no halogenated derivatives of tetraborane-10 have been well characterized. Since only relatively few derivatives of tetraborane-10 have been reported,[4,5] and since a halogen derivative was desired for other work in this laboratory, study of the reaction of bromine with tetraborane-10 was undertaken. Under controlled conditions at low temperatures, a 2-bromotetraborane-10 has been prepared and characterized.

Experimental

Preparation of B_4H_9Br.—Approximately 10 mmoles of bromine was introduced into a small glass flask using a hypodermic syringe to measure and transfer the liquid. The flask was chilled with liquid nitrogen, evacuated, and warmed, and the bromine was allowed to transfer by condensation into a 1-l. reaction flask. Tetraborane-10 from laboratory stock was purified by fractional condensation and an excess (approximately 30 mmoles) condensed into the flask on top of the solid bromine. The flask was sealed from the vacuum system, warmed slowly to near 0°, and then immersed in a salt–ice bath (about −15°) until the bromine color disappeared. From 12 to 18 hr. was generally required before the color had completely faded. The flask was reattached to the vacuum system, opened, evacuated, and subjected to a series of trap to trap fractional condensation steps. Hydrogen bromide and unreacted tetraborane-10 passed a −80° trap which retained the desired product. The entire −80° fraction was further fractionated through a special low-temperature column in which between 2 and 3 mmoles of 2-bromotetraborane was separated from boron tribromide and possible other impurities.[6]

Analysis.—Owing to the thermal instability of the compound an analysis of a weighed sample was not attempted. A suitable small sample of material was collected in a thin-walled ampoule placed at the exit of the fractionating column. The ampoule was sealed off and placed in a flask containing a similar ampoule of water. The flask was evacuated and sealed off, and both ampoules were broken by shaking. The hydrolysis was carried to completion by heating to 100° for 24 hr. Hydrogen was measured volumetrically, and both hydrogen bromide and boric acid were determined by titrating the strong acid produced, then adding *d*-mannitol and titrating the boric acid complex by the identical pH method. The ratio of boron to bromide to hydrogen was 4.01:1.00:10.01, in good agreement with the 4:1:10 required by the balanced equation for hydrolysis reaction.

To determine the molecular weight, a sample of the material was quickly vaporized in a calibrated U-tube, the pressure quickly measured, and the entire contents of the tube transferred to a weighing tube. The observed molecular weight, 135.2, agreed adequately with the theoretical 132.3.

Melting Point.—The melting point of 2-bromotetraborane was found to be −37.1 ± 0.5° in three determinations using the Stock plunger method.[2]

Vapor Pressures.—Freshly purified 2-bromotetraborane-10 was distilled directly from the fractionating column into a U-tube with attached manometer. Vapor pressures were measured at several temperatures with the U-tube cooled by suitable slush baths. The temperature of each bath was checked with a vapor pressure thermometer. The measured value at 25.5° was rendered somewhat uncertain by decomposition during the time necessary for measurement. The experimental points were used to determine the equation

$$\ln P_{\mathrm{mm}} = 18.31 - 8822/RT$$

by a least-squares fit. The calculated boiling point is 110°, and Trouton's constant has a normal value of 23 cal. mole^{-1} deg.$^{-1}$. Experimental vapor pressures (given as mm.) were: −36.2°, 0.65; −23.3°, 1.55; −19.0°, 2.20; 0.0°, 9.90; 25.5°, 32.

Nuclear Magnetic Resonance Spectra.—Both proton and ^{11}B spectra were observed with a Varian DP-60 spectrometer operating at 60 and 19.3 Mc./sec., respectively. Samples were maintained at about −20° in each case to avoid decomposition. As usual, the proton spectrum is complex and similar to that of tetraborane. In the absence of spin saturation studies, no further comments seem justified at the present time. The ^{11}B spectrum consists of a low-field doublet at δ +1.5 (relative to the diethyl etherate of boron trifluoride), J = 149 c.p.s.; a triplet at δ 10.0, J = 130 c.p.s.; and a high-field doublet at δ +34.7, J = 160 c.p.s., in relative intensities close to the 1:1:2 expected for a 2-substituted product. Both the triplet and the high-field doublet showed signs of further splitting of about 31 and 39 c.p.s., respectively, arising from the influence of bridge protons. This splitting was insufficient to resolve clearly the individual peaks but the coupling to the 1(3) borons clearly exceeded the coupling to the 2(4) borons. It is interesting to observe that the complex 1(3) resonance of tetraborane itself is reduced to a simpler structure in the substituted case. The cause of the complex splitting in tetraborane-10 itself is treated elsewhere and in any event is sufficiently complex so that no simple interpretation can be given of the reduction of fine structure in the substituted molecule.[7]

Discussion

The n.m.r. spectrum clearly establishes that this derivative is 2-substituted but it should be pointed out that in principle two isomers of 2-bromotetraborane-10 could exist. It seems likely that the more stable isomer will have the bromine in an equatorial (relative to the twofold axis of the unsubstituted molecule) position since considerable steric repulsion between the bromine and a 4 hydrogen might occur if the former were axial. On the other hand such stereochemistry might account for the rapid decomposition of the molecule. The argument is by no means clear and an X-ray study has been undertaken by others to clarify this point.

Acknowledgment.—Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

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(1) Studies of Boranes XV; for paper XIV of this series see R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y.

(4) C. A. Lutz, and D. M. Ritter, *Can. J. Chem.*, **41**, 1344 (1963).

(5) B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

(6) J. Dobson and R. Schaeffer, "Studies of Boron–Nitrogen Compounds. IX," to be published elsewhere.

(7) J. D. Baldeschweiler, *et al.*, to be published.

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Role of Water in the Reaction of Fluorine with Trifluoroacetic Acid to Produce Trifluoroacetyl Hypofluorite

BY GARY L. GARD AND GEORGE H. CADY

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Ever since it was found that water[1] increased the yield of trifluoroacetyl hypofluorite by the reaction of

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(1) G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953).

fluorine with trifluoroacetic acid, questions regarding its role in the process have remained unanswered. This paper[1] states: "Usually the product could be obtained without adding water. However, in the case of the last cylinder of fluorine used in the study, almost none of the explosive substance (CF_3COOF) was formed unless water vapor was added." The purpose of the present work was: (1) to determine whether water is actually needed, (2) to obtain some measure of its effect, and (3) to explain its role.

Experimental

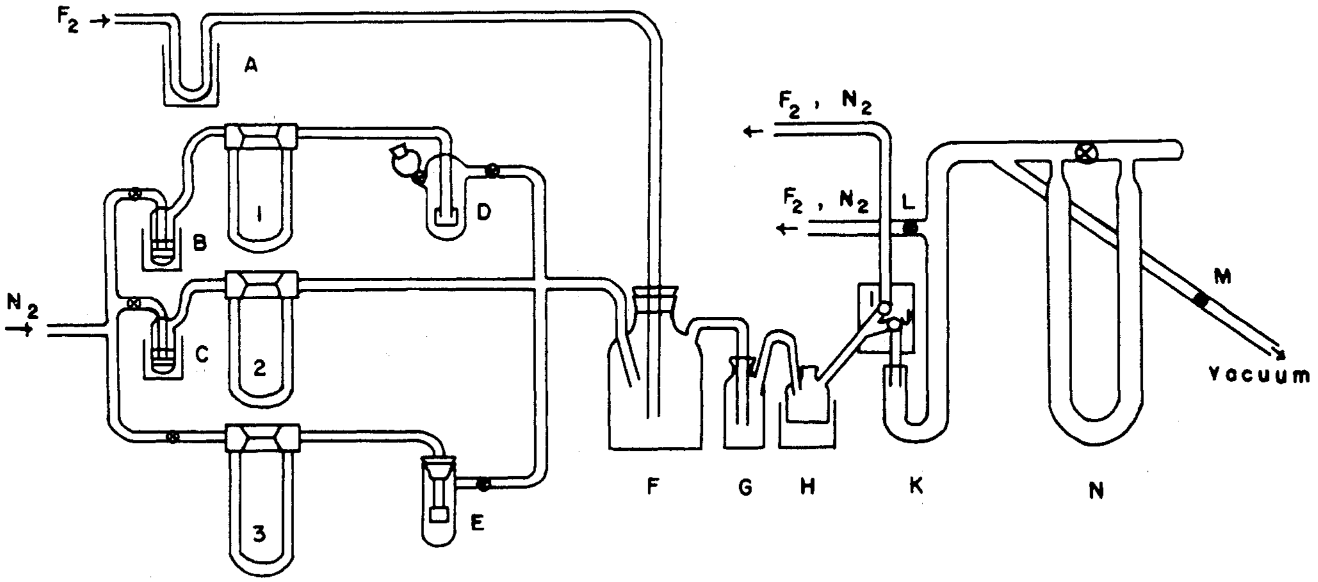

Figure 1.

Figure 1 shows the equipment used for this study. The inlets and outlets for fluorine and nitrogen are shown on the drawing. Water-pumped nitrogen was dried by passing it through traps B and C which were packed with glass wool and cooled to −183°. Fluorine was passed through Monel metal trap A (0.5-in. Monel tubing bent into a U shape) cooled also to −183° and entered the reactor, F, near the bottom. Bubblers D and E contained trifluoroacetic acid and water, respectively, held at constant temperature near 19°. The polyethylene reaction vessels, F (1026 ml.) and G (505 ml.), were maintained at 24.0 ± 1.2°. Trap H (275 ml.) was maintained at −30.0 ± 5° to condense HF and CF_3COOH but to allow CF_3COOF (b.p. −25°) to pass. Flow meters 1, 2, and 3 were used to measured the flow of streams of nitrogen gas, and the total flow rate for nitrogen was not less than 16.9 l./hr. nor more than 18.7 l./hr. Fluorine entered the system at a rate of 1.1 l./hr. (at room temperature) or 0.045 mole/hr. The residence time of gases in the reactors was about 5.2 min. In all of the experiments, the flow rate for trifluoroacetic acid was close to 0.026 mole/hr. Various flow rates of water vapor were used.

When making a run, constant flow rates and temperatures were maintained for a sufficient period, usually about 0.25 hr. after each change in flow rates, to permit a steady state to be reached. During this time, the gas stream passed from the system through valve I. After reaching a steady state, valve I was closed and metal valve J and glass stopcock L were opened to allow the gas stream to pass through trap K (cooled to −183°), where CF_3COOF condensed. After a collection time of 1 min., valves J and L were closed and I was opened. The materials in trap K, which were volatile at −183°, were then pumped away through stopcock M. After closing M, trap K was quickly warmed to room temperature and pressure was measured using manometer N, in which the mercury was protected by Kel-F oil. A Tesla coil leak tester was then held near the tube, and the spark caused the CF_3COOF to decompose into CF_4 and CO_2. The pressure was again measured and the increase in pressure was taken to be equal to the pressure of CF_3COOF. In a typical case the pressure changed from 43.7 to 58.4 mm., indicating 14.7 mm. of CF_3COOF. The part of the system involving trap K was then flushed in preparation for the next sample. Since three measured streams of nitrogen entered the reactor, it was possible to maintain a constant total flow of nitrogen and to vary the concentration of entrained water vapor.

In one run when no water was added, fluorine and dry nitrogen were allowed to sweep through the system for 2 hr. before starting the flow of trifluoroacetic acid vapor. After adding the acid and allowing the system to reach a steady state, a sample was taken. No explosive product was found, and only about 0.27 ml. (at STP) of nonexplosive gas was collected.

In another run without water, the results were similar but the volume of nonexplosive gas was 1.2 ml. Such experiments show that not more than a trace of trifluoroacetyl hypofluorite, CF_3COOF, was produced. Since the 1.2-ml. volume was only about one-fourth of the average volume, 4.1 ml., of gaseous products obtained when water was used at a rate of 0.0085 mole/hr. or more, it follows that only a small fraction of the trifluoroacetic acid reacted with fluorine in the absence of water.

The product from all runs contained nonexplosive substances. While these were not identified for each run, the nonexplosive compounds collected in trap K probably were largely CF_4 and CO_2, known products of the decomposition of trifluoroacetyl hypofluorite. As the amount of water in the reacting mixture was increased, the yield of these nonexplosive products increased and reached a substantially constant maximum value of about 0.007 mole/hr. If this material were composed of equal volumes of CF_4 and CO_2 it could mean that about half of the trifluoroacetyl hypofluorite had decomposed in the reactors before the stream of gas reached trap K.

After developing a satisfactory operating procedure, several series of runs were made using various flow rates for water vapor. The results are shown with sufficient accuracy in Figure 2. It is obvious from this figure that the production of trifluoroacetyl hypofluorite was greatly favored by adding water to the reacting mixture. It also appears that the addition of water beyond a certain limit was of little or no increased value. This limit, about 0.0085 mole/hr. in these experiments, corresponded to relative molar flow rates of fluorine to acid to water of about 5:3:1. (It was not learned whether the yield of the hypofluorite might be increased above about 15% by increasing the concentration of fluorine or lengthening the time of residence in the reactor.)

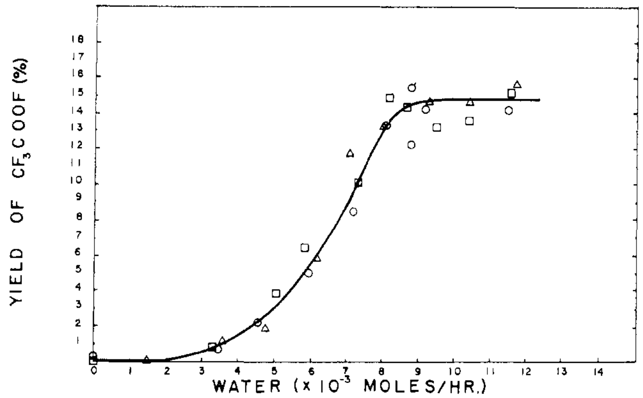

Figure 2.

Discussion

Although the experiments just described clearly indicate that the formation of trifluoroacetyl hypofluorite and of nonexplosive products such as CF_4 and CO_2 is greatly accelerated by water vapor, the exact role of water is still unclear. It may reasonably be assumed that water reacts either with the acid or with fluorine to give an intermediate which then gives the hypofluorite. Such an intermediate may be a gaseous hydrate of the acid or it may be a substance formed by the reaction of fluorine with water. The known products from fluorine and water are hydrogen fluoride, oxygen, and oxygen difluoride. None of these appears to be an intermediate responsible for producing CF_3-COOF. A mixture of oxygen difluoride with trifluoroacetic acid vapor was found to stand at room temperature essentially without reacting. Menefee and Cady[2] have shown that hydrogen fluoride vapor does not accelerate the formation of pentafluoropropionyl hypofluorite from fluorine and pentafluoropropionic acid as does water. Oxygen lacks the presence of fluorine needed to form trifluoroacetyl hypofluorite from trifluoroacetic acid. This state of affairs leaves the authors guessing that an active intermediate is involved in the reaction and that it may be a hydrate of trifluoroacetic acid, atomic fluorine, ·OF radical, HOF molecule, or some other unknown species. It is not clear why increasing the ratio of molecules of water to acid above 1:3 failed to increase the yield of trifluoroacetyl hypofluorite.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research with funding by ARPA.

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[2] A. Menefee, Thesis, University of Washington, 1953, p. 6.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF
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The Synthesis of Disilanylphosphine and Disilylphosphine in a Silent Electric Discharge

BY SUDARSHAN D. GOKHALE AND WILLIAM L. JOLLY

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We previously observed that the two isomers of Si_2PH_7 (disilanylphosphine, $Si_2H_5PH_2$, and disilylphosphine, $(SiH_3)_2PH$) were formed when a mixture of silane and phosphine was passed through an ozonizer-type silent electric discharge tube.[1] These compounds have such similar volatilities that we were unable to separate them by ordinary vacuum-line techniques. Disilanylphosphine was isolated by gas chromatography, but disilylphosphine decomposed on the chromatographic column. In this note, we report silent-electric-discharge methods for preparing both disilylphosphine and disilanylphosphine, each free from the other. Disilylphosphine was prepared from a mixture of silane and silylphosphine, and disilanylphosphine was prepared from a mixture of disilane and phosphine. The methods are based on the fact that, when a stream of molecules passes rapidly through a silent electric discharge, the molecules generally do not undergo drastic fragmentation and rearrangement. Because the molecular fragments more or less retain their original configurations, it is possible to predict the structures of new molecules that are formed by the combination of the molecular fragments. Thus by a suitable choice of starting materials, it is possible to tailor-make molecules.

Experimental

Reagents.—Disilane was prepared from silane by a previously described silent-electric-discharge process.[2] Silylphosphine was prepared by circulating a 1:1 mixture of silane and phosphine through an ozonizer tube at −78° and a product-collecting trap at −112°.[3] The crude product was distilled into a series of traps at −95, −130, and −196°. A mixture of silylphosphine and disilane collected in the −130° trap; the disilane was preferentially vaporized from the trap by pumping into a −196° trap as the trap gradually warmed up. The latter fractions, whose infrared spectra showed them to consist of pure silylphosphine, were saved, and the earlier fractions were subjected to a second fractionation. Traces of trisilane in the silylphosphine were removed by passage through a −112° trap. By this procedure, about one-third of the silylphosphine in the original product mixture was isolated with a purity estimated at greater than 99%.

Electric Discharge Reactions.[3]—The discharge tube was kept at 0° and the product-collecting trap at −45°. The volume of the discharge system was 1.5 l. At the end of each run, the contents of the discharge apparatus was fractionally condensed in traps at −95 and −196°. The material which collected in

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[1] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).

[2] E. J. Spanier and A. G. MacDiarmid, *ibid.*, **2**, 215 (1963).

[3] For a discussion of the ozonizer-type discharge, see J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962), and W. L. Jolly, Chapter 5 in "Technique of Inorganic Chemistry," Vol. 1, H. B. Jonassen and A. Weissberger, Ed., 1963, p. 179.