empirical formula $CH_{4.5}B_2O_4$, which might well represent a mixture of, substantially, metaboric acid (HBO_2) and polymethylene $(CH_2)_n$. The X-ray diffraction pattern indicated a mixture of orthoboric acid and an additional phase which could not be identified, but the orthoboric acid must have been formed by inadvertent exposure of the X-ray sample to moisture; orthoboric acid is unstable under the conditions used in the vacuum distillation and would have been dehydrated to metaboric acid.[7]

(2) **Triethyl Orthoborate.**—At the end of the pyrolysis, the flask and dewar trap were cooled to −78° and all gases volatile at that temperature removed by pumping. The flask and trap were warmed to room temperature and the apparatus pumped again, any material volatile at room temperature being caught in a U-trap cooled to −78°. This trap then was sealed off and removed. It contained a few ml. of a colorless liquid and some white solid, presumably diboron trioxide. Several sections of the pyrolysis system also were coated with this white solid. The liquid was examined by infrared spectroscopy and found to contain ethanol, acetal, and a small amount ($\sim$10%) of ethyl borate. The pot residue consisted of a dark gummy solid, 99.4% of which was volatile in methanol and presumed to be metaboric acid.

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The Infrared Spectrum of NF_2

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The dissociation of tetrafluorohydrazine (N_2F_4) to difluoramino radicals (NF_2) has been demonstrated recently.[1,2] The results of our investigation of the infrared spectrum of the difluoramino free radical are given below.

When equilibrium mixtures of N_2F_4 and NF_2 are heated in a conventional infrared cell to increase the proportion of NF_2, profound changes in the infrared spectrum are observed. The 1010 cm.$^{-1}$ band of N_2F_4 is found to decrease drastically while smaller decreases are found at 960 and 740 cm.$^{-1}$. A large increase is found between 940 and 910, with smaller increases at 990–970 and 735–730 cm.$^{-1}$. It is not possible to distinguish the bands, however, because of severe overlapping by N_2F_4 bands at 1010, 960, and 735 cm.$^{-1}$.

To increase the resolution of the NF_2 spectrum, a compensating technique was used to cancel the N_2F_4 spectrum. A short cell (2-cm.) was filled to a high pressure of N_2F_4 and placed in the reference beam of a Perkin–Elmer Model 21 with a rock salt prism. A long cell (1 or 10-m.) was placed in the sample beam and a much lower pressure (where the relative concentration of NF_2 is large) admitted to just cancel the N_2F_4 peaks. In Fig. 1b, the long cell pressure was about 0.2 mm. at 25°. The short cell pressure was adjusted until the characteristic N_2F_4 maximum at 960 cm.$^{-1}$ was indistinct in the difference spectrum. The 10-m. cell then was heated to 110°; from equilibrium data[2] the N_2F_4 was 70% dissociated, hence there were about 5 NF_2 molecules per N_2F_4 in the long cell. In some instances N_2 or He was admitted to the long cell to reduce pressure broadening effects, but little difference was noted.

Under the above conditions the observed spectrum should be that due to NF_2 alone. Strong bands were found at 920, 980, and 730 cm.$^{-1}$ with a weak, rather broad peak at 1100 cm.$^{-1}$. These peaks were observed to increase with increasing temperature and decrease again on cooling.

The observed spectrum is similar to that of OF_2,[3] which has its three infrared active fundamentals at 929 (ν_1), 826 (ν_3), and 461 (ν_2). The ν_2 "scissors" of NF_2 appears to be surprisingly high in frequency, particularly in view of the values[4,5] of 666 and 650 cm.$^{-1}$ for ν_2 of CF_2. Limitations in cell optics prevented study below 650 cm.$^{-1}$. In view of the lack of detail in the absorptions observed insufficient data were available to calculate meaningful force constants.

Our results are in partial agreement with those of Schoen, Lide, and Mann,[6,7] who observed two regions of absorption at 1075 and 940 cm.$^{-1}$ by

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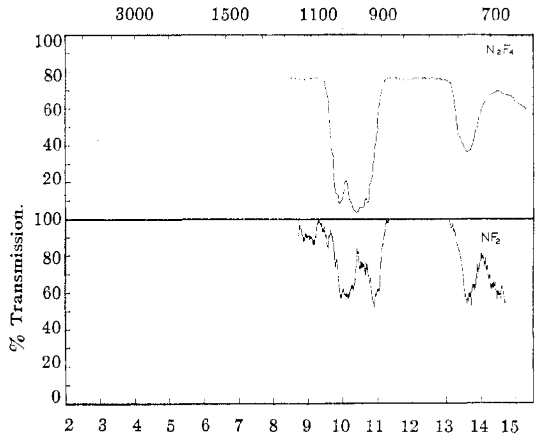

Fig. 1.—Infrared absorption of N_2F_4 and NF_2.

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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