

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. An intermediate 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 afforded in good yield and purity, as evidenced by melting point analysis. The infrared spectra of both compounds show characteristic peaks which are compared and contrasted.

Introduction

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) 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 Arrhenius definition of acids and bases rigorously requires the presence of water.

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.

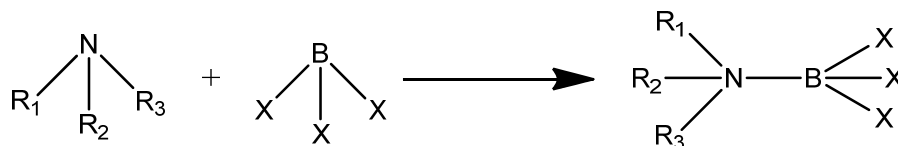


Figure 1. Reaction of an Amine with a Borane.

In this report, a Lewis acid-base adduct is prepared from *tert*-butylamine hydrochloride and sodium tetaborohydride (Figure 2). The resulting compound is characterized by melting point and IR spectroscopy and compared and contrasted to the *tert*-butylamine hydrochloride starting material.

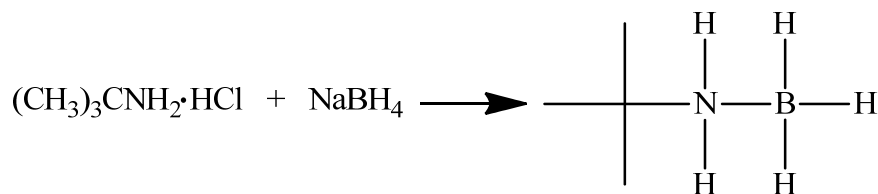


Figure 2. The Reaction to Produce *tert*-Butylamine: Borane Adduct.

Methods

tert-Butylamine hydrochloride (**1**) – *tert*-Butylamine (1.0 mL, 0.6900g) was added to 10 mL of absolute ethanol. While stirring, 12 M HCl (0.80 mL) was added dropwise over a period of 2 m. The solution was stirred for 5 m, then the stir bar was removed and the solution evaporated to dryness. The resulting solid was collected and stored for the following synthesis. Yield: 0.6930 g (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) and 5 mL of THF. To the stirred mixture, NaBH₄ (0.2773 g) was added in small portions over a period of 5 m. The flask was loosely capped with a septum and the mixture stirred for 2 h. The mixture was then filtered and the filtrate evaporated to dryness. Hexanes (10 mL) were added to the colorless residue and the resulting mixture was filtered, washed with hexanes and air dried. Yield: 0.4997 g (92%). 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 NaBH₄ 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** were collected with an ATR attachment and are shown in Figures 3 and 4, respectively.

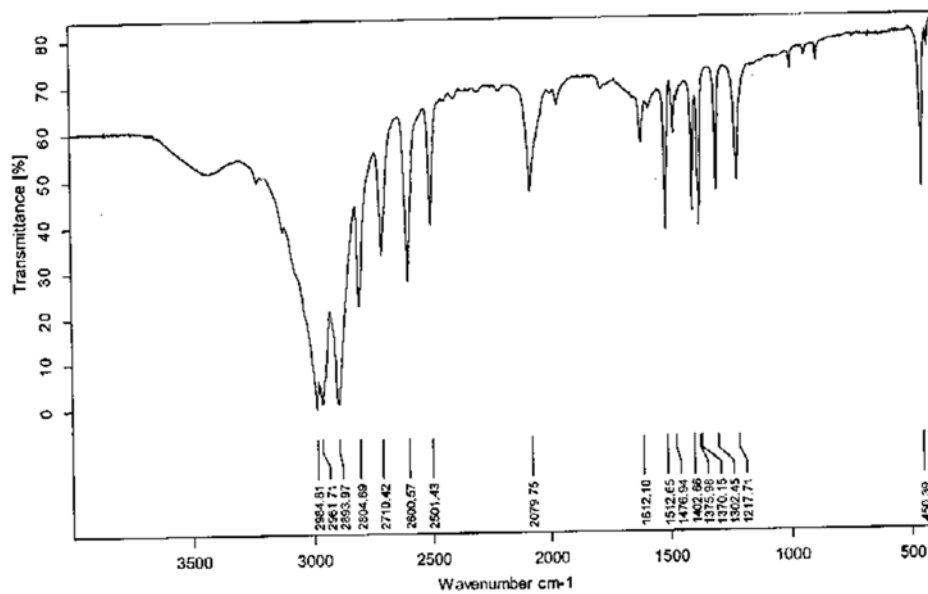


Figure 3. Infrared Spectrum of *tert*-Butylamine Hydrochloride.

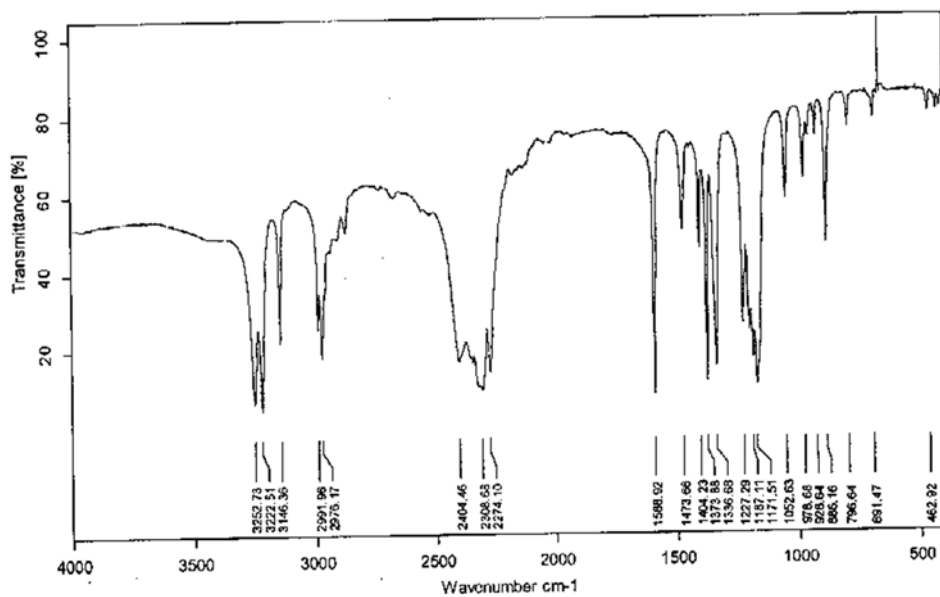


Figure 4. Infrared Spectrum of *tert*-Butylamine: Borane Adduct.

Discussion

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), suggesting that the compound is not pure. A 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.

<i>tert</i> -Butylamine Hydrochloride			<i>tert</i> -Butylamine: Borane Adduct		
Band Position (cm ⁻¹)	Intensity	Assignment	Band Position (cm ⁻¹)	Intensity	Assignment
2985	strong	N–H stretch	3253	strong	N–H stretch
2962	strong		3223	strong	
2894	strong		2976	strong	C–H(sp ³)
2805	medium		2404	strong	B–H stretch
2710	medium		2309	strong	
2601	medium		2274	strong	
2501	medium		1589	strong	bend
1612	weak	bend	1474	weak	bend
1403	medium	bend	1404	weak	
1376	medium		1172	strong	

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.

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 experienced a shift 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.

Conclusion

A Lewis acid-base adduct was successfully prepared and characterized by IR spectroscopy. Characteristic peaks in the spectrum of the product prove the formation of the adduct through the presence of B–H stretches as well as a B–N bend.

References

- ¹ Atkins, P.; Jones, L. *Chemical Principles: The Quest for Insight*; 2nd. Ed; W. H. Freeman and Co.: New York, NY, 2002; p. F88.
- ² Heinrich, N; Hasso, B. *Chem. Ber.*; **1960**; 93, 928-38.
- ³ Moore, J. W.; Stanitski, C. L.; Jurs, P. C. *Chemistry: The Molecular Science*; Harcourt College Publishers: New York, NY, 2002; pp. 728-734.
- ⁴ Rogers, G. E. *Descriptive Inorganic, Coordination, and Solid-State Chemistry*; 2nd Ed.; Brooks/Cole Publishing: Toronto, Canada, 2002; p. 58.