Inorganic Synthesis with Electric Discharges

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Electric discharge reactions which yield thermodynamically unstable products are of interest to synthetic chemists because such products are often difficult to prepare by other methods. Many fascinating compounds of unusual structure have been isolated from discharge reactions. Although such syntheses usually have low efficiencies, the general techniques are nevertheless of interest to chemists who hope to discover new types of compounds. In this paper, we shall consider some important types of reactions which can be effected with the aid of electric discharges, together with some recent examples of these reactions.

Conversion of Simple Molecules into Higher Homologs

When simple volatile hydrides are passed through an ozonizer-type discharge tube near atmospheric pressure or through a glow discharge at low pressure, fairly good yields are obtained of the higher homologs of the hydrides. For example, both silane and germane can be converted to their respective higher hydrides; silanes as high as Si_8H_{18} and germanes as high as Ge_9H_{20} are formed. Similarly, arsine may be converted to diarsine. A wide variety of boron hydrides, including B_9H_{15}, $B_{10}H_{16}$, $B_{20}H_{16}$, B_6H_{12} and B_8H_{12}, has been prepared in electric discharges. In all these reactions, hydrogen is a by-product, and there is no tendency for back-reaction of the hydrogen with the product molecules.

When the volatile halides, $SiCl_4$, $GeCl_4$, and BCl_3, are passed through a glow discharge at low pressure, small yields of the higher homologs, Si_2Cl_6, Ge_2Cl_6 and B_2Cl_4, are obtained if provision is made to separate the products from the by-product chlorine by fractional condensation. (Chlorine reacts readily with the product molecules to reform the starting materials.) However, the yields are much improved if a reducing agent which can react with chlorine is included in the discharge zone or immediately after the discharge zone. Mercury and copper wool have been found to be very effective reducing agents for this purpose. In fact, P_2Cl_4 can be obtained from a discharge in H_2 + PCl_3 or from a PCl_3 discharge followed by copper wool, whereas no P_2Cl_4 has been obtained in the absence of the reducing agents.

Conversion of Mixtures into More Complicated Molecules

When mixtures of relatively simple hydrides are passed through an electric discharge, higher molecular weight ternary hydrides are formed. Thus by using appropriate mixtures of SiH_4, GeH_4, PH_3, and AsH_3, it has been possible to prepare, among other things, SiH_3GeH_3, SiH_3PH_2, SiH_3AsH_2, GeH_3PH_2, and GeH_3AsH_2. By using a silent electric discharge, which does not cause drastic fragmentation and rearrangement, it is possible, within limits, to tailor-make molecules. Thus a mixture of SiH_3PH_2 and SiH_4 yields $(SiH_3)_2PH$, and a mixture of Si_2H_6 and PH_3 yields $Si_2H_5PH_2$.

Passage of diborane-acetylene mixtures through an electric discharge yields carboranes as the major volatile products, including 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and at least six B-methylated derivatives of these plus C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$. The reaction of SiH_4 and $(CH_3)_2O$ in a silent electric discharge yields mainly a series of inseparable mixtures, but a fair yield of $Si_2H_5CH_3$ can be isolated.

A fascinating series of oxygen fluorides (O_2F_2, O_3F_2, O_4F_2, O_5F_2 and O_6F_2) has been prepared by subjecting mixtures of oxygen and fluorine to electric discharge at very low temperatures. All these compounds are very unstable, and, on warming, they decompose to oxygen and fluorine. Nitrogen trifluoride, AsF_5, and F_2 when subjected to a glow discharge at low temperatures yields NF_4AsF_6. This material is a relatively stable material which is fairly well characterized.

The only reported method for the preparation of a xenon compound that does not involve the use of elementary fluorine or some fluorinating agent almost as difficult to handle as fluorine, is the electric discharge synthesis of XeF_2 from Xe and CF_4. The carbon-containing by-products of the reaction were not identified.

Controlled Reactions of Atoms and Radicals with Other Species

In the discharge methods discussed above, all the reactant species are passed through an electric discharge. However many synthetically useful reactions can be carried out in the absence of a discharge by allowing a stream of atoms or radicals (prepared in an electric discharge) to impinge on various compounds. For example, atomic hydrogen is a very reactive species which has been used for the preparation of hydrides and for carrying out reductions. A promising field of study is the reaction of atomic hydrogen with aqueous solutions. In basic solutions, the hydrogen atoms yield electrons, and the method furnishes a convenient method for studying the reducing effects of the aqueous electron.

Atoms and radicals act as electrophilic reagents. The atoms O, Cl, Br, I, and N favor attack at polarizable donor atoms. Thus atomic nitrogen reacts with divalent sulfur compounds (H_2S, CS_2, OCS, S_8, S_2Cl_2 and SCl_2) to yield sulfur-nitrogen compounds, whereas no sulfur-nitrogen compounds are formed in the reaction of N atoms with SO_2, $SOCl_2$, and SO_3. The reaction with S_2Cl_2 gives fair yields of the interesting molecule NSCl.

Equipment

Most of the readily-available laboratory equipment for producing electric discharges is suitable only for relatively small-scale operation, involving only a gram or two of material. Such equipment, and the corresponding low yields, is satisfactory for the preparation of new compounds in amounts satisfactory for identification purposes. But in order for electric discharge syntheses to be useful for the preparation of mole quantities of materials, as are the usual synthetic methods, it will be necessary to have a marked break-through in the development and marketing of these instruments.