**EXPANDED BENCHTOP PROTOCOL FOR THE COLOMERIC TITRATION OF BORON CHLORIDE AND BROMIDE**

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**Abstract**

Expansion and modification upon previous uses of N,N-dimethylaniline (DMA) as a colorimetric titrant for boron tribromide now allows for the quantification of boron trichloride. This technique is now a general method for titration of BX$_2$ (X = Cl, Br). In CH$_2$Cl$_2$, the initial complex exhibits an increasingly blue color before reaching a sharp yellow endpoint upon addition of catalytic quantities of Lewis acid.

Keywords: boron trihalides, titration, Lewis acid, colorimetric indicator, boron

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**Introduction**

Boron trihalide (BX$_3$) reagents play an important role in organic synthesis.$^{1-5}$ Their strong Lewis acid character allows for diverse chemistry from the classic ether cleavage reaction (established in 1942) to more modern alkyne-activated annihilations.$^{2,3,5}$ Like organolithiums and Grignard reactions, the use of BX$_3$ reagents requires precise knowledge of the concentration of the reagent. However, unlike organometallic reagents, where numerous titration methods are available, benchtop quantification protocols for BX$_3$ reagents are scarce (Figure 1).$^{6-8}$ Additionally, BX$_3$ reagents are commonly purchased as a solution and degrade rapidly to produce boric acid and HX. Therefore, a fast and reliable benchtop titration method is needed to ensure correct stoichiometric addition of Lewis acid to substrate.

Recently, we and others reported the first colorimetric protocol for titrating boron tribromide.$^9$ This methodology uses DMA, which in a CH$_2$Cl$_2$ solution is colorless. Upon addition of BBr$_3$ (1 equivalent) the solution turns blue indicating a 1:1 DMA-BBr$_3$ adduct. Upon addition of catalytic amounts of the Lewis acid, the solution reaches a yellow endpoint. While this approach works well for boron tribromide, it did not prove a reliable method for other boron-based Lewis acids, namely boron trichloride due to weak or unobservable color changes.

Yet, BCl$_3$ is well known for its C-O bond cleavage reactions, but recently is employed to activate alkynes towards electrophilic addition.$^{10-14}$ Additionally, BCl$_3$ is known to borylate arenes in the presence of catalytic quantities of AlCl$_3$. The polarizability of the boron-chlorine bonds found in BCl$_3$ combined with its versatility as both a catalyst and source of chlorine in reactions explain the utility of this reagent.

Our interest in the boron trihalide class of reagents stems from developing a deeper understanding of ether cleavage as well as expanding the scope of annulation reactions to generate larger fused rings motifs.$^2$ Due to the continued and expanding interest in BX$_3$ (X = Cl, Br), we sought to expand our prior method for titrating boron tribromide. The modified technique increases the concentration of DMA, thus expanding this technique from quantifying only BBr$_3$ to now include BCl$_3$ solutions. Additionally, the modified protocol exhibits reliable and reproducible results across both reagents.

**Experimental Methods**

**General Procedures**

Boron trihalides are highly corrosive and should be handled under inert atmosphere. 1.0 M BCl$_3$ and BBr$_3$ in CH$_2$Cl$_2$ and N,N-dimethylaniline (≥99.5% purity) were purchased from Sigma-Aldrich. Anhydrous CH$_2$Cl$_2$ was obtained from a solvent system. Additional concentrations of BCl$_3$ and BBr$_3$ were prepared by adding the appropriate amount of 1.0 M solution by syringe to an oven-dried, septum-capped 10-mL volumetric flask under inert (nitrogen or argon) atmosphere, and diluting with anhydrous CH$_2$Cl$_2$.

**Titration Protocol**

An oven-dried reaction vessel charged with a magnetic stirbar was placed under an inert atmosphere. N,N-dimethylaniline (0.1 mL, 0.789 mmol) and anhydrous CH$_2$Cl$_2$ (0.5 mL) were added to the vessel. The BCl$_3$ solution was placed under inert atmosphere and drawn into a gastight syringe and was subsequently added dropwise to the reaction vessel. The color changed from clear to increasingly blue (or pink as noted in Table 1, entry 5) until reach-

![Figure 1: Commonly employed organometallic titrants.](image)

**Scheme 1:** BCl$_3$ efficiently cleaves C-O bonds$^{11}$ and active alkynes toward electrophilic cyclization.$^{14}$
ing a distinct yellow endpoint upon addition of one drop of BCl\textsubscript{3} solution (Figure 2). The volume of BCl\textsubscript{3} solution added was used to calculate the concentration of the solution, using a 1:1 molar ratio of N,N’-dimethylaniline to BCl\textsubscript{3}.

**Results and Discussion**

The titration is carried out at a concentration of 0.16 M DMA / CH\textsubscript{2}Cl\textsubscript{2} solution (1) and the solution is placed under an inert atmosphere. Our initial trials focused on CH\textsubscript{2}Cl\textsubscript{2} since this solvent is commonly used for C-O bond cleavage and annihilation reactions. The addition of one equivalent of BCl\textsubscript{3} results in a blue solution due to the Lewis acid-base interaction (2). Upon addition of catalytic quantities of BCl\textsubscript{3}, the solution quickly reaches a yellow endpoint presumably due to the loss of the BCl\textsubscript{3}-DMA adduct and subsequent borylation of DMA’s aromatic ring (3).\textsuperscript{16}

The results of the titration methods are highlighted in Table 1. To test the limits of this methodology, several different concentrations of BCl\textsubscript{3} ranging from 0.1 M to 1.0 M were titrated (Table 1, entries 1-5). Each solution was run in triplicate to confirm consistency and reproducibility. Each trial performed saw an increasingly intense blue color as more BCl\textsubscript{3} was added, with the exception of 0.25 M, which turned pink, until a sharp yellow endpoint was reached with the addition of one drop of BCl\textsubscript{3} solution. The group is further exploring the seemingly concentration dependent pink color noted in the 0.25 M trial, although the variation in initial solution color did not impact the accuracy of the titration method or the fact that the addition of catalytic quantities of BCl\textsubscript{3} created a yellow solution. At too low of a concentration, demonstrated by Entry 5 of Table 1, the concentration of the BCl\textsubscript{3} solution could not be determined through visible color change, indicating there is a lower limit for the application of this protocol.

Titration of BCl\textsubscript{3} in heptane initially produced a cloudy pale blue solution before forming a thick white precipitate which prevented the appearance of the yellow endpoint. However, precipitation did not occur when a 1 M BCl\textsubscript{3} in m-xylene was titration; rather this solution produced clear blue midpoints and a vibrant yellow endpoint.

Furthermore, and not surprisingly, the increase in concentration of DMA, which allows for BCl\textsubscript{3} titration, does not affect quantification of BBr\textsubscript{3}, as shown in Table 2. The original and modified procedure show good agreement in their observed molarity at the 1 M and 0.25 M concentrations. Unfortunately, however, the use of DMA as a titrant, does not allow for BF\textsubscript{3} etherate quantification regardless of the concentration of the titrant.

In summary, modification of a previously reported protocol that uses DMA as a titrant for BBr\textsubscript{3}, now allows for quantification of BCl\textsubscript{3} solutions. This methodology is easily conducted from inexpensive commercially available materials and provides a clear color changes and defined endpoint.

**Acknowledgments**

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**References**


**Table 1. Titrations of boron trichloride solutions.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Expected Molarity</th>
<th>Solvent</th>
<th>Number of trials</th>
<th>Observed Molarity</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1 M</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>n = 3</td>
<td>0.98±0.02</td>
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<td>2</td>
<td>0.66 M</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>n = 3</td>
<td>0.63±0.03</td>
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<tr>
<td>3</td>
<td>0.33 M</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>n = 3</td>
<td>0.32±0.01</td>
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<tr>
<td>4</td>
<td>0.25 M</td>
<td>CH\textsubscript{2}Cl\textsubscript{2}</td>
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<td>0.22±0.04</td>
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<tr>
<td>5</td>
<td>0.10 M</td>
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<td>N/A</td>
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<td>6</td>
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<td>heptane</td>
<td>n = 3</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>1 M</td>
<td>m-xylene</td>
<td>n = 4</td>
<td>0.97±0.02</td>
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**Table 2. Titrations of boron tribromide solutions.**

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<tr>
<th>Entry</th>
<th>Expected Molarity</th>
<th>Concentration of DMA</th>
<th>Number of trials</th>
<th>Observed Molarity</th>
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<td>1.0±0.06</td>
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<tr>
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<td>0.53</td>
<td>n = 3</td>
<td>0.24±0.05</td>
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<tr>
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<td>0.25 M</td>
<td>1.6 M</td>
<td>n = 3</td>
<td>0.25±0.01</td>
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