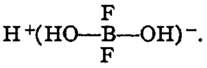
Proof of Structure of Dihydroxyfluoboric Acid.—The analyses and molecular weight determinations indicated a compound having a molecular formula H_3BF_2O. The presence of one strongly acidic hydrogen atom was indicated by the fact that dihydroxyfluoboric acid reacted in molar proportions with sodium chloride forming hydrogen chloride. The resulting sodium salt lost water, which indicates the attachment of two hydroxyls to the same atom. The presence of the two hydroxyl groups was shown by the fact that one mole of dihydroxyfluoboric acid reacted with two moles of acetyl chloride to form hydrogen chloride, acetic acid–boron fluoride ($CH_3COOH_2\cdot BF_3$), acetic acid and a solid compound identical with that obtained from acetic anhydride. This derivative crystallized from hot acetyl chloride in the form of long needles having a melting point of 202–203°, and contained boron and fluorine in the ratio of approximately one to one. It formed a white solid compound on treatment with mercuric oxide, which was insoluble in acetyl chloride. Further work is being done at present in order to establish the structure of this acetoxy derivative. The acid characteristics of dihydroxyfluoboric acid are further indicated by its reactivity toward alkali hydroxides and carbonates and by its catalytic effect on esterification reactions.

On the basis of this information we may write the following tentative structure for dihydroxyfluoboric acid:



$$H^+(HO\text{—}\overset{F}{\underset{F}{B}}\text{—}OH)^-.$$

Summary

1. A new liquid, anhydrous, inorganic acid of the hydroxyfluoboric type has been prepared.

2. Several methods of preparation have been given.

3. A structure has been assigned it tentatively.

4. Some of its properties and acidic reactions have been studied.

5. Some of its possibilities as a catalytic agent have been mentioned.

6. Pure metaboric acid has been prepared and its melting point has been determined.

Notre Dame, Indiana Received January 10, 1935

[Contribution from the Metcalf Chemical Laboratory of Brown University]

Photochemical Studies. XXI. The Absorption Spectrum of Germane

By H. E. Mahncke and W. Albert Noyes, Jr.

The decomposition of germane sensitized by mercury vapor has been investigated.[1] At the same time it was observed that germane could be decomposed photochemically in the absence of mercury vapor by the action of radiation from a hydrogen discharge tube which had traversed thin layers of quartz. The final products in both cases were metallic germanium and hydrogen. No absorption due to germane was found with the aid of a quartz spectrograph (2100–7000 Å.).

In the present investigation the absorption spectrum of germane has been photographed in the fluorite region and estimates made of the absorption coefficients at several wave lengths. An attempt has been made to determine the nature of the primary step in the direct photochemical decomposition of germane.

I. Experimental

The preparation and purification of the germane have been described.[1,2,3] Due to the fact that metallic germanium is deposited during photochemical decomposition of the germane, it was not deemed advisable to use this substance in the vacuum grating spectrograph. The present study was made, therefore, with a small fluorite spectrograph of the type described by Cario and Schmidt-Ott.[4] It was modified slightly so that four exposures could be taken on one plate without breaking the vacuum. The spectrograph was evacuated by a butyl phthalate diffusion pump.

A water-cooled hydrogen discharge tube of the type described by Bay and Steiner[5] was used as a light source. It was operated on two kilowatts without a condenser in the secondary circuit.

The absorption cell was of Pyrex, 6.3 mm. in length, one end of which was waxed directly to the window of the discharge tube, while the other was similarly fastened to the window of the spectrograph.

Eastman Ultraviolet Sensitive plates were used.

Qualitative estimates of absorption coefficients were made by the method of varying times of exposure.[6] The results are admittedly very inaccurate, but serve to give the order of magnitude.

II. Results

With fluorite windows on the cell the photochemical decomposition proceeded very rapidly and the windows of the absorption cell became opaque due to the deposited germanium. With

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[1] Romeyn and Noyes, This Journal, **54**, 4143 (1932).

[2] Kraus and Carney, *ibid.*, **56**, 765 (1934).

[3] Teal, Ph.D. Thesis, Brown University, 1930. The germane used in these experiments was prepared by Dr. Teal.

[4] Cario and Schmidt-Ott, *Z. Physik*, **69**, 719 (1931).

[5] Bay and Steiner, *ibid.*, **45**, 337 (1927).

[6] Weigert, "Optische Methoden der Chemie," Akademische Verlagsgesellschaft, Leipzig, 1927, p. 223.

quartz windows 1.5 mm. in thickness exposures down to 1550 Å. could be obtained without undue decomposition.

No bands were observed, the absorption being apparently continuous at all pressures. Table I gives the last line of the Lyman bands obtained at a series of pressures, the absorption being practically complete for all wave lengths below these limits.

TABLE I

APPROXIMATE LIMITS OF ABSORPTION

Pressure, mm.	0.87	2.48	5.00	10.00
Wave length, Å.	1577	1596	1623	1667

Table II gives estimates of the absorption coefficient k in the formula $I = I_0 e^{-kpd}$ where p is expressed in millimeters of mercury and d is in centimeters.

TABLE II

APPROXIMATE ABSORPTION COEFFICIENTS

Abs. coeff.	0.16	0.094	0.068	0.03
Wave length	1623	1639	1642	1657

III. Discussion

The continuous absorption observed indicates that the upper electron states of germane, at least as far as the region investigated is concerned, are repulsive. In this respect germane is analogous to methane, which shows only continuous absorption down to 850 Å.[7] The same seems to be true of all pentatomic tetrahedral molecules so far investigated.

Since the heat of sublimation of metallic germanium is unknown, there is no way of calculating the average heat of formation of the germanium–hydrogen bonds in germane. By very rough comparison with other hydrides it might be expected to be about 2 electron volts. That the value is probably low is further borne out by the relatively low thermal stability of GeH_4. The germanium atom in this compound has a completed group of electrons, $(4s)^2 (4p)^6$. It is impossible to change the quantization of one of these electrons without change of principal quantum number. All of the resulting states thus produced would be expected to be repulsive.

Two possible primary processes may be visualized.

$$GeH_4 + h\nu = GeH_3 + H \qquad (1)$$
$$GeH_4 + h\nu = GeH_2 + H_2 \qquad (2)$$

If the process is represented by equation (1) and the heat of dissociation is very much less than the approximate value of 7 electron volts obtained from the absorption spectrum, either the products must possess high kinetic energy, or one of them (necessarily the GeH_3) will be in an excited state, or both. Since the promotion of one of the electrons will be necessary for the formation of an excited state, one would expect a fairly high excitation energy for the GeH_3 group. Dissociation by equation (1) would seem to be most probable, although since the heat of dissociation of hydrogen is probably more than twice as large as the heat of dissociation of the germanium–hydrogen bond, equation (2) may not be ignored.

Some effort was made to determine which of the two possible mechanisms was correct. The ortho–para hydrogen conversion was used first in an effort to detect the presence of hydrogen atoms. The results were inconclusive for a number of reasons. However, it is possible that the heat of activation of the reaction $H + H_2(o) = H_2(p) + H$[8] is considerably higher than for the reaction $H + GeH_4 = H_2 + GeH_3$ so that hydrogen atoms would have such a transitory existence as to be unable to cause much conversion. A few experiments were carried out, therefore, with the object of finding out whether hydrogen atoms would cause decomposition of germane. The primary process in ammonia decomposition is probably $NH_3 + h\nu = NH_2 + H$.[9] The low quantum yield for this decomposition is probably due, at least in part, to a recombination of NH_2 and H.[10] When the hydrogen atoms are removed by other molecules the quantum yield for ammonia decomposition is increased.[11] When ammonia mixed with germane is exposed to radiation absorbed only by the ammonia, the rate of formation of gas uncondensed by liquid air is more rapid than when ammonia at the same pressure is exposed alone. Table III presents typical data.

When the ratio GeH_4/NH_3 was 0.32, the ratio of the pressure change to that in pure ammonia was 3.7, while when $GeH_4/NH_3 = 1.61$, the ratio of pressure changes was 3.2. It seems obvious that some of the intermediates of the ammonia decomposition (probably NH_2 or H or both) cause germane to decompose. This is further proved by the fact that deposits of metallic germanium could

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[7] See Duncan and Howe, *J. Chem. Physics*, **2**, 851 (1934).

[8] A. Farkas, *Z. physik. Chem.*, **10B**, 419 (1930); Geib and Harteck, *ibid.*, Bodenstein Festband, 849 (1931); L. Farkas and Harteck, *ibid.*, **25B**, 257 (1934).

[9] See Dixon, *Phys. Rev.*, **43**, 711 (1933).

[10] *Cf.* Evans and Taylor, *J. Chem. Physics*, **2**, 732 (1934); Jungers and Taylor, *ibid.*, **2**, 373 (1934).

[11] Bacon and Duncan, THIS JOURNAL, **56**, 336 (1934).

TABLE III

PHOTOCHEMICAL DECOMPOSITION OF AMMONIA AND GERMANE

Run	Initial NH_3, mm.	Pressure of GeH_4, mm.	dp/dt uncondensed by liquid air av. 3 hours mm./hr. × 10^4	Source
1	1.1	0	5.7	H_2 discharge through 1.5 cm. air. Windows waxed on
2	0	1.5	0	
3	1.2	0.38	19.0	
4	0.94	0	3.0	Same except all quartz cell
5	0	1.4	0	
6	0	1.1	0	
7	0.98	1.58	10.3	
8	1.02	1.98	38	Zn spark through 7 cm. air
9	1.02	1.98	665	Zn spark through 3 cm. air
10	0	2.16	56	
11	0	1.72	0	Same through 6.5 cm. water
12	0.98	1.78	10	
13	.94	0.84	1	No light

be observed when the ammonia–germane mixtures were exposed to radiation which did not cause the germane alone to decompose. The variations in germane pressure did not affect appreciably the rate of gas evolution. While the proof is not conclusive, these facts indicate that hydrogen atoms may not be able to have a long independent existence in the presence of GeH_4. This is also in agreement with the previous finding[1] that hydrogen does not inhibit the sensitized decomposition of germane as much as would be expected from its effect in quenching the fluorescence of mercury vapor.

Other attempts were made to detect the presence of hydrogen atoms. Molybdenum trioxide is known to be reduced to a blue oxide by the action of hydrogen atoms. Illumination of germane in the presence of a thin film of molybdenum trioxide gave no conclusive evidence of a blue color, even though the metallic germanium was clearly visible. When the germane was decomposed by a spark, no reduction seemed to take place until the germane had largely decomposed. This may be taken as further evidence for the relatively short existence of hydrogen atoms in germane.

While the primary step represented by equation (1) seems more reasonable than that shown by (2), we have been unable to prove definitely which mechanism is correct. It has been shown, however, that hydrogen atoms if formed would be difficult to detect. In the photochemical decomposition of germane reaction (1) would be followed, therefore, by

$$GeH_4 + H = GeH_3 + H_2 \qquad (3)$$

The weakness of the germanium–hydrogen bond compared to that of the hydrogen–hydrogen bond would probably lead to the decomposition of GeH_3 into Ge and 3/2 H_2 either in the gas phase or on the walls.

The mechanism suggested for the photochemical decomposition of germane involves short chains. That the chains are not long is indicated by the relative rates of gas evolution in ammonia alone and in ammonia mixed with germane and the fact that the rate of pressure increase does not depend markedly on the germane pressure.

Summary

1. Germane shows no banded absorption at wave lengths longer than 1550 Å. It does show continuous absorption extending from about 1700 Å. to shorter wave lengths.

2. Attempts were made to determine the nature of the primary step in photochemical decomposition of germane. Experiments show that failure in these attempts may be due to the fact that hydrogen atoms react readily with germane and would not have a long independent existence.

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