Synthesis and Characterization of *tert*-Butylamine:Borane, a Lewis Acid-Base Adduct

Abstract

A Lewis acid-base adduct of *tert*-butylamine and borane was prepared and characterized over the course of two laboratory sessions. The intermediate, $(CH_3)_3CNH_2 \cdot HCl$, was prepared during the first week and the adduct was prepared the second week. The intermediate and product were characterized by melting point and IR spectroscopy. Both were obtained in good yield. Purity was inferred from melting point analysis. Characteristic peaks in the infrared spectra of both compounds are compared and contrasted.

Introduction

Gilbert N. Lewis first proposed his theory of acids and bases in 1923 and he developed it more completely in 1938 in an effort to find more encompassing, generalized definitions.[1,2] In the Lewis theory of acids and bases, one is concerned only with the donation of electron pairs (bases) or the acceptance of electron pairs (acids). These definitions eliminate the need for proton donors or acceptors (typical of the Brønsted-Lowry definition[3]) or even the presence of solvent. In order to utilize the Brønsted-Lowry theory, some sort of protic solvent, often water, is required to be present. The Arrenhius definition of acids and bases rigorously requires the presence of water.[4]

Lewis's definition allows for a ready description of the formation of adducts between two stable compounds in terms of acid-base pairs. In general, one need only place a compound containing a free lone pair of electrons in the presence of a compound that is electron deficient and has an open site in its coordination sphere to produce an adduct. This process has been utilized to prepare and study a wide variety of adducts between various amines and boranes as shown in Figure 1.
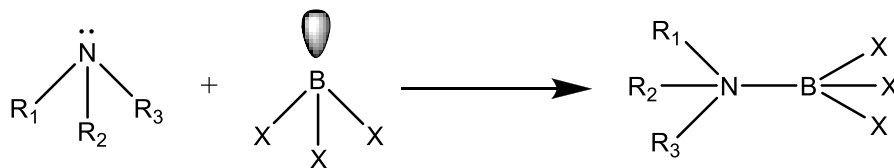
Figure 1. Reaction of an Amine (Lewis base) with a Borane (Lewis acid) R_1, R_2, R_3 = H or any alkyl group; X = a halogen.

This report describes how to prepare a Lewis acid-base adduct from *tert*-butylamine hydrochloride and sodium tetraborohydride (Figure 2). The resulting compound is characterized by melting point and IR spectroscopy, and the product's properties are compared and contrasted to those of the *tert*-butylamine hydrochloride starting material.
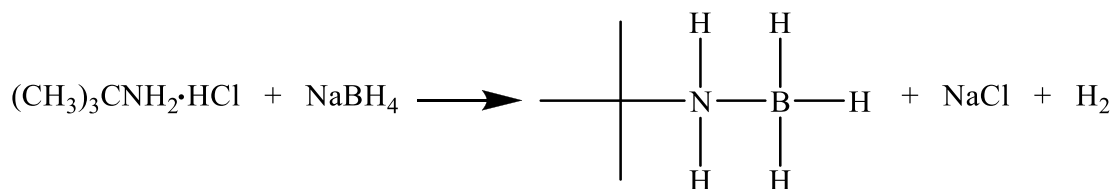

Figure 2. The Reaction to Produce *tert*-Butylamine:Borane Adduct.

Methods

All chemicals were purchased from Aldrich and used as received. Unless otherwise noted, all reactions were carried out under ambient laboratory conditions. Melting points were determined using a Mel-Temp melting point apparatus. Infrared spectra were collected on a Bruker Tensor 27 FTIR spectrometer, using an attenuated total reflectance (ATR) apparatus.

tert-Butylamine hydrochloride (**1**) – *tert*-Butylamine (1.0 mL, 0.6900g, 9.448×10^{-3} mol) was added to 10 mL of absolute ethanol. While stirring, 12 M HCl (0.80 mL, 9.6×10^{-2} mol) was

added dropwise over a period of 2 min. The solution was stirred for 5 min, then the stir bar was removed and the solution was evaporated to dryness. The resulting solid was collected and stored for the following synthesis. Yield: 0.6930 g (6.327 x 10^{-3} mol, 66.71%). m.p. > 200°C. IR (cm^{-1}, KBr): 2985 (s), 2962 (s), 2894 (s), 2805 (m), 2710 (m), 2601 (m), 2501 (m), 2080 (w), 1612 (w), 1513 (m), 1477 (w), 1403 (m), 1376 (m), 1370 (m), 1302 (w), 1218 (w), 450 (w).

tert-Butylamine:borane (**2**) – A round-bottom flask was charged with **1** (0.6902, 6.273 x 10^{-3} mol) and 5 mL of THF. To the stirred mixture, NaBH$_4$ (0.2773 g, 7.30 x 10^{-3} mol) was added in small portions over a period of 5 min. During the addition, bubbles were observed evolving from the reaction mixture and a colorless precipitate formed. The flask was capped loosely with a septum and the mixture was stirred for 2 h. Then the mixture was filtered and the filtrate was evaporated to dryness. Hexanes (10 mL) were added to the colorless residue and the resulting mixture was filtered, washed with hexanes (2 x 5 mL) and air dried. Yield: 0.4997 g (5.744 x 10^{-3} mol, 91.60%). m.p. = 73°C. IR (cm^{-1}, KBr): 3253 (s), 3223 (s), 3146 (m), 2992 (m), 2976 (s), 2404 (s), 2309 (s), 2274 (s), 1589 (s), 1474 (w), 1404 (w), 1374 (s), 1337 (s), 1227 (m), 1187 (s), 1172 (s), 1053 (w), 979 (w), 929 (w).

Results

The Lewis acid-base adduct **2** was prepared in excellent yield (92%) from NaBH$_4$ and **1**, which itself was prepared in good yield (67%) the previous week. The melting points of **1** and **2** were found to be >200°C and 73°C, respectively. The infrared spectra of **1** and **2** are shown in Figures 3 and 4, respectively.

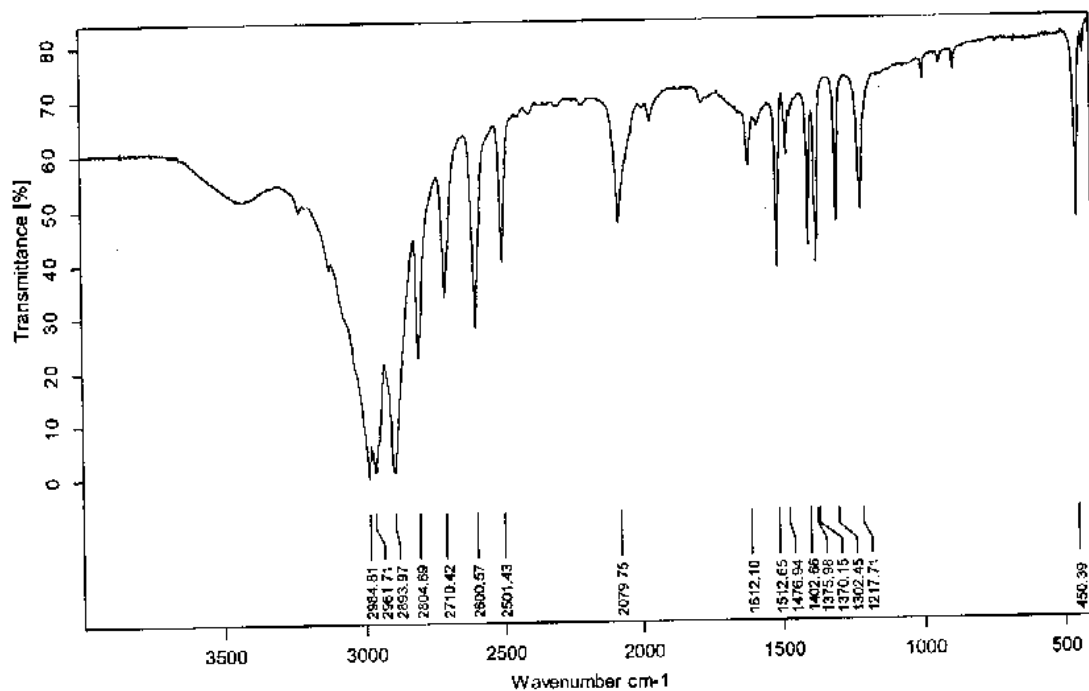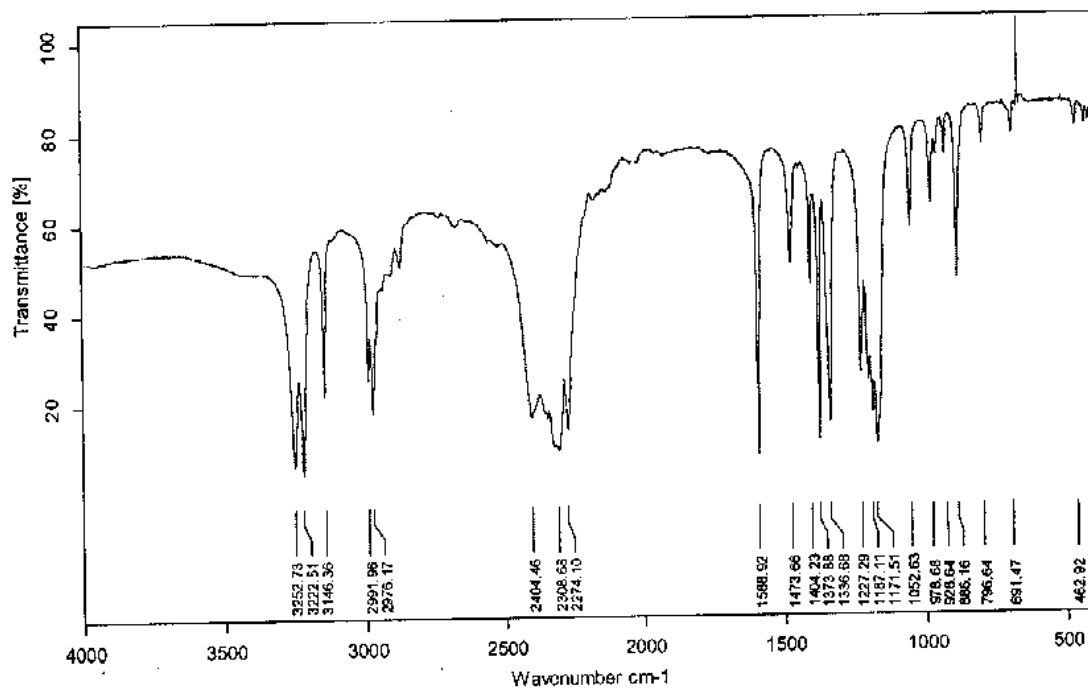**Figure 3.** Infrared Spectrum of *tert*-Butylamine Hydrochloride (**1**).

Figure 4. Infrared Spectrum of *tert*-Butylamine:Borane Adduct (**2**).

<u>Discussion</u>

The melting point of **1** is above the range reasonably detected by the melting point apparatus, as would be expected for a salt with strong ionic interactions. The melting point of **2** is below that reported in the literature (98 °C),[5] suggesting that the compound is not pure. The impurity is most likely excess $NaBH_4$. Another possible contaminant is water, although such contamination must be minimal since the characteristic broad peak for water in the infrared spectrum at ca. 3300 cm^{-1} is not observed.

The assignment of the key peaks in Figures 3 and 4 is made in Table 1.

tert-Butylamine Hydrochloride			*tert*-Butylamine:Borane Adduct		
Band Position (cm^{-1})	Intensity	Assignment	Band Position (cm^{-1})	Intensity	Assignment
2985	strong		3253	strong	N–H
2962	strong		3223	strong	stretch
2894	strong	N–H	2976	strong	C–H(sp^3)
2805	medium	stretch*	2404	strong	
2710	medium		2309	strong	B–H stretch
2601	medium		2274	strong	
2501	medium		1589	strong	NH$_2$ bend
1612	weak	NH$_2$ bend	1474	weak	
1403	medium		1404	weak	CH$_3$ bend
1376	medium	CH$_3$ bend			
			1172	strong	B–N bend
* These peaks are in combination with the C–H stretches from the *tert*-butyl group.					

Table 1. Assignment of Peaks from Figures 3 and 4.

The IR spectrum of **1** shows a distinct set of peaks from *ca.* 2890 to 2990 cm^{-1} that are characteristic of N–H stretches. There is also evidence of a small broad peak at *ca.* 3400 cm^{-1} that may be attributed to contamination of the sample by water. This contamination is not unexpected, since hydrochloride salts of amines are typically hygroscopic.

The IR spectrum of **2** shows a set of peaks at *ca.* 2275 to 2400 cm^{-1} that are indicative of terminal B–H stretches. The N–H stretching peaks have become sharper and have shifted in energy to *ca.* 3200 cm^{-1}. Several more peaks appear in the region from 1000 to 1500 cm^{-1}. This region is where bending modes are detected and some correlations can be made between the peaks seen for **1** and **2**. For example, the IR spectrum of **1** shows a peak at 1403 cm^{-1} which has shifted to 1404 cm^{-1} in the IR spectrum of **2**. Any additional peaks in this region can be attributed to B–N or B–H bending.

Conclusion

A Lewis acid-base adduct was successfully prepared and characterized by IR spectroscopy. Characteristic peaks in the spectrum of the product indicate successful formation of the adduct through the presence of B–H stretches as well as a B–N bend. Further evidence could be provided by ^{1}H NMR or by IR studies where hydrogen atoms are replaced by deuterium.

References

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[4]   Atkins, P.; Jones, L. *Chemical Principles: The Quest for Insight;* 2nd. Ed; W. H. Freeman and Co.: New York, NY, 2002; p. F88.

[5]   Heinrich, N; Hasso, B. *Chem. Ber.;* **1960**; *93*, 928-38.