967); *Chem. Abstr.*, **68**, 75338 (1968).
(9) P. B. Ayscough and H. J. Emeleus, *J. Chem. Soc.*, 3381 (1954).
(10) H. Siebert, *Z. Anorg. Allg. Chem.*, **273**, 161 (1953).
(11) W. J. C. Dyke, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 463 (1930).
(12) C. H. Bamford, D. L. Levi, and D. M. Newitt, *J. Chem. Soc.*, 468 (1946).
(13) F. Ostwald, *Z. Anal. Chem.*, **197**, 309 (1963).
(14) W. J. Lehmann, C. O. Wilson, and I. Sharpiro, *J. Chem. Phys.*, **28**, 777 (1958).
(15) A. Stock and F. Zelder, *Ber. Deut. Chem. Ges.*, **54**, 531 (1921).
(16) A. D. Norman and W. L. Jolly, *Inorg. Syn.*, **11**, 15 (1968).
(17) R. C. Taylor and A. R. Grimes, *Spectrochim. Acta*, **10**, 419 (1958).
(18) A. Stock and E. Kuss, *Ber. Deut. Chem. Ges.*, **47**, 3113 (1914).
(19) T. Wentink and V. H. Tiensuu, *J. Chem. Phys.*, **28**, 826 (1958).
(20) M. Green and G. A. Martin, *Trans. Faraday Soc.*, **48**, 416 (1952).
(21) D. A. Daws and G. Bottger, *J. Chem. Phys.*, **34**, 689 (1961).
(22) E. Pohland and H. Harlus, *Z. Anorg. Allg. Chem.*, **207**, 242 (1932).
(23) J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959).
(24) (a) H. A. Skinner, Ed., "Experimental Thermochemistry," Vol. II, Interscience, New York, N. Y., 1962; (b) S. Sunner and I. Wadso, *Acta Chem. Scand.*, **13**, 97 (1959).
(25) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.
(26) J. L. Mills and L. C. Flukinger, *J. Chem. Educ.*, **50**, 636 (1973).
(27) G. W. Mappes, S. A. Fridmann, and T. P. Fehlner, *J. Phys. Chem.*, **74**, 3307 (1970). Over ten values for the dissociation of diborane into borane units have been reported. We have chosen what appears to be the most generally accepted recent value, although the use of other values would not appreciably change our results.
(28) F. G. A. Stone and A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 286 (1954).
(29) H. C. Brown and M. Gerstein, *J. Amer. Chem. Soc.*, **72**, 2923 (1950); H. C. Brown, N. D. Taylor, and M. Gerstein, *ibid.*, **66**, 431 (1944).
(30) R. H. Harris, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1952.
(31) F. Hewitt and A. K. Holliday, *J. Chem. Soc.*, 530 (1953).
(32) S. Sujishi, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1949.
(33) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, **93**, 6014 (1971).
(34) K. J. Alford, E. O. Bishop, P. R. Carey, and J. D. Smith, *J. Chem. Soc. A*, 2574 (1971).
(35) E. A. Fletcher, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1952.
(36) G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 146 (1945).
(37) M. L. Denniston and D. R. Martin, *J. Inorg. Nucl. Chem.*, in press.
(38) H. C. Brown and R. R. Holmes, *J. Amer. Chem. Soc.*, **78**, 2173 (1956).
(39) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 164 (1956).
(40) W. A. G. Graham and F. G. A. Stone, *Chem. Ind. (London)*, 319 (1956).
(41) D. E. Young, G. E. McAchran, and S. G. Shore, *J. Amer. Chem. Soc.*, **88**, 4390 (1966).
(42) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963).

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Microwave Spectra of Trimethylamine–Borane. The Boron–Nitrogen Distance and Molecular Dipole Moment

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The $J = 2 \rightarrow 3$ and $J = 3 \rightarrow 4$ transitions for eight isotopic species of trimethylamine–borane were measured. The nitrogen coordinates in the principal axes systems of $Me_3{}^{14}N \cdot {}^{11}BH_3$ and $Me_3{}^{14}N \cdot {}^{11}BD_3$ were determined by the double-substitution method. In combination with previous studies this gave the following structural parameters: $d(BN) = 1.638 \pm 0.01$ Å, $d(CN) = 1.483 \pm 0.01$ Å, $\angle CNB = 109.9 \pm 1°$. The dative bond lengths and stabilities of $Me_3N \cdot BH_3$ and $Me_3N \cdot BF_3$ were discussed. A dipole moment of 4.84 ± 0.1 D was determined for $Me_3N \cdot BH_3$.

Introduction

The dative bond distance in compounds of the type $X_3A \cdot BY_3$ (A = group V, B = group III elements) is ordinarily expected to decrease as the stability to dissociation of the complex increases. A test of this assumption has been recently made for the series $(CH_3)_3P \cdot BH_3$,[2a] $CH_3PH_2 \cdot BH_3$,[2a] $H_3P \cdot BH_3$,[2b] $F_3P \cdot BH_3$,[3] and $F_2PH \cdot BH_3$.[4] While the relationship seems to hold for the first three compounds, $F_3P \cdot BH_3$ is an exception. Although it is less stable than the methylated phosphine adducts, its P–B bond distance is about 0.07 Å shorter. Gas-phase structural data have heretofore not been precise enough to permit careful tests of the bond length–stability relationship for similar boron–nitrogen adducts. Three trimethylamine adducts have been studied in the gas phase. For $(CH_3)_3N \cdot B(CH_3)_3$, which is readily dissociated, the N–B distance appears to be long (>1.65 Å).[5] For $(CH_3)_3N \cdot BF_3$, which is undissociated at room temperature, a value of 1.636 ± 0.004 Å is reported.[6] For $(CH_3)_3N \cdot BH_3$, which is also undissociated but more stable than $(CH_3)_3N \cdot BF_3$ (see Discussion), there have been three gas-phase structure studies. An early electron diffraction report gave 1.62 ± 0.05 Å.[7] More recent investigations by microwave spectroscopy reported 1.65 ± 0.02 Å[8] and 1.609 Å, or 1.637 Å,[9] with preference expressed for the 1.609 Å value.

The purpose of our investigation was to determine a more accurate value for the B–N distance in $(CH_3)_3N \cdot BH_3$ in order to compare it with that in $(CH_3)_3N \cdot BF_3$ and to examine the bond length–stability relationship for the two adducts. The previous MW investigations differed in their estimates of this distance because (1) no spectra from nitrogen-15 species were observed,[10] (2) the nitrogen atom lies very near the center of mass, and (3) vibration–rotation interaction effects which occur upon isotopic substitution are apparently quite large for several of the deuterated species that were employed in the structure deductions. These factors make it difficult to locate the nitrogen atom accurately. We have obtained a more accurate B–N bond length by measuring the spectra of four ^{15}N-enriched species and by using the double-substitution procedure to analyze the data.[11] This procedure (previously applied to a small number of linear and asymmetric-top molecules) is prescribed to minimize isotopic vibration–rotation effects and to locate atoms near principal rotational axes accurately.

Experimental Section

Samples. The samples were prepared by using standard vacuum-line procedures.[12] The $J = 3 \rightarrow 4$ transition of $Me_3{}^{14}N \cdot {}^{11}BH_3$ and the transitions of $Me_3{}^{14}N \cdot {}^{10}BH_3$ were measured from a sample containing 93% ^{10}B–7% ^{11}B. The $J = 2 \rightarrow 3$ transition of $Me_3{}^{14}N \cdot {}^{11}BH_3$ was obtained from a sample containing a mixture of BH_3, BD_3, etc., but the normally occurring abundances of boron-10 and -11. The $Me_3{}^{15}N \cdot BH_3$ transitions were measured with a sample containing about 99% ^{15}N and 90% ^{10}B–10% ^{11}B. A sample containing the same enrichments for nitrogen and boron but >95% deuterium was employed for $Me_3{}^{15}N \cdot BD_3$. The transitions for $Me_3{}^{14}N \cdot BD_3$ were measured with a sample containing >95% deuterium and the normal 81:19 ratio of boron-10:boron 11.