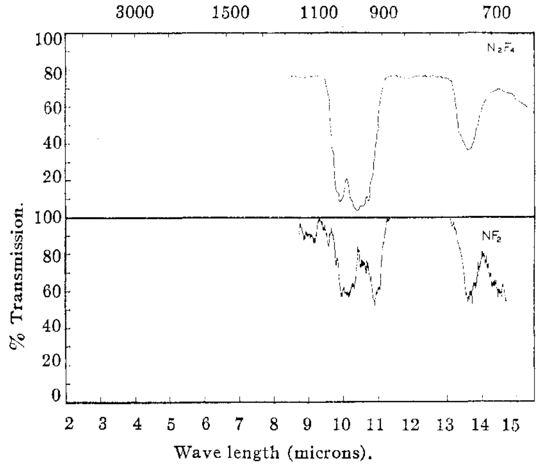

Fig. 1.—Infrared absorption of N_2F_4 and NF_2.

simply heating N_2F_4 in an infrared cell. By this technique the combined spectra of N_2F_4 and NF_2 are obtained.

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The Conversion of Silane to Higher Silanes in a Silent Electric Discharge[1a]

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It has been reported that when silane, SiH_4, is passed through a hot tube it is partly converted to disilane, Si_2H_6.[2] In a somewhat similar reaction it has been found that when SiH_4 is heated with certain hydrocarbons, small quantities of higher silanes are formed.[3] Irradiation of SiH_4 containing mercury vapor and hydrocarbons by a mercury lamp also gives small quantities of higher silanes.[3] When SiH_4 and water vapor were subjected to an electric discharge no higher silanes were obtained.[4] With SiH_4 alone the chief products were hydrogen, a solid silicon subhydride of composition $SiH_{1.2-1.7}$, and small quantities of higher silanes.[5]

Since the action of an electric discharge on both B_2H_6 and GeH_4 yields relatively large amounts of volatile boranes[6] and germanes,[7] respectively, it appeared that the analogous reaction involving SiH_4 warranted further study since it might serve as a useful method of preparation of higher silanes from SiH_4.

The present investigation shows that SiH_4 may be converted in an ozonizer type electric discharge to a mixture of higher volatile silanes (63% yield) in addition to solid silicon subhydrides and hydrogen. The mixture of higher volatile silanes contains Si_2H_6 (66%), Si_3H_8 (23%), and higher silanes (11%). The conversion was carried out in an easily constructed automatic recycling apparatus from readily obtainable equipment. The yields of higher silanes are so good that this method appears to be the most convenient and practical process for their production since the starting material, SiH_4, can be easily obtained in high yields from $SiCl_4$ and $LiAlH_4$.[8] The preparation of Si_2H_6 by the reduction of Si_2Cl_6 (which is not as readily available as $SiCl_4$) does not give high yields of the desired silane,[9] whereas the preparation of higher silanes from magnesium silicide and acid involves first the preparation of the silicide.[10]

Experimental

All work was carried out in a Pyrex glass vacuum system. Temperatures below 0° were measured by an iron-constantan thermocouple standardized by the National Bureau of Standards. Infrared spectra were run on a Perkin-Elmer Infracord spectrophotometer (Model 137B) employing a sodium chloride optical system. Measure-

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ments were made on the gaseous phase at 25° with the sample confined in a 10-cm. cell fitted with 4-mm. potassium bromide windows cemented with glyptal resin. SiH_4 was prepared by the reduction of $SiCl_4$ with $LiAlH_4$.[8]

In preliminary experiments it was observed that SiH_4 could be converted to higher silanes in reasonably good yields merely by touching a glass tube of the vacuum system through which SiH_4 was passing with the tip of a standard tesla coil, "leak detector."[11] The SiH_4 was allowed to vaporize from one trap and was condensed in an adjacent trap surrounded by liquid nitrogen, the tesla coil point being applied to the glass tubing an inch or two above the level of the liquid nitrogen. After several such passes the higher silanes were separated from SiH_4 by passage through a trap held at −134°. Although this method was satisfactory for the preparation of small quantities of Si_2H_6 and Si_3H_8 (~130 mg.; 33% yield), the following apparatus was used for the preparation of larger quantities of these and other higher silanes.

An automatic Toepler pump[12] of 250-ml. capacity was used to pump SiH_4 through an ozonizer and then through two traps immersed in baths held at approximately −134°. The higher silanes formed in the ozonizer were removed by the cold baths and the hydrogen formed in the reaction together with unchanged SiH_4 then was automatically recycled through the ozonizer. A 2-l. surge bulb was incorporated into the apparatus in order to minimize pressure fluctuations caused by the operation of the Toepler pump, which was adjusted to cycle 500 ml. of gas per min. The ozonizer was constructed from an all-glass Pyrex condenser (water jacket 250 mm. long; outer diameter of water jacket 19.0 mm.; outer diameter of inner tube 12.0 mm.; thickness of glass 1.0 mm.). The outer surface of the water jacket was wrapped with aluminum foil, and a cork was placed in the smaller end of the inner tube which then was filled with copper sulfate solution. A wire which dipped into this solution then was attached to one secondary terminal of a 7500-v. neon sign transformer,[13] and a wire from the other terminal of the secondary coil of the transformer was wrapped around the aluminum foil.

In a typical experiment 1.895 g. of SiH_4 (mol. wt.: found, 32.2; calcd., 32.12; purity confirmed by infrared spectrum[14]) was circulated through the apparatus for 5 hr. The pressure in the system at the start of the experiment was 143 mm. (minimum) on the downstroke of the Toepler pump and 156 mm. (maximum) on the upstroke. After removing hydrogen, recycling was continued for an additional 1 hr. Some yellowish-brown powder, assumed to be silicon subhydrides, had formed in and near the exit of the ozonizer.

The volatile products of the reaction were passed through a trap at −96° and then into a trap surrounded by liquid nitrogen. On holding the condensate in the latter trap at −134°, SiH_4 (0.669 g., mol. wt.: found, 32.6; calcd., 32.12; confirmed by infrared spectrum[14]) distilled off. The material remaining was almost pure Si_2H_6 (0.510 g., mol. wt.: found, 63.2; calcd., 62.23). Further distillation through a −96° trap gave a sample of pure Si_2H_6 (mol. wt.: found, 62.5, confirmed by infrared spectrum[15]; vapor pressure at −69.01°: found, 50.2 mm.; calcd.,[16] 50.71 mm.; calcd.,[17] 49.40 mm.).

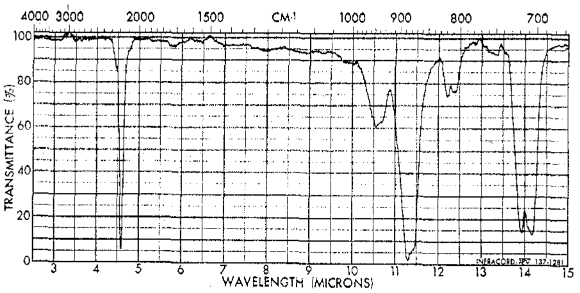

Figure 1.

After passing the condensate in the −96° trap through a −46° and then into a −196° trap the most volatile fraction was found to consist of almost pure Si_3H_8 (0.144 g., mol. wt.: found, 93.4; calcd., 92.33). A slightly less volatile material also was obtained which appeared to be an approximately equimolar mixture of Si_3H_8 and Si_4H_{10} (0.065 g., mol. wt.: found, 107.4; calcd. for Si_3H_8, 92.33; calcd. for Si_4H_{10}, 122.44). Further purification of the Si_3H_8 fraction gave a sample of mol. wt. 93.0 (vapor pressure at −23.72°: found 26.2 mm.; calcd.[18] 26.2 mm.). The infrared spectrum of pure Si_3H_8 (4.0 mm. pressure) is given in Fig. 1 and its absorption maxima are: 2180 $cm.^{-1}$, s (Si–H-stretch); 948 $cm.^{-1}$, m; 884 $cm.^{-1}$, vs; 819 $cm.^{-1}$, m; 808 $cm.^{-1}$, m; 747 $cm.^{-1}$, w; 717 $cm.^{-1}$, d.s.; 705 $cm.^{-1}$, d.s.

From the condensate in the −46° trap a little impure Si_4H_{10} (0.01 g., mol. wt.: found, 130; calcd., 126.4) was obtained in addition to 0.039 g. of higher silanes which exerted a vapor pressure of 3.2 mm. at room temperature. The vapor in equilibrium over this liquid had a molecular weight of 161 (calcd. for Si_5H_{12}, 152.55).

In an attempt to increase the yield of Si_3H_8 and higher silanes, the −134° traps in the recycling apparatus were replaced by −96° traps. As expected, the percentage of Si_3H_8 and Si_4H_{10} in the higher silane mixture increased but the over-all yield of higher silanes was reduced. The greatest weight of Si_3H_8 and higher silanes per experiment was obtained when the −134° traps were used.

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(12) Delmar Scientific Co., Maywood, Illinois.

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Nitrile Derivatives of Chromium Group Metal Carbonyls

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It has been reported that nitrile complexes of the group VIB metal carbonyls are prepared