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INORGANIC SYNTHESIS WITH ELECTRIC DISCHARGES

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May 1967

Inorganic Synthesis with Electric Discharges

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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 SiCl_4 , GeCl_4 and BCl_3 are passed through a glow discharge at low pressure, the higher homologs, Si_2Cl_6 , Ge_2Cl_6 and B_2Cl_4 , 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 PCl_3 . If a glow discharge is established in a stream of PCl_3 vapor in the absence of a reducing agent,

Table 1.

Electric Discharge Syntheses of Volatile Hydrides

Starting Material	Electric Discharge	Products Isolated	References
SiH_4	Ozonizer	Si_2H_6 , Si_3H_8 , Si_4H_{10} ,* Si_5H_{12} ,* Si_6H_{14} ,* Si_7H_{16} ,* Si_8H_{18} .	15,50
GeH_4	Ozonizer	Ge_2H_6 , Ge_3H_8 , Ge_4H_{10} ,* Ge_5H_{12} ,* Ge_6H_{14} ,* Ge_7H_{16} ,* Ge_8H_{18} , Ge_9H_{20}	7,8,15,16
AsH_3	Ozonizer	As_2H_4	
B_2H_6	Ozonizer; Glow discharge between Cu electrodes	B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , B_9H_{15}	14,32
B_5H_9 (+ H_2)	Glow discharge between Cu electrodes	$\text{B}_{10}\text{H}_{16}$ + ...	20
B_5H_9 (+ B_2H_6 + H_2)	Glow discharge between Cu electrodes	B_8H_{12} + ...	10
$\text{B}_{10}\text{H}_{14}$ (+ H_2)	Glow discharge between Cu electrodes	$\text{B}_{20}\text{H}_{16}$ + ...	13
* Isomers observed			

the vapor leaving the PCl_3 discharge contains PCl_5 and probably one or more of the following species: P , P_2 or PCl . No P_2Cl_4 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 P_2Cl_4 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 SiH_4 and PH_3 through an ozonizer discharge, one obtains a mixture of the compounds SiH_3PH_2 , $\text{Si}_2\text{H}_5\text{PH}_2$, and $(\text{SiH}_3)_2\text{PH}$, as well as P_2H_4 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 SiH_3PH_2 and SiH_4 yields $(\text{SiH}_3)_2\text{PH}$, and a mixture of Si_2H_6 and PH_3 yields $\text{Si}_2\text{H}_5\text{PH}_2$. The conversion of acetylene-boron hydride mixtures into carboranes involves

Table 2.

Electric Discharge Syntheses of Halides

Starting Material	Reducing Agent	Products Isolated	References
BCl_3	none	B_2Cl_4	
	Hg	B_2Cl_4	56,57
	Zn		53
	Cu	B_2Cl_4	58
BI_3	none	B_2I_4 , B_xI_y , $(\text{BI})_x$	43
AlI_3	none	$(\text{AlI})_x$	44
SiCl_4	Hg	$\text{Si}_n\text{Cl}_{2n+2}$	55
	Si	$\text{Si}_n\text{Cl}_{2n+2}$	29
GeCl_4	none	Ge_2Cl_6	25,47
	Cu	Ge_2Cl_6	27
PCl_3	none	P_xCl_y , PCl_5	27
	H_2	P_2Cl_4	4,41
	Hg	P_2Cl_4	12
	Cu	P_2Cl_4	27
	P_4	P_2Cl_4	41
TiCl_4	H_2	TiCl_3	24

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 $\text{SiCl}_3\text{BCl}_2$ as a by-product from the mercury discharge synthesis of B_2Cl_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_2F_2 (40), O_3F_2 (3,30,31), O_4F_2 (22), O_5F_2 (54) and O_6F_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

Reagents	Electric Discharge	Products Isolated	References
$\text{SiH}_4 + \text{GeH}_4$	ozonizer	SiH_3GeH_3	51
$\text{SiH}_4 + \text{PH}_3$	ozonizer	SiH_3PH_2 , $\text{Si}_2\text{H}_5\text{PH}_2$, $(\text{SiH}_3)_2\text{PH}$	9,17
$\text{Si}_2\text{H}_6 + \text{PH}_3$	ozonizer	$\text{Si}_2\text{H}_5\text{PH}_2$	18
$\text{SiH}_3\text{PH}_2 + \text{SiH}_4$	ozonizer	$(\text{SiH}_3)_2\text{PH}$	18
$\text{SiH}_4 + \text{AsH}_3$	ozonizer	SiH_3AsH_2 , Si_2AsH_7	9
$\text{GeH}_4 + \text{PH}_3$	ozonizer	GeH_3PH_2 , Ge_2PH_7 , Ge_3PH_9 , GeP_2H_6	9
$\text{GeH}_4 + \text{AsH}_3$	ozonizer	GeH_3AsH_2	9
$\text{SiH}_4 + \text{CH}_3\text{OCH}_3$	ozonizer	$\text{CH}_3\text{Si}_2\text{H}_5$	1
$\text{B}_5\text{H}_9 + \text{C}_2\text{H}_2$	ozonizer	$\text{B}_3\text{C}_2\text{H}_5$, <u>sym</u> - $\text{B}_4\text{C}_2\text{H}_6$, <u>unsym</u> - $\text{B}_4\text{C}_2\text{H}_6$, $\text{B}_5\text{C}_2\text{H}_7$	45,46
$\text{B}_2\text{H}_6 + \text{C}_2\text{H}_2$	glow discharge between Cu electrodes	$\text{B}_3\text{C}_2\text{H}_5$, <u>sym</u> - $\text{B}_4\text{C}_2\text{H}_6$, $\text{B}_5\text{C}_2\text{H}_7$ + methyl derivs.	19

the unusual compound $\text{NF}_4^+\text{AsF}_6^-$ was prepared by subjecting a mixture of NF_3 , AsF_5 and F_2 to a glow discharge at -78° (23). In contrast to the polyoxygen fluorides and krypton difluoride, NF_4AsF_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 CF_4 through a microwave discharge and obtained good yields of 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 involved. 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 H_2 and B_5H_9 to give $B_{10}H_{16}$ involved the abstraction of the apical H atom from B_5H_9 followed by coupling of two B_5H_8 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 PH_3 , only H_2 and red phosphorus were observed as products (59). However, the reaction was studied only at 73° and higher, at which temperatures P_2H_4 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 reaction of atomic hydrogen with various transition metal oxides to form reduced oxides (35). In the case of TiO_2 and ZrO_2 , hydrogen-containing oxides of empirical composition $H_{0.2}TiO_{1.3}$ and $H_{0.2}ZrO_{1.66}$ were obtained. Zirconium difluoride has been prepared by the action of atomic hydrogen on thin layers of ZrF_4 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).

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

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

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 (H_2S , CS_2 , OCS , S_8 , S_2Cl_2 and SCL_2) yield a variety of sulfur-nitrogen compounds. On the other hand, sulfur compounds containing sulfur atoms with a positive formal charge (SO_2 , $SOCl_2$, and SO_3) yield no sulfur-nitrogen compounds. The reaction of atomic nitrogen with S_2Cl_2 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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