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INORGANIC SYNTHESIS WITH ELECTRIC DISCHARGES

William L. Jolly

May 1967
Inorganic Synthesis with Electric Discharges

William L. Jolly

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Introduction

Electric discharge reactions often yield thermodynamically unstable products, of unusual structure, that are difficult to prepare by other methods (26,28). Such reactions are of great interest to chemists who hope to discover new types of compounds. Nevertheless, electric discharges are not yet a favorite laboratory technique among synthetic chemists. There are three reasons for this unpopularity of electric discharges. (a.) In contrast to conventional synthetic equipment (flasks, heaters, stirrers, etc.), electric discharge apparatus is fairly complicated and time-consuming in use. (b.) Apparatus large enough to give decent yields of product is fairly expensive. (c.) The art of predicting the course of discharge reactions is primitive and unreliable. It is to be hoped that the first two problems can be solved by electrical engineers
and apparatus manufacturers. The third problem must be solved by physical and synthetic chemists. In this review, we shall try to systematize briefly the available knowledge and to point out likely directions for future research.

Conversion of Simple Molecules into Higher Homologs

The simplest hydrides and halides of boron, silicon, germanium, phosphorus and arsenic can be decomposed in electric discharges to form mixtures of the corresponding higher molecular weight compounds. The energetics and experimental technique for the hydride reactions are quite different from those for the halide reactions, and we shall discuss these two classes of reactions separately.

Hydrides

The decomposition of a simple hydride into hydrogen and a higher hydride is an exothermic process; therefore when the reaction products leave the discharge zone there is no tendency for back-reaction to the starting material. Of course, inasmuch as reactions of molecular hydrogen are generally quite slow at ordinary temperatures, it is unlikely that any appreciable back-reaction would occur even if the decomposition were endothermic. The absence of back-reaction simplifies the experimental procedure, because there is no need to rapidly quench the reaction products and no need to remove the hydrogen from the vapors leaving the discharge.

The usual procedure in preparations of polysilanes and polygermanes is to circulate the simple hydride through an ozonizer-type discharge
until practically all of it has decomposed and the gas being circulated is principally hydrogen. The product hydrides are trapped out in a suitable cold trap in the gas circuit. If the desired product vapors were allowed to continually circulate through the discharge, the product would eventually be decomposed completely to hydrogen and a very high molecular weight, essentially non-volatile, product. The average molecular weight of the product can be adjusted by varying the cold trap temperature - the colder the trap, the lower the average molecular weight.

In Table 1, some of the higher molecular weight hydrides which have been prepared from simple hydrides are listed.

**Halides -**

When the volatile halides SiCl₄, GeCl₄ and BCl₃ are passed through a glow discharge at low pressure, the higher homologs, Si₂Cl₆, Ge₂Cl₆ and B₂Cl₄, are formed along with elementary chlorine. These higher halides may be isolated if the vapors emerging from the discharge are passed through suitable cold traps for separating the halides from chlorine by fractional condensation. However, a great deal of back-reaction occurs, and the yields are low. If the apparatus is modified so that a suitable reducing agent is present in the discharge zone or immediately after the discharge zone, the yields are greatly improved. Mercury and copper wool have been found to be very effective reducing agents for this purpose.

The effectiveness of including a reducing agent in the apparatus is dramatically shown by experiments with PCl₃. If a glow discharge is established in a stream of PCl₃ vapor in the absence of a reducing agent,
**Table 1.**

Electric Discharge Syntheses of Volatile Hydrides

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Electric Discharge</th>
<th>Products Isolated</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>Ozonizer</td>
<td>Si₂H₆, Si₃H₈, Si₄H₁₀, *</td>
<td>15,50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si₅H₁₂, *Si₆H₁₄, * Si₇H₁₆, *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si₈H₁₈</td>
<td></td>
</tr>
<tr>
<td>GeH₄</td>
<td>Ozonizer</td>
<td>Ge₂H₆, Ge₃H₈, Ge₄H₁₀, *</td>
<td>7,8,15,16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge₅H₁₂, *Ge₆H₁₄, *</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ge₇H₁₆, *Ge₈H₁₈, Ge₉H₂₀</td>
<td></td>
</tr>
<tr>
<td>AsH₃</td>
<td>Ozonizer</td>
<td>As₂H₄</td>
<td></td>
</tr>
<tr>
<td>B₂H₆</td>
<td>Ozonizer; Glow discharge between Cu electrodes</td>
<td>B₄H₁₀, B₅H₉, B₅H₁₁, B₆H₁₀,</td>
<td>14,32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B₇H₁₅</td>
<td></td>
</tr>
<tr>
<td>B₅H₉ (+ H₂)</td>
<td>Glow discharge between Cu electrodes</td>
<td>B₁₀H₁₆ + ***</td>
<td>20</td>
</tr>
<tr>
<td>B₅H₉ (+ B₂H₆ + H₂)</td>
<td>Glow discharge between Cu electrodes</td>
<td>B₆H₁₂ + ***</td>
<td>10</td>
</tr>
<tr>
<td>B₁₀H₁₄ (+ H₂)</td>
<td>Glow discharge between Cu electrodes</td>
<td>B₂₀H₁₆ + ***</td>
<td>13</td>
</tr>
</tbody>
</table>

* Isomers observed
the vapor leaving the PCl₃ discharge contains PCl₅ and probably one or more of the following species: P, P₂ or PCl. No P₂Cl₄ is obtained, even by fractional condensation of the vapors. However, by including a reducing agent (hydrogen, mercury, copper or phosphorus) in or near the discharge, fairly good yields of P₂Cl₄ have been obtained.

A brief summary of some electric discharge halide syntheses is given in Table 2.

Conversion of Mixtures into More Complicated Molecules

When a binary mixture of relatively simple molecules is subjected to an electric discharge, various types of reactions are possible, including simple coupling with the elimination of fragments, and the transfer of an atom or group from one species to another.

Hydrides -

When mixtures of relatively simple hydrides are passed through an electric discharge, higher molecular weight ternary hydrides are formed. For example, by passing a mixture of SiH₄ and PH₃ through an ozonizer discharge, one obtains a mixture of the compounds SiH₂PH₂, Si₂H₅PH₂, and (SiH₃)₂PH, as well as P₂H₄ and various polysilanes (9,17). The ozonizer (or silent electric discharge) is mild in its action on molecules, and it does not cause drastic fragmentation and rearrangement. There is some evidence that, by the judicious choice of reagents, it can be used for the preparation of specific isomers (18). Thus a mixture of SiH₃PH₂ and SiH₄ yields (SiH₃)₂PH, and a mixture of Si₂H₆ and PH₃ yields Si₂H₅PH₂. The conversion of acetylene-boron hydride mixtures into carboranes involves
### Table 2.

**Electric Discharge Syntheses of Halides**

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Reducing Agent</th>
<th>Products Isolated</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC13</td>
<td>none</td>
<td>B2Cl4</td>
<td>56,57</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>B2Cl4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>B2Cl4</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>B2Cl4</td>
<td>58</td>
</tr>
<tr>
<td>BI3</td>
<td>none</td>
<td>B2I4, BxIy, (BI)x</td>
<td>43</td>
</tr>
<tr>
<td>All3</td>
<td>none</td>
<td>(AlI)x</td>
<td>44</td>
</tr>
<tr>
<td>SiCl4</td>
<td>Hg</td>
<td>Si₂Cl₂n±2</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>Si</td>
<td>Si₂Cl₂n±2</td>
<td>29</td>
</tr>
<tr>
<td>GeCl4</td>
<td>none</td>
<td>Ge₂Cl₆</td>
<td>25,47</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Ge₂Cl₆</td>
<td>27</td>
</tr>
<tr>
<td>PCl₃</td>
<td>none</td>
<td>PₓClₙ, PCl₅</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>P2Cl₄</td>
<td>4,41</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>P2Cl₄</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>P2Cl₄</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>P₄</td>
<td>P2Cl₄</td>
<td>41</td>
</tr>
<tr>
<td>TiCl₄</td>
<td>H₂</td>
<td>TiCl₃</td>
<td>24</td>
</tr>
</tbody>
</table>
relatively deep-seated molecular rearrangements. The ozonizer is fairly inefficient in effecting such reactions, and the more powerful glow-discharge between copper electrodes is preferred for such purposes (19).

A summary of some electric discharge syntheses of ternary hydrides is given in Table 3.

**Halides**

The author is aware of only one example of the preparation of a ternary halide in an electric discharge. Massey and Urch (34) obtained a very small sample of impure SiCl$_2$BCl$_2$ as a by-product from the mercury discharge synthesis of B$_2$Cl$_4$. The silicon probably originated from the quartz discharge cell used. It appears that the essentially unexplored study of mixtures of halides in electric discharges is worthy of study.

**Fluorides**

Some remarkable compounds have been prepared by subjecting mixtures of various species with elementary fluorine to glow discharges. Both static and circulating systems have been employed, and the products of the reactions have been effectively removed from the possible destructive action of the discharge by holding the discharge tube at a temperature low enough to cause the condensation of the product. Thus, by subjecting mixtures of oxygen and fluorine to the action of a glow discharge between copper electrodes at 60-77°K, the compounds O$_2$F$_2$ (10), O$_3$F$_2$ (3, 30, 31), O$_4$F$_2$ (22), O$_5$F$_2$ (54) and O$_6$F$_2$ (54) have been prepared. The higher members of this series are extremely unstable compounds that decompose to their elements even at 90°K. Using a similar apparatus at 86°K, krypton and fluorine have yielded the very reactive species KrF$_2$ (21, 42). Recently
Table 3.

Electric Discharge Syntheses of Ternary Hydrides

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Electric Discharge</th>
<th>Products Isolated</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ + GeH₄</td>
<td>ozonizer</td>
<td>SiH₃GeH₃</td>
<td>51</td>
</tr>
<tr>
<td>SiH₄ + PH₃</td>
<td>ozonizer</td>
<td>SiH₃PH₂, Si₂H₅PH₂, (SiH₃)₂PH</td>
<td>9, 17</td>
</tr>
<tr>
<td>Si₂H₆ + PH₃</td>
<td>ozonizer</td>
<td>Si₂H₅PH₂</td>
<td>18</td>
</tr>
<tr>
<td>SiH₃PH₂ + SiH₄</td>
<td>ozonizer</td>
<td>(SiH₃)₂PH</td>
<td>18</td>
</tr>
<tr>
<td>SiH₄ + AsH₃</td>
<td>ozonizer</td>
<td>SiH₃AsH₂, Si₂AsH₇</td>
<td>9</td>
</tr>
<tr>
<td>GeH₄ + PH₃</td>
<td>ozonizer</td>
<td>GeH₃PH₂, Ge₂PH₇, Ge₃PH₉, GeH₆</td>
<td>9</td>
</tr>
<tr>
<td>GeH₄ + AsH₃</td>
<td>ozonizer</td>
<td>GeH₃AsH₂</td>
<td>9</td>
</tr>
<tr>
<td>SiH₄ + CH₃OCH₃</td>
<td>ozonizer</td>
<td>CH₃Si₂H₅</td>
<td>1</td>
</tr>
<tr>
<td>B₅H₉ + C₂H₂</td>
<td>ozonizer</td>
<td>B₅C₂H₅, sym-B₄C₂H₆, unsym-B₄C₂H₆, B₅C₂H₇</td>
<td>45, 46</td>
</tr>
<tr>
<td>B₂H₆ + C₂H₂</td>
<td>glow discharge</td>
<td>B₃C₂H₅, sym-B₄C₂H₆, B₅C₂H₇, B₅C₂H₇ + methyl derivs.</td>
<td>19</td>
</tr>
</tbody>
</table>
the unusual compound \( \text{NF}_4^+\text{AsF}_6^- \) was prepared by subjecting a mixture of \( \text{NF}_2, \text{AsF}_5 \) and \( \text{F}_2 \) to a glow discharge at \(-78^\circ \) (23). In contrast to the polyoxygen fluorides and krypton difluoride, \( \text{NF}_4^+\text{AsF}_6^- \) is stable and non-volatile at 25°.

The synthesis of a rare gas fluoride ordinarily involves the use of elementary fluorine and the concomitant special equipment used in handling fluorine. However Milligan and Sears (37) have described a fluorination technique which avoids the use of fluorine and consequently deserves serious consideration as a general method. They passed mixtures of xenon and \( \text{CF}_4 \) through a microwave discharge and obtained good yields of \( \text{XeF}_2 \).

**Controlled Reactions of Atoms and Radicals**

The syntheses discussed in the preceding section are characterized by the reaction of a mixture of species in an electric discharge. This procedure sometimes leads to the formation of unwanted by-products that complicate the isolation of pure products. These side reactions can partially be avoided by allowing a stream of atoms or radicals (prepared in an electric discharge) to impinge on various compounds in the absence of a discharge. This procedure is somewhat inefficient because of inevitable losses of the atoms or radicals while in transit from the discharge zone, but it affords considerable control over the nature of the products formed.

**Atomic Hydrogen**

Many reactions of atomic hydrogen with organic compounds have been studied (52). It is generally agreed that the primary reaction with
saturated hydrocarbons is hydrogen abstraction, whereas with alkyl halides
and alkenes halogen atom abstraction and hydrogen atom addition are in-
volved. Relatively few reactions of atomic hydrogen with gaseous inorganic
compounds have been studied (48). Apparently no controlled reaction of
atomic hydrogen with a boron hydride has been studied. Possibly the
reported reaction of a mixture of H₂ and B₅H₉ to give B₁₀H₁₆ involved
the abstraction of the apical H atom from B₅H₉ followed by coupling of
two B₅H₆ radicals (20). It would be interesting to see if other similar
coupling reactions can be effected by atomic hydrogen. In a study of
the reaction of atomic hydrogen with PH₃, only H₂ and red phosphorus were
observed as products (59). However, the reaction was studied only at
73° and higher, at which temperatures P₂H₄ is kinetically unstable (11).
Possibly useful yields of higher phosphines could be obtained by working
at lower temperatures.

The reactions of atomic hydrogen with the elements has been reviewed
by Siegel (48). In many cases hydrides are formed, but the reactions
with metals are often complicated by the heat liberated by the surface-
catalyzed atom recombination reaction. McTaggart has reported the reac-
tion of atomic hydrogen with various transition metal oxides to form
reduced oxides (35). In the case of TiO₂ and ZrO₂, hydrogen-containing
oxides of empirical composition H₀.₂TiO₁.₃ and H₀.₂ZrO₁.₆₆ were obtained.
Zirconium difluoride has been prepared by the action of atomic hydrogen
on thin layers of ZrF₄ at elevated temperatures (36).

A number of interesting reactions have been studied by passing
streams of atomic hydrogen through aqueous solutions (5,6). In a typical
procedure, hydrogen gas at 20-30 mm. pressure is pumped through an
electric discharge, through the experimental solution (cooled to reduce
evaporation), and through a cold trap to retain volatile products.
Dissolved atomic hydrogen sometimes acts as an oxidizing agent, by
hydrogen abstraction from organic molecules, or together with the aqueous
proton as in the oxidation of ferrous ion \((5,6)\):

\[
\text{Fe}^{2+} + H + H^+ \rightarrow \text{Fe}^{3+} + H_2
\]

With many inorganic species (such as \(\text{Co}(III)\) complexes, nitrate ion, and
ferricyanide), atomic hydrogen acts as a reducing agent, with formation
of the aqueous proton \((38)\). For example,

\[
\text{Co(NH}_3)_6^{3+} + H \rightarrow \text{Co(NH}_3)_6^{2+} + H^+
\]

Recently it has been recognized that atomic hydrogen and the aqueous
electron are two distinct reducing species, interconvertible by adjust-
ment of the pH \((2)\):

\[
\text{H}_{aq} + \text{OH}^- \rightarrow \text{e}_{aq}^- + \text{H}_2\text{O}
\]

The application of these reagents to synthetic problems has not yet been
attempted. Possibly the effect of hydrogen atoms on aqueous systems
can be studied by using a static ozonizer discharge containing aqueous
solutions. It has been demonstrated that ceric ions may be reduced to
cerous ions and that ferrous ions are oxidized to ferric ions (with
formation of hydrogen peroxide) by simple exposure of the appropriate
solutions to a silent electric discharge \((60)\). These reactions are
believed to involve the formation of H atoms and OH radicals.
Atomic Nitrogen

Atomic nitrogen, like most atoms and radicals (39), acts as an electrophilic reagent which favors attack at polarizable donor atoms. This behavior is apparent from a study of the reaction of atomic nitrogen with various sulfur compounds (49). Divalent sulfur compounds (H2S, CS2, OCS, S2, S2Cl2 and SCl2) yield a variety of sulfur-nitrogen compounds. On the other hand, sulfur compounds containing sulfur atoms with a positive formal charge (SO2, SOCl2, and SO3) yield no sulfur-nitrogen compounds. The reaction of atomic nitrogen with S2Cl2 was found to give good yields of the unusual molecule NSCl.

Recently it has been shown that when atomic nitrogen is passed through aqueous solutions, it can effect a variety of oxidation-reduction reactions (33).

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Literature Cited


(40) Ruff, O., Menzel, W., Z. anorg. allgem. Chem., 211, 204 (1933).
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