The reaction of potassium germyl with boron trimethyl

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THE REACTION OF POTASSIUM GERMYL WITH BORON TRIMETHYL*

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Potassium germyltrihydroborate, KGeH₃BH₃, was prepared and characterized in this laboratory [1]. Two other germylborates, LiGePh₃BPh₃ [2] and LiGeEt₃BPh₃ [3], are known, and there is evidence that similar species, KGeH₃BX₃, are the initial products of reaction between potassium germyl, KGeH₃, and several BX₃ compounds (X = I, Cl, OMe) [4]. In this note we describe the reaction between KGeH₃ and boron trimethyl to form the adduct KGeH₃BMe₃.

Experimental

Standard vacuum-line techniques were used for the manipulation of the volatile compounds. In a typical reaction a measured amount of BMe₃ was condensed into a 150-ml vessel containing an aliquot (ca. 5 ml) of a standard solution of KGeH₃ in diglyme [5]. The reaction vessel was slowly warmed from -196° to 0° and held at that temperature, with stirring. Subsequently the vessel was cooled to -196°, and any non-condensible gas was removed with a Toepler pump, measured in a gas buret, and analyzed by mass spectroscopy on a Granville-Phillips 750 quadrupole mass spectrometer. Products volatile at 0° were then removed, separated by trap-to-trap distillations, and identified from vapor pressure measurements and infrared spectroscopy on a Perkin-Elmer Model 137 spectrophotometer.

Water and dilute hydrochloric acid were successively distilled into the reaction vessel, and in each case the volatile products were
analyzed and measured as above. In a separate series of runs, 1:1 mixtures of the reactants were sealed in nmr tubes, and the reaction was followed at 0° by recording \(^1\)H nmr spectra sequentially on a Varian T-60 or HA-100 spectrometer.

Results and Discussion

The potassium germyl solutions reacted with boron trimethyl at 0° to produce clear colorless solutions which became straw-colored after several hours. Generally a trace of germane, equivalent to ca 1\% of the germanium, was the only volatile product. When more than an equimolar amount of BMe\(_3\) was used (run 6), the excess BMe\(_3\) was recovered. Hydrolysis of the final reaction mixture gave hydrogen, germane, and digermane, in the amounts shown in Table 1. The data taken as a whole are consistent with the initial formation of the germyl-trimethylborate ion:

\[
\text{GeH}_3^- + \text{BMe}_3 \rightarrow \text{GeH}_3\text{BMe}_3^- \quad (1)
\]

In run 1, which was quenched one minute after mixing the reactants, germane was the major hydrolysis product. Presumably the following hydrolysis occurred in this case.

\[
\text{GeH}_3\text{BMe}_3^- + \text{H}_2\text{O} \rightarrow \text{GeH}_4 + \text{HOBMe}_3^- \quad (2)
\]

In every other run, relatively large amounts of hydrogen and digermane formed in the hydrolysis reaction. We believe that these hydrolysis products are evidence of a disproportionation of the GeH\(_3\)BMe\(_3\)\(^-\) ion.
Table 1. The Reaction of Potassium Germyl with Boron Trimethyl at 0°

<table>
<thead>
<tr>
<th>Run</th>
<th>Reaction Time (hrs)</th>
<th>Reactions (mmole)</th>
<th>Volatile Hydrolysis Products (mmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>KGeH₃</td>
<td>BMe₃</td>
</tr>
<tr>
<td>1</td>
<td>a</td>
<td>3.24</td>
<td>3.25</td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>0.65</td>
<td>0.50</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>1.23</td>
<td>0.69</td>
</tr>
<tr>
<td>5</td>
<td>2.5</td>
<td>0.63</td>
<td>0.59</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>0.63</td>
<td>1.56</td>
</tr>
<tr>
<td>7</td>
<td>6.0</td>
<td>3.52</td>
<td>3.40</td>
</tr>
<tr>
<td>8</td>
<td>6.0</td>
<td>3.68</td>
<td>3.68</td>
</tr>
<tr>
<td>9</td>
<td>47</td>
<td>1.09</td>
<td>0.94</td>
</tr>
<tr>
<td>10</td>
<td>140</td>
<td>0.65</td>
<td>0.62</td>
</tr>
</tbody>
</table>

a solution frozen one minute after complete melting; never reached 0°
This disproportionation explains the low yields of germane which, in runs 2-10, were always close to the amounts expected from hydrolysis of the excess GeH$_3^-$ (GeH$_3^-$ + H$_2$O $\rightarrow$ GeH$_4$ + OH$^-$). The disproportionation products presumably underwent hydrolysis according to reactions 4 and 5.

\[
\text{HBMMe}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{HOBMe}_3^- \hspace{2cm} (4)
\]

\[
\text{Ge}_2\text{H}_5\text{BMe}_3^- + \text{H}_2\text{O} \rightarrow \text{Ge}_2\text{H}_6 + \text{HOBMe}_3^- \hspace{2cm} (5)
\]

Reaction 3 has several analogues in germanium chemistry [6]. For example, GeH$_3$BH$_3^-$ is known to disproportionate in the presence of diborane [1]:

\[
2 \text{GeH}_3\text{BH}_3^- \xrightarrow{\text{B}_2\text{H}_6} \text{BH}_4^- + \text{Ge}_2\text{H}_5\text{BH}_3^- \hspace{2cm} (6)
\]

These conclusions are supported by the $^1$H nmr study of the 1:1, KGeH$_3$:BMe$_3$ reaction. Because the solvent peaks lie close to the GeH resonance region only the protons of methyl groups attached to boron were readily observed. Resonances attributable to GeH$_3^-$ or BMe$_3^-$ were not observed in the initial spectrum at 0°, indicating a complete and rapid 1:1 reaction. Three singlets were observed however at -0.35, -0.48 and -0.59 8 (chemical shifts given in parts per million, to low field of internal TMS). The peak at -0.35 8 disappeared after 30 min at 0° and is assigned to GeH$_3$BMe$_3^-$. The peak at -0.46 8 is assigned to HBMMe$_3^-$, found in an independent experiment to have a methyl resonance at -0.48 8. The singlet at -0.58 8, possibly associated with a broad features at 2.78 8, is assigned to Ge$_2$H$_5$BMe$_3^-$. 

\[
2 \text{GeH}_3\text{BMe}_3^- \rightarrow \text{HBMMe}_3^- + \text{Ge}_2\text{H}_5\text{BMe}_3^- \hspace{2cm} (3)
\]
Except in runs 1 and 2, the germanium was never fully recovered in the form of volatile products; some of it ended up in an intractable precipitate which formed when excess water or acid was added to the reaction mixture. (In runs 7, 8, and 9 the sum of the germanium and any boron in the residue was determined by volumetric analysis [7]. In these runs, the total recovery of germanium plus boron (as GeH₄, Ge₂H₆, BMe₃, and residue) was 104, 98, and 103 percent respectively.) Furthermore, the amount of hydrogen liberated on initial hydrolysis always exceeded the amount of digermane formed. (From equations 3, 4, and 5, one would expect these amounts to be equal.) To explain these data, we tentatively suggest that GeH₃BMe₃⁻ and Ge₂H₅BMe₃⁻ undergo the following type of hydrolysis in competition with reactions 2 and 5.

\[
\text{Ge}_n\text{H}_{2n+1}\text{BMe}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Ge}_n\text{H}_{2n} + \text{HOBMe}_3^- \quad (7)
\]

Dilution of the solution with water caused precipitation of the germanium-containing polymer:

\[
\text{Ge}_n\text{H}_{2n} \rightarrow \frac{n}{x} (\text{GeH}_2)_x \quad (8)
\]

According to equations 4, 5, and 7, hydrolysis should have converted all the boron to HOBMe₃⁻, which can be converted to BMe₃ by acid:

\[
\text{HOBMe}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{BMe}_3 \quad (9)
\]

Indeed, the acid hydrolyses generally did give quantitative recovery of the BMe₃. (In a few irreproducible cases, up to 20% of the boron remained in the residue, probably as a result of accidental oxidation.)
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