accounted for by assuming the presence of moisture in the gases in contact with the beryllium oxide (flame gases, etc.).

3. The volatilization rate increases with increasing temperature.

4. The volatilization does not occur in the cases of beryl or magnesia.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 1, 1948

[CONTRIBUTION FROM THE GENERAL ELECTRIC CO. RESEARCH LABORATORY]

The Distillation of Mixtures Containing Diborane and the Identification of Two Azeotropes

BY LEWIS V. MCCARTY[1]

Depending upon the method of manufacture diborane may be contaminated with hydrogen halides, boron halides and ethane. Thus in Schlesinger's[2] and Stock's[3] methods of preparation hydrogen chloride and boron trichloride, and hydrogen bromide and boron tribromide are possible contaminants. In Schlesinger's later preparation[4] ethane might also contaminate the diborane. In other reactions described by Hurd[5] boron trifluoride as well as boron trichloride and hydrogen chloride may be impurities. A knowledge of the various possible mixtures of diborane with these materials becomes important both for the purification of diborane and the analytical distillation of the products of the reactions.

Experimental

Apparatus.—The apparatus used to perform the distillations was the Automatic Recording Low Temperature Fractional Distillation Apparatus, Hyd Robot Model, Serial No. H 576, manufactured by the Podbielniak Centrifugal Super Contactor Company. The entering stopcock of the "Super Cool" column was attached to a vacuum line that was equipped with bulbs of known volume. This part of the system was not thermostated, and all measurements of the gases entered into the column were made at room temperature. All values reported in the tables, however, have been reduced to 0° and 760 mm. Samples were mixed in the column by entering each gas separately. No van der Waals corrections were applied to any of the gases. The time under total reflux was ordinarily about thirty minutes to one hour long.

Chemical Analysis.—In Expt. 1 of Table I a chemical analysis was made for hydrogen chloride. This was accomplished by freezing a known volume of the gases into a sample bulb and then expanding through two bubblers of distilled water. A slow stream of dry nitrogen was used to prevent water from sucking back into the sampling bulb. The water was analyzed for hydrogen chloride by titration with a sodium hydroxide solution to a methyl orange end-point.

Materials.—The hydrogen chloride and diborane used in Expt. I, Table I, were distilled and only the middle cuts were saved. All boron trichloride was distilled prior to use. The diborane, ethane and boron trifluoride of Tables III and IV were distilled before use. All other hydrogen chloride and diborane as well as the hydrogen bromide came from tanks in which the impurities were known to be mainly gases not condensable in liquid nitrogen. Accordingly, the purification procedure for these samples was to freeze some gas into a bulb in liquid nitrogen, and then pump on the bulb.

Results

The System Hydrogen Chloride–Diborane.—A few preliminary runs (not reported here) with rather impure materials served to indicate that an azeotrope was formed having the approximate composition 26–30% hydrogen chloride and 70–74% diborane. This material boiled at about −94° at 760 mm., 1.5° lower than the value for diborane, −92.5°.

In order to get an accurate value for the composition of the azeotrope at 760 mm., samples of distilled hydrogen chloride and diborane were used in Expt. 1 of Table I. It will be noticed that in this experiment the difference between the total volume of gas used and that found is only 2 cc. in 4,934. This is fortuitous as will be found by an inspection of other data in this and subsequent tables. Sometimes less and sometimes more gas was found than was originally used. This is attributed to solution and possibly reaction in some cases with the stopcock grease of the Podbielniak apparatus. Apiezon L was the lubricant used. In making calculations on azeotrope composition, it is convenient to have the total volumes found agree with the total volumes used. If there is a discrepancy, it is assumed to be due to the causes mentioned, and the volumes found are pro-rated with an appropriate factor to bring them into agreement with the volumes used. It is then a simple matter to make the azeotrope composition calculations. The value for the azeotrope at 755 mm. was found to be 29.9% hydrogen chloride on a molar basis. When 1984 cc. of the azeotrope at S.T.P. was analyzed for hydrogen chloride in water solution,[6] 0.957 g. of hydrogen chloride was found. This corresponds to 29.6 mole per cent. in the azeotrope.

Experiments 2, 3 and 4 of Table I are determinations of the azeotrope composition at a lower pressure (205–208 mm.). The average of the three determinations of the composition is 26.2% hydrogen chloride and 73.8% diborane. The boiling point of the azeotrope at 207 mm. is about −114.5°, whereas for pure diborane at 207 mm. the boiling point is −113°.

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[1] This work was done on Army Ordnance Contract TU1-2000.

[2] Schlesinger and Burg, THIS JOURNAL, 53, 4321 (1931).

[3] Stock and Sütterlein, *Ber.*, 67B, 407 (1934).

[4] Finholt, Bond and Schlesinger, THIS JOURNAL, 69, 1199 (1947).

[5] Hurd, *ibid.*, 71, 20 (1949).

[6] Analysis courtesy of L. B. Bronk.

TABLE I

THE SYSTEM HCl–B_2H_6

Expt.	HCl used, cc.	B_2H_6 used, cc.	Azeotrope found. cc.	B. p. of azeotrope. °C.	HCl found, cc.	B. p. of HCl, °C.	Dist. pres., mm.	% in azeotrope HCl	B_2H_6
1[b]	2470	2464	3513	− 94	1419	− 85	755	29.9[a]	70.1
2[c]	939	1142	1523	−115.5	512	−106	205	26.7	73.3
3[b]	1106	1242	1646	−114.5	674	−105.5	207	25.5	74.5
4[b]	1004	1244	1666	−114.5	554	−105.5	208	26.3	73.7

[a] 1984 cc. of azeotrope analyzed for hydrochloric acid by solution in water and titration, 29.6% of hydrochloric acid on a molar basis. [b] HCl entered into column first. [c] B_2H_6 entered into column first.

The System Boron Trichloride–Diborane.—Data for the single experiments on this system are: cc. B_2H_6 used, 1262; cc. B_2H_6 found, 1280 b. p. −93.5°, 750 mm.; cc. BCl_3 used, 1173; cc. BCl_3 found, 1183, b. p. +11.5°, 750 mm. The data on the gas found as compared to that put into the distillation column checks sufficiently closely so that an azeotrope probably does not exist.

The System Hydrogen Chloride–Boron Chloride.—Although this system does not include diborane, it was considered important because of the ternary system which follows: cc. HCl used, 1274; cc. HCl found, 1271, b. p. −85.5° 754 mm.; cc. BCl_3 used, 934; cc. BCl_3 found, 945, b. p. +11.5°, 754 mm. Somewhat more BCl_3 was found than used to make up the sample, but the amount is within the experimental error.

The System Hydrogen Chloride–Diborane–Boron Trichloride.—The data for this ternary system are: cc. BCl_3 used, 1208; cc. BCl_3 found, 1228, b.p. +12.5°, 752 mm.; cc. B_2H_6 used, 1249; cc.* azeotrope found, 1782, b.p. −95.5°, 752 mm.; cc. HCl used, 1246; cc. HCl found, 713, b.p. −85.5°, 752 mm. (*Composition from these data, 29.9% HCl, 70.1% B_2H_6.) There was slightly more boron trichloride found than used, but again this is most likely to be experimental error. It does not apparently form a ternary azeotrope with the other components, nor does it influence the composition of the hydrogen chloride–diborane azeotrope.

TABLE II

THE SYSTEM B_2H_6–HBr

Expt.	HBr used, cc.	B_2H_6 used, cc.	HBr found, cc.	B. p. of HBr, °C.	B_2H_6 found, cc.	B. p. of B_2H_6, °C.	Dist press. mm.
1	1194	932	1188	−84	941	−108	298
2	1058	1040	1062	−83.5	1012	−108	309
3	1199	528	1219	−67.5	496	− 93.5	753
4	2315	2060	2280	−67.5	2013	− 94	756

TABLE III

THE SYSTEM B_2H_6–C_2H_6

Expt.	B_2H_6 used, cc.	B_2H_6 found, cc.	C_2H_6 use cc.	C_2H_6 found, cc.	B. p. of B_2H_6, °C.	B. p. of C_2H_6, °C.	Dist. press.. mm.
1[a]	1121	1179	975	902	− 92	− 88	753
2[b]	772	776	130	135	− 92	− 88	753
3[a]	1287	1270	133	147	− 92	− 88	753
4[a]	1260	1258	131	121	−121	−118	102
5[b]	618	590	127	116	−120.5	−117.5	99
6[b]	740	744	132	114	−121.5	118.5	100

[a] C_2H_6 entered into column first. [b] B_2H_6 entered into column first.

The System Hydrogen Bromide–Diborane.—The conclusion drawn from the data presented in Table II is that no azeotrope exists at the pressures studied. The system is somewhat difficult to study because of the relatively high melting point of the hydrogen bromide, −86°.

The System Diborane–Ethane.—Table III presents the data for the distillation of known samples of diborane–ethane. Experiment 1 does not show very good agreement between the amount of materials used and found in the analysis. This was blamed on insufficient reflux time rather than on the formation of an azeotrope. Accordingly, two hours of reflux time was allowed before taking off any gas from the top of the distillation column in all other experiments. There does not seem to be any general trend dependent upon which liquid, ethane or diborane, wets the packing of the column first. There does not seem to be any trend dependent upon the size of the sample or the ratio of diborane to ethane. The conclusion drawn is that there is no azeotrope in the system.

The System Diborane–Boron Trifluoride.—For the experiments of Table IV a total reflux time of two hours was allowed before any gas was taken off the top of the distillation column. As can be seen from the data the composition of the azeotrope formed is reasonably constant regardless of which material is in excess or entered into the column first. The average of the three

TABLE IV

THE SYSTEM B_2H_6–BF_3

Expt.	B_2H_6 used, cc.	BF_3 used, cc.	Azeotrope found, cc.	B_2H_6 found, cc.	BF_3 found, cc.	B. p. of azeotrope, °C.	B. p., °C. of B_2H_6	BF_3	Dist. press., mm.	% in azeotrope B_2H_6	BF_3
1[a]	1295	1279	2193	357	..	−105.5	−92	...	755	42.2	57.8
2[b]	1261	1092	1841	500	..	−106	−92.5	...	745	41.0	59.0
3[a]	1036	2573	2476	...	1108	−106	....	−100	760	41.6	58.4

[a] B_2H_6 entered into column first. [b] BF_3 entered into column first.

values determined is 41.6% diborane and 58.4% boron trifluoride, and the boiling point at atmospheric pressure is about −106°.

Summary

The systems $HCl-B_2H_6$, $B_2H_6-BCl_3$, $HCl-BCl_3$, $HCl-B_2H_6-BCl_3$, $HBr-B_2H_6$, $B_2H_6-C_2H_6-C_2H_6$ and $B_2H_6-BF_3$ have been studied.

An azeotrope containing 70.1% B_2H_6 and 29.9% HCl and boiling at −94° at atmospheric pressure has been identified. The presence of BCl_3 does not affect the $HCl-B_2H_6$ azeotrope.

An azeotrope containing 41.6% B_2H_6 and 58.4% BF_3 and boiling at −106° at atmospheric pressure has been identified.

None of the other systems studied show azeotrope formation.

SCHENECTADY, N. Y. RECEIVED NOVEMBER 18, 1948

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA 18, PENNSYLVANIA]

Ultraviolet Absorption Spectra of Nicotine, Nornicotine and Some of Their Derivatives

BY MARGARET L. SWAIN, ABNER EISNER, C. F. WOODWARD AND B. A. BRICE

Nicotine and its analog, nornicotine, and the myosmines and nicotyrines derived from them as dehydrogenation products, represent interesting examples of series of compounds possessing progressively increasing conjugated unsaturation of the cyclic type. Characteristic and similar ultraviolet absorption spectra for the two parent compounds and for the pairs of analogs obtained at each successive dehydrogenation step may therefore be expected. Such spectra determined on preparations of high purity should be useful as a means of further characterizing the compounds, provide a test of the correctness of assigned structures, and furnish a possible method of assay and analysis. Although the increasing practical importance of nicotine has prompted an intensive study of the chemistry of the alkaloid and its derivatives during recent years, no spectroscopic studies using modern photoelectric instruments have been reported. The only available absorption curves are those for nicotine published by Purvis[2] and Dobbie and Fox[3] and others during the early years of the century. A systematic determination of the ultraviolet spectra of pure preparations of nicotine, nornicotine, their dehydrogenated derivatives, and a few related compounds has therefore been carried out.

The wave length positions of the clearly defined maxima and minima occurring in the spectra of the compounds in a number of solvents and the specific extinction coefficients at these maxima and minima are listed in Table I. Molecular extinction coefficients at the maxima are also listed to permit comparison on a molar basis. Absorption curves for all the compounds in 95% ethanol solution and for representative compounds in acidified 95% ethanol are shown in Figs. 1 to 9.

As might be expected, the absorption curves of nicotine (A, Fig. 1) and nornicotine (A, Fig. 5) are almost identical in shape and in position of maxima and minima. The observed difference in specific extinction coefficients is apparently entirely due to the diluent effect of the methyl group occurring on the pyrrolidine ring of nicotine; on a molecular basis the extinction coefficients are nearly identical. The spectra of nicotine and nornicotine show the close relationship to the ultraviolet spectrum of pyridine (A, Fig. 2) that was to be expected. Differences between the curves of the alkaloids and that of pyridine, namely, a bathochromic shift of about 5 mμ in the position of the chief maximum, an elevation in molecular extinction coefficient, and a loss in fine structure, are of the kind to be anticipated as a result of substitution of the pyrrolidine ring on the pyridine nucleus. Addition of acid produces similar exaltations of the absorption maxima, depressions of the minima, and loss of fine structure in nicotine (B, Fig. 1) and nornicotine (A, Fig. 7) as it does in pyridine (B, Fig. 2).

Introduction of an additional double bond in conjugation with the pyridine ring as in myosmine (B, Fig. 5) results in a further shift of the pyridine absorption to longer wave lengths, accompanied by the appearance of a new strong, structureless band at 234 mμ. Presumably this latter band represents the bathochromic shifting through conjugation of the pyridine absorption normally lying below 200 mμ. An ever greater shift toward the red is exhibited in the spectrum of metanicotine (A, Fig. 4), in which the pyrrolidine ring has been opened and the introduced unsaturation conjugated with the pyridine nucleus occurs in an open chain. As is generally the case, the conjugation of ring and open chain unsaturation possessed by metanicotine also produces a substantially higher intensity of absorption than does the equivalent ring to ring conjugated unsaturation of myosmine. The spectrum of the comparison compound, 3-vinylpyridine (A, Fig. 6),

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(1) One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Purvis, *J. Chem. Soc.*, **97**, 1035 (1910).

(3) Dobbie and Fox, *ibid.*, **103**, 1193 (1913).