[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. VII. Evidence of the Transitory Existence of Borine (BH_3): Borine Carbonyl and Borine Trimethylammine

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On account of its position in the periodic system and the composition of its most widely known compounds, boron has generally been regarded as a trivalent element; its hydrides therefore might have been expected to have the "normal" formulas BH_3, B_2H_4, B_3H_5, etc. Actually, however, the simplest known hydride of boron is diborane (B_2H_6), a substance whose formula is characteristic of some compounds of tetravalent elements. This formula has not as yet been explained by any generally accepted rules of molecular structure, nor has there been any obvious reason for the failure of all previous attempts to find evidence for the existence (whether stable or transitory) of the "normal" hydrides, or borines. It is therefore of interest to discover what conditions may be sufficient for the existence of such borines and their derivatives.

Progress in this direction is now given new impetus by the discovery of a gaseous compound having the molecular formula BH_3CO. This new substance is produced by the treatment of diborane with carbon monoxide (present in great excess), which acts according to the equation $B_2H_6 + 2CO \rightleftarrows 2BH_3CO$. The reaction reaches equilibrium rapidly at 100°; at room temperature, the reverse reaction is slow enough to permit the isolation and study of the product. The molecular formula was established by observing the volumes of diborane and carbon monoxide produced by the decomposition of a known volume of the gas; the result was checked by hydrolytic analysis, and by the determination of the vapor density.

The initial rate of decomposition of BH_3CO at room temperature is relatively high, but decreases very rapidly, long before the final equilibrium is reached. The inhibiting agent is the carbon monoxide produced by the reaction; the other product, diborane, has no appreciable effect upon the rate in the early stages of the process. These observations suggest that the reaction occurs in two steps, the first of which results in the transitory existence of the hitherto unknown compound borine, according to the equation $BH_3CO \rightleftarrows BH_3 + CO$. This presumably rapid and easily reversible reaction is carried forward by the removal of borine, as a result of the almost irreversible secondary reaction $2BH_3 \rightleftarrows B_2H_6$,[2] a reaction whose rate determines the rate of the entire process in its early stages. As the concentration of carbon monoxide increases, during the course of the whole reaction, its increasing effectiveness in reversing the primary reaction makes the borine less and less available for the secondary reaction, whose rate therefore decreases rapidly.

This interpretation implies the transitory existence of molecules of borine, and at the same time suggests that its isolation is not feasible. Since we are, therefore, unable to present this most direct proof of its existence, we offer the following additional indirect evidence. Any substance capable of uniting with molecules of borine to form a compound more stable than BH_3CO, should displace carbon monoxide from BH_3CO. Ammonia might have been expected to react in this manner, for it is known to form many stable addition products by reaction with "normal" boron compounds, but the actual reaction of ammonia with BH_3CO does not liberate carbon monoxide. Instead, there appears a solid material, stable at room temperature, having the empirical composition represented by the formula $BH_3CO(NH_3)_2$.[3] Considering that this result might be due to the labile character of hydrogen in ammonia, we tried the effect of trimethylamine upon BH_3CO and found that it displaces the carbon monoxide rapidly and completely at ordinary temperature, according to the equation, $BH_3CO + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3$

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[1] Presented in condensed form at the Chicago Meeting of the National Academy of Sciences, Nov. 17, 1936.

[2] Our reason for supposing this reaction to be nearly irreversible is based upon an experiment by Stock and Kusz, *Ber.*, **56B**, 799 (1923), in which a sample of diborane was heated as high as 155°, without showing the slightest evidence of the formation of borine. Our only evidence that the reaction is reversible at all, is the fact that BH_3CO actually is formed from diborane and carbon monoxide.

[3] This material is in need of further investigation. It reacts with sodium in liquid ammonia to produce the quantity of hydrogen corresponding to two ammonium ions per molecule of BH_3CO, and therefore appears to have the character of a dibasic acid. Nevertheless, it is not yet possible to decide whether it is a pure compound, or a mixture of substances formed by the decomposition of BH_3CO during its reaction with ammonia.

+ CO. This reaction is in agreement with our assumption of the transitory existence of borine. The high speed of this displacement seems to justify the conclusion that the reaction $BH_3CO \rightleftarrows BH_3 + CO$ is far more rapid than the association of borine to form diborane.[4]

The reactions here described support the assumption that BH_3CO has the structure of a "borine carbonyl," a compound in which borine and carbon monoxide are joined by a coördinate link consisting of electrons furnished by the carbon monoxide.[5] Another structure which might be considered is $\mathrm{H:\overset{H}{\ddot{B}}:\overset{H}{\ddot{C}}::\ddot{O}:}$, which is an aldehyde type. Aside from the difficulty that such a substance should not easily produce diborane and carbon monoxide, there is the positive objection that it would be expected to add diborane, as acetaldehyde and other organic compounds containing the $=C=O$ group have been found to do.[6] The absence of such a reaction makes the aldehyde structure highly improbable. Other alternative structures which might suggest themselves seem too unlikely for discussion.

The compound $(CH_3)_3NBH_3$, borine trimethyl*ammine*, is extraordinarily stable. During the determinations of molecular weight and vapor tensions, it was heated for hours at a time at temperatures as high as 125°, without showing the slightest sign of a change in physical properties.

The studies here presented are being continued along several major lines. One of these is the investigation of the behavior of the alkyl diboranes and some of the higher boranes with carbon monoxide and with trimethylamine. The methyl derivatives of diborane already have been found to react with carbon monoxide, but the result is a series of compounds far different from BH_3CO.[7] In addition to this program, we are searching for other compounds which, like carbon monoxide and trimethylamine, may unite with the borine molecule to form compounds capable of isolation and study. These lines of work should lead to a better understanding of the nature of the boron hydrides and of the numerous "addition compounds" which they seem to be capable of forming.

Experimental Part[8]

Preparation of Borine Carbonyl.—Comparison of the results of a number of preliminary experiments showed that the equilibrium represented by the equation $B_2H_6 + 2CO \rightleftarrows 2BH_3CO$ is closely approached in fifteen minutes at 90°, but that less severe heating is not adequate for the purpose. Longer heating, or the same duration at a higher temperature, leads to no improvement in the yield; on the contrary, the increased production of less volatile material[9] involves a loss. At room temperature the reaction is very slow: after three hours the yield was only 1% of that obtained from a parallel experiment in which equilibrium was attained at 100°.

This preliminary study was followed by experiments in which mixtures of diborane with high concentrations of carbon monoxide[10] were heated in bomb tubes. In each of these experiments, a known quantity of diborane, and then a much larger, measured volume of carbon monoxide were condensed into the bomb at −210°.[11] The bomb was sealed off, removed from the low temperature bath, and inverted just as the diborane melted, in order that the liquid running down might evaporate and mix thoroughly with the carbon monoxide. Adequate mixing was made still more certain by allowing the tube to remain for ten hours or longer at room temperature, before the reaction was carried on by a twenty-minute heating in a steam-bath. After the heating, the bomb was cooled to −196°, and the contents introduced into the vacuum apparatus by means of the vacuum tube opener. In two of these experiments, in which data for the calculation of the equilibrium constant were recorded, the first fraction of the carbon monoxide was analyzed for hydrogen by combustion. The diborane and the borine carbonyl were isolated with un-

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[4] The compound $(CH_3)_3NBH_3$ is also formed very easily by the action of trimethylamine upon diborane, even at temperatures as low as −110°. This reaction probably does not depend entirely upon the dissociation of diborane to free borine molecules at such a low temperature; it is more reasonable to suppose that the trimethylamine acts upon diborane directly. Similarly, trimethylamine may react directly with BH_3CO. On account of this possibility, the formation of $(CH_3)_3NBH_3$ is not in itself a clear proof of the free existence of borine.

[5] For the present purpose, we consider it unnecessary to decide whether the carbon atom or the oxygen atom is linked directly to boron. Our use of the term "carbonyl" is solely a matter of convenience.

[6] These results have not yet been published. We have found that diborane reacts rapidly with acetaldehyde to give diethoxyborine, with acetone to give a compound which seems to be diisopropoxyborine, and far more slowly with methyl formate to give dimethoxyborine. The aldehyde and ketone reactions are completed in ten minutes at room temperature.

[7] Experimental work of F. L. McKennon.

[8] The high vacuum methods used in this work have been described quite adequately in the papers of Stock and in earlier papers of this series. All volumes mentioned in this paper refer to gases at standard conditions.

[9] This material in itself is worthy of further study. Like borine carbonyl, it begins to decompose rapidly at room temperature, and this initial reaction is soon hindered by the carbon monoxide which it produces. Unlike BH_3CO, the material produces a white, non-volatile solid which turns brown when heated. These observations suggest a carbonyl of a boron hydride fragment heavier than BH_3.

[10] The diborane was prepared by our usual method [Schlesinger and Burg, THIS JOURNAL, **53**, 4321 (1931)]. The carbon monoxide was prepared *in vacuo* by the action of hot sulfuric acid upon formic acid, and purified by distillation from a tube at −196° to a receiver at −210° (liquid nitrogen, whose temperature had been lowered by pumping).

[11] The uncondensed carbon monoxide was removed by a Töpler pump and measured over mercury. The purity of the sample was checked by combustion of tbis remainder.

usual care,[12] and the purity of each was checked before the volume was measured. The conditions and results of the bomb tube experiments are shown in Table I. Comparison of the last experiment with the others, shows very clearly the value of a high concentration of carbon monoxide.

TABLE I

Conditions			Results				
Capacity of bomb, cc.	Volume of B_2H_6	Volume of CO	Volume of BH_3CO	Residual volume of B_2H_6	Residual volume of CO	Volume of H_2	Volume of less volatile material
93.0	73.7	297	36.3	49.0	258	5	2.7
87.3	82.4	305	38.6	54.4	263	6.5	3.4
61.5	70.7	670	77.8	24.9	(585)	...	...

All volumes in this table are expressed in cc.

The equilibrium constant for the reaction $B_2H_6 + 2CO \rightleftharpoons 2BH_3CO$ may be calculated from the data of the first two experiments in Table I. Expressing the concentrations in terms of partial pressures (in mm.), we have from the first experiment

$$K = (P_{CO}^2 \times P_{B_2H_6})/P_{BH_3CO}^2 = 2.8 \times 10^4$$

The second experiment gave the result $K = 3.0 \times 10^4$. Neither result is to be regarded as very precise, because the side reactions, the possible lack of perfect mixing, the chance that equilibrium was not perfectly attained, and even some slight decomposition of the borine carbonyl during purification, all must be considered as sources of error. The tendency is toward high results; we therefore consider the lower value to be more dependable, and take it to represent a maximum value of the constant.

This result means that a sample of pure BH_3CO, having an initial pressure of 200 mm. at 100°, would be approximately 95% decomposed if brought to equilibrium at that temperature (secondary and side reactions neglected).

Physical Properties.—The uniformity of various samples of the new compound was indicated by the consistent checking of the vapor tension of 25.4 mm. at −111.8° (m. p. of carbon disulfide). As a further check on the uniformity of the material, the melting points of three separately purified samples were measured by the magnetic plunger method of Stock.[13] The three readings of the carbon tetrafluoride vapor tension thermometer were 382, 382 and 381 mm., corresponding to −137.0, −137.0 and −136.97°.

In addition to these tests, the vapor tensions at a number of different temperatures were measured, and the results found to be consistent with the Clapeyron equation. The rapid decomposition of the vapor made such measurements difficult, but it was possible, by rapid establishment of the thermal equilibrium, by very fast readings of the temperature and pressure, and by careful repurification between measurements, to obtain satisfactory check values. In order to establish equilibrium rapidly enough, it was necessary to choose samples so small that the thermal capacity of the liquid would be negligible. It was thus possible to obtain each reading within half a minute after warming the sample from −196°. The values, corrected for the expansion of mercury above 0°, are shown in Table II. The equation representing them is $\log_{10} p_{\mathrm{mm.}} = 7.85 - (1040/T)$, from which we calculate the normal boiling point to be −64°, the heat of vaporization 4750 cal./mole, and the Trouton constant 23.0 cal./deg. mole. The high value of the Trouton constant suggests that the complete curve relating $\log p$ to $1/T$ would be slightly concave downward, and that the true boiling point may be one or two degrees higher.

TABLE II

$t°$	−137	−122	−121.2	−120.3	−112.8	
$p_{\mathrm{mm.}}$ (obsd.)	1.4	9.0	9.7	10.7	22.5	
$p_{\mathrm{mm.}}$ (calcd.)	1.6	9.3	10.0	11.1	23.0	
$t°$	−111.8	−103.5	−95.6	−87.5	−87.2	−78.8
$p_{\mathrm{mm.}}$ (obsd.)	25.4	52.8	98.6	175	181	314
$p_{\mathrm{mm.}}$ (calcd.)	25.4	51.9	98.2	177	180	316

Analyses and Molecular Weight.—The most direct evidence of the identity of the new compound came from a quantitative experiment on its decomposition.

The sample was allowed to stand at room temperature for an hour. The carbon monoxide was then removed (through a trap at −196°) by a Töpler pump, and collected over mercury in a gas-measuring tube. The material in the trap was warmed again to room temperature, and the process of decomposing the original substance, and removing the carbon monoxide, was repeated again and again until the mixture no longer gave off more than traces of carbon monoxide. The latter stages of the process were facilitated by heating the mixture to 50°.

A 23.9-cc. sample thus yielded 24.1 cc. of non-condensable gas, 10.4 cc. of diborane, 0.7 cc. of material less volatile than the original sample, and a residue of 0.5 cc. of the original substance. The non-condensable material was analyzed by combustion and found to consist of 22.2 cc. of carbon monoxide and 1.9 cc. of hydrogen. The hydrogen and the least volatile material were unavoidable results of the heating.

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(12) The material less volatile than borine carbonyl seemed to be trapped out completely at −120°; its elimination was made certain by passing the more volatile materials very slowly through a trap at −145°. Nearly all of the borine carbonyl condensed in pure condition at −155°, but the purification of the diborane required a very slow distillation through a U-tube at −165°. The fraction trapped out at that temperature required further separation.

(13) Stock, *Ber.*, **50**, 157 (1917).

TABLE III

Time, min.		0	0.5	1.5	2.5	3.5	4.5	5.5	6.5	7.5	10.5
Pressure, mm.		161.3	162.3	164.3	165.3	166.0	167.1	168.2	168.8	169.3	170.3
% decomposed[a]		0	1.2	3.7	5.0	5.8	7.2	8.6	9.3	10.0	11.2
Time	17.5	27.5	57.5	87.5	118	148	210	270	360	450	520
Pressure	171.2	172.4	174.4	176.0	177.2	178.0	180.2	181.8	183.5	184.5	186.0
% decomp.	12.3	13.8	16.2	18.2	19.7	20.7	23.4	25.4	27.5	28.8	30.6

[a] The percentage decomposed at each point was calculated by dividing the total increment of pressure (multiplied by 100) by one-half the initial pressure.

Neglecting these side-reaction products, the results give the empirical molecular formula $B_{0.89}H_{2.82}(CO)_{0.96}$. The neglected material could easily represent the difference between this empirical result and the rounded formula, BH_3CO. At the same time, there could be some doubt that the observed quantities represented all of the material in the original sample, for non-volatile products could have remained unobserved in the form of a thin film on the glass walls of the container. The results therefore were supplemented by a determination of the molecular weight.

The molecular weight was calculated from the vapor density, determined in the usual manner. The sample (20.0 cc.) had a weight of 37.5 mg.: the molecular weight therefore was 42.0 (theoretical for BH_3CO, 41.85; considering the instability of the substance, such close agreement probably was fortuitous).

The formula BH_3CO was checked more definitely by the complete hydrolysis of a measured sample of the pure compound, followed by the combustion of the non-condensable gases and the titration of the boric acid. A 15.95-cc. sample, which was inclosed in a 250-cc. bulb with a liberal excess of water and heated for three hours at 100°,[14] produced 47.3 cc. of hydrogen, 15.7 cc. of carbon monoxide, and 16.0 "cc."[15] of boric acid. These results agree well enough with the expected equation $BH_3CO + 3HOH \longrightarrow B(OH)_3 + 3H_2 + CO$, to remove any doubt concerning the molecular formula of the compound.

The Rate of Decomposition.—The change in the rate of the reaction $2BH_3CO \longrightarrow 2CO + B_2H_6$, at room temperature, was studied by observing the relation of the total pressure to the time. The reaction evidently was not simple, for there occurred 8% decomposition during the first five minutes, 11% in ten minutes, 13% by the end of twenty minutes and only 13.8% at the half-hour point: a further eight-hour period was required to reach 30% decomposition. The detailed results are shown numerically in Table III, which records the progress of the decomposition of a 17.8-cc. sample at 23°, and graphically by curve I in Fig. 1.

The small rate of change toward the end of this experiment was shown not to be due to a close approach to equilibrium, by the behavior of the mixture after it had been heated for four hours at 50–60°. This treatment caused the extent of decomposition to increase from 30.6 to 78%. Nevertheless, the decomposition continued after the resulting mixture had been cooled to 24°.

The cause of the rapid decrease in the velocity of decomposition was made clear by further observations of the pressures registered by the same sample, after the carbon monoxide (accumulated in the course of the experiment described above) had been removed by pumping through a trap at −196°. The materials condensed (6.8 cc. B_2H_6, 3.7 cc. BH_3CO, and a trace of less volatile material) were returned to the reaction tube. The results of observations at 24° are shown in Table IV, and as curve II in Fig. 1. The sharp change in the behavior of the sample, as a result of removing carbon monoxide, leaves but little doubt that carbon monoxide is the main cause of the rapid slowing of the rate of decomposition, for the new rate curve is much like the original.[16]

The effect of carbon monoxide was tested more

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[14] The use of such a large bulb, and the drastic heating, seemed to be necessary for complete hydrolysis, since a somewhat smaller sample, heated with water for half an hour at 100°, in a space of 17 cc., was only 92% hydrolyzed. Hydrolysis thus appears to be an indirect reaction, in which a product of the decomposition (borine or diborane) is the material reacting with water. The high concentration of carbon monoxide built up in the smaller tube would stabilize the BH_3CO to such a degree as to account for the observed difficulty of hydrolysis.

[15] The symbol "cc." is used to represent the standard gas volume equivalent to a substance determined by titration.

[16] The rate of decomposition was considerably higher at any point in the present experiment than at the corresponding point in the original experiment. The difference no doubt was due mainly to the fact that the smaller sample in the same space built up a far lower partial pressure of carbon monoxide.

TABLE IV

Time, min.	0	0.5	1.0	3.0	8.0	16	23
Pressure, mm.	104.5	105.5	106.0	107.0	108.3	109.0	109.5
% decomposed[a]	0	6	9	15	23	27	30
Time, min.	32	43	53	76	191	270	546
Pressure, mm.	110.0	110.3	110.5	111.0	112.8	113.5	114.5
% decomposed[a]	33	34.5	36	39	49	54	59.5

[a] The % decomposed was calculated by dividing the total increment of pressure (multiplied by 100) by half the estimated initial partial pressure of BH_3CO (that is, by 0.5 × 33.6). It may be that the decomposition of the trace of less volatile material contributed to the rise of pressure: if so, these calculated values might be high by as much as 10 units. This uncertainty has no effect upon our conclusions, for a suitable correction would not alter the character of the curve.

directly in an experiment in which borine carbonyl and carbon monoxide were allowed to mix by diffusion at −80° (during twelve hours), after which the mixture was suddenly warmed to room temperature. The relation of the total pressure to the time was then observed as before.

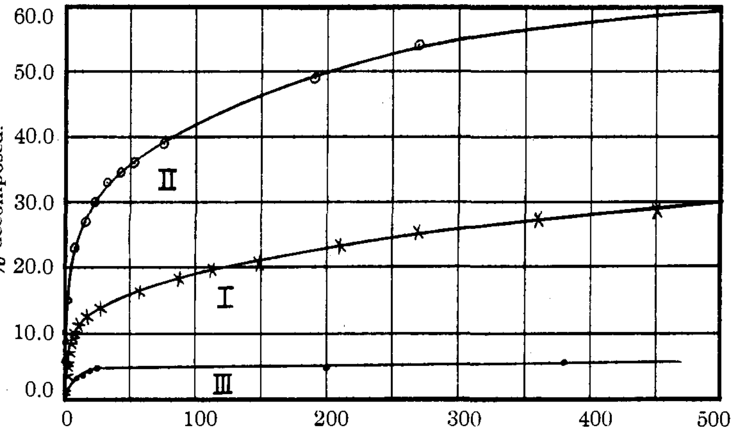

Fig. 1.

Table V shows the results obtained with such a mixture of 15.0 cc. BH_3CO and 22.2 cc. of carbon monoxide at 26°.

TABLE V

Time, min.	0	10	15	20	25	200	380
Pressure, mm.	320	322	322.3	322.7	322.8	323	323.5
Partial pressure of BH_3CO (calcd.)	120	116	115.4	114.6	114.2	114	113
% decomposition	0	3.3	3.8	4.5	4.8	5.0	5.8

At the end of this experiment, the diborane was isolated and measured as 0.4 cc., corresponding well with the 3.5 mm. increase of pressure. The rather rapid beginning of the decomposition probably is best explained by supposing that the mixing was not thorough enough for a perfect result.

Comparison of these results (curve III, Fig. 1) with those of the other rate experiments, fully confirms the conclusion that carbon monoxide is the inhibitor in the decomposition of borine carbonyl.

The Action of Ammonia upon Borine Carbonyl.—The original purpose in the treatment of borine carbonyl with ammonia was discussed in the introduction. The experimental details are as follows.

A pure sample of borine carbonyl (20.5 cc.) was treated with a large excess (114.1 cc.) of sodium-dried ammonia, at −124°. After an hour, the temperature was raised gradually to −80°, and the excess ammonia sublimed off into a trap at −196°. No trace of uncondensed gas was observed during this process. The solid residue now contained three moles of ammonia per mole of borine carbonyl originally used: this ratio was further decreased by warming the residue slowly to room temperature and condensing the ammonia liberated in the process. This second stage in the removal of ammonia was accompanied by the formation of 0.25 cc. of non-condensable gas, and a small sublimate of slightly volatile material. The solid residue in the original reaction tube now had an empirical formula approximating $(BH_3CO)_{0.9}(NH_3)_{2.07}$. It appeared to be fairly stable at room temperature.

In considering the possible ways in which ammonia might add to borine carbonyl, without liberating carbon monoxide, it seemed worth while to learn whether the product contained any ammonium ions. Accordingly, we tried the action of sodium upon a fresh sample of the material, dissolved in liquid ammonia.

The new sample was made from 14.0 cc. of borine carbonyl and a large, undetermined excess of ammonia. The solid was washed down to the bottom of the reaction tube by melting ammonia which had been condensed above it, and the solution was frozen during the introduction of 36.1 mg. of pure sodium (by a technique which blank tests had previously shown to be suitable for the purpose). When the solution was melted (allowing the sodium to enter the liquid phase at −77°), there occurred a very rapid reaction which produced one gram atom of hydrogen per gram molecule of borine carbonyl originally used. A secondary reaction produced a second gram atom of hy-

TABLE VI

Temperature, °C.	−77	−79	−77	−50	−49
Total time, min.	4	45	180	1560	3060
Total H_2, cc.	7.16	7.30	7.50	14.50	15.08
Ratio of H-atoms to BH_3CO used	1.02	1.04	1.04	2.07	2.16

drogen in the course of a day. The course of the whole reaction is shown in Table VI.

The excess over two atoms of hydrogen is properly to be attributed to amide formation.

The sodium reaction thus demonstrated that the product of addition of ammonia to borine carbonyl contains two ammonium ions per molecule of borine carbonyl. The question whether the material is a diammonium salt or a mixture of two salts, has not been decided.

Borine Trimethylammine

Preparation.—The reaction of trimethylamine with borine carbonyl appears to require temperatures as high as those at which the decomposition of the latter compound is observable. For example, there is no observable displacement of carbon monoxide by trimethylamine at −80° , but the reaction proceeds very rapidly at room temperature.

Thus 14.0 cc. of borine carbonyl and 25.0 cc. of trimethylamine, condensed into the tubulature of a reaction bulb (which was sealed while the reactants remained at −196°), and then warmed suddenly to room temperature, produced the solid material so rapidly that there was no further change after one minute. The reaction bulb was opened by a tube-opener, and the carbon monoxide was passed through a trap at −196°, by means of a Töpler pump, and measured as 14.2 cc. The residual trimethylamine was isolated by distillation through a trap at −80°, and measured as 10.8 cc.; the quantity which reacted hence was 14.2 cc., in perfect agreement with the quantity of carbon monoxide. The solid product therefore had the empirical composition $(CH_3)_{3x}(NBH_3)_x$, within the probable error.

Physical Properties and Molecular Weight.—The vapor tensions at various temperatures, and the total volumes of samples used in the determinations of the molecular weight, were measured by the aid of the device represented in Fig. 2. During such work, the sample contained in the bulb B registers its pressure upon the adjacent manometer, whose mercury levels are compared by means of a cathetometer. The complete immersion of the parts containing the sample makes it possible to work at elevated temperatures. In order to introduce or remove the sample, the mercury is lowered in the manometer to the point M, by applying a pump connection at P, and opening the ground-glass valve V.

The measurements so obtained for the vapor tensions of the solid product of the reaction of borine carbonyl and trimethylamine, were corrected for the varying density and vapor tension of mercury at different temperatures. The results are presented in Table VII. In the course of these measurements, the *melting point* was observed to lie between 94 and 94.5°.

TABLE VII

$t°$	23	27	34	39	51	60.3	69.5	77.6	82.7
$p_{mm.}$ (obsd.)	0.8	1.0	1.5	2.6	5.5	9.4	18.7	28.5	37.9
$p_{mm.}$ (calcd.)	0.7	1.0	1.6	2.4	5.5	10.1	17.8	28.4	37.8
$t°$	86.8	96.9	99.3	104.0	111.2	117.2	118.7	119.7
p (obsd.)	47.8	76.5	84.7	101.7	130.0	159.8	166.0	171.8
p (calcd.)	47.9	78.2	85.3	101.4	130.6	160.0	167.5	173.4

The values of the vapor tension below the melting point led to the equation $\log_{10} p_{mm.} = 10.187 - 3061/T$. The values above the melting point gave the equation $\log_{10} p_{mm.} = 7.846 - 2202/T$. Eliminating log p from these equations and solving for T gives a calculated melting point of 94°, in close agreement with direct observation. The heat of vaporization below the melting point is calculated to be 13,991 cal./mole, and above the melting point, 10,064 cal./mole. The calculated *heat of fusion* therefore is 3927 cal./mole. From the equation corresponding to the vapor tensions above the melting point, we calculate the Trouton constant to be 22.7 and the normal *boiling point*, 171°. The slightly high value of the Trou-

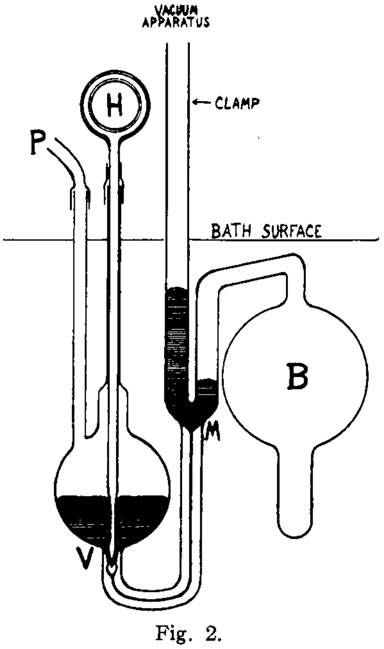

Fig. 2.

ton constant suggests that the true boiling point may be as much as one degree higher.

The sharpness of the melting point, and the character of the vapor tension curves, left no doubt of the uniformity of the material.

The molecular weight was determined by weighing portions of the sample in a small, detachable bulb with stopcock (the grease was not in the least affected), and then measuring the volume by the aid of the special device described above. The data and results of two such determinations are presented in Table VIII. The volume measurements for both of these samples were carried out at temperatures only a little way above the condensation points for the pressures observed; it is therefore reasonable that the results are somewhat higher than the value 72.85, calculated for the formula of borine trimethylammine, $(CH_3)_3NBH_3$.

TABLE VIII

Vol. of bulb, cc.	Temp., °C.	Corr. press.	Sample vol., cc.	Sample wt., mg.	Mol. wt.
118.0	120.0	111.0	11.97	39.6	74.0
118.6	99.5	74.9	8.56	28.6	74.8

This new compound forms hexagonal crystals which may appear in a variety of shapes, from long needles to short lumps having the appearance of broken quartz. Observations indicated that it is very stable, for it was heated at 125° for hours at a time, without the least permanent effect.

The Reaction of Diborane with Trimethylamine.—Diborane is absorbed by trimethylamine (present in 50% excess) rapidly and completely at any temperature at which the latter exerts an appreciable vapor tension. After removal of the excess of trimethylamine, there remains a solid residue having the empirical constitution and properties of borine trimethylammine. It was thought possible that the primary product of the reaction might be an analog of the ammonium salt which is formed by the absorption of diborane by solid ammonia under similar conditions, but an investigation of the behavior of the product toward sodium in liquid ammonia, soon gave an answer to the contrary.[17] The details of an experiment representing these observations are as follows.

A 7.1-cc. sample of diborane was condensed completely upon 20.8 cc. of trimethylamine in the bottom of a plain vertical tube. The tube was then warmed from −196 to −110°; the pressure developed by the evaporated diborane diminished practically to zero during five minutes. The excess trimethylamine was then distilled off at −80°, and measured as 6.5 cc. The residue hence had the empirical constitution $B_2H_6 \cdot 2N(CH_3)_3$, or $BH_3 \cdot N(CH_3)_3$, within the probable error.

Ammonia was now distilled into the tube, in quantity sufficient to form 3–4 cc. of solution, and approximately 20 mg. of pure sodium was introduced into the tube, which was kept full of pure hydrogen and at −196° during the process. After the tube was resealed and evacuated, it was warmed to −75°; the melting ammonia dissolved the sodium and the solid compound. During five minutes at −75°, the solution yielded 0.185 cc. of hydrogen; after half an hour the total hydrogen was only 0.203 cc. It appears reasonable to attribute the hydrogen to impurity, rather than to any appreciable quantity of trimethylammonium ion.

After the solvent ammonia had been removed (by distillation at −60°), the residual solid compound was sublimed into the device represented in Fig. 2, and found to exert a vapor tension of 86 mm. at 100°; the melting point was 95°. The volume was measured as 13.2 cc. These results left no doubt that the product of reaction of diborane with trimethylamine is borine trimethylammine. In addition, the molecular weight of a similar sample, which had not been exposed to sodium in liquid ammonia, was measured as 75.6, in good agreement with the values obtained for samples derived from borine carbonyl.

The behavior of trimethylamine toward diborane is thus found to be strikingly different from that of ammonia. At the present time, we see no very clear explanation for the wide contrast between the two reagents.

Acknowledgments.—Credit is due to David M. Ritter for the initial experiment on the reaction of diborane with trimethylamine. We wish also to acknowledge the aid of a grant from the National Research Council, for liquid nitrogen used in this work.

Summary

The new compounds borine carbonyl, BH_3CO, and borine trimethylammine, $(CH_3)_3NBH_3$, have been prepared and characterized. The former decomposes easily, to form diborane and carbon monoxide; the variation in the rate of this decomposition is such as to suggest that free molecules of borine, BH_3, may be involved in the process. Borine trimethylammine, a very stable compound, is formed very easily by the action

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(17) The diammoniate of diborane reacts with sodium in liquid ammonia to produce hydrogen; the experimental details and conclusions will be published in a separate paper. The product of the reaction of diborane with trimethylamine at low temperature does not react at all with sodium in liquid ammonia. The difference cannot be due to a failure of trimethylammonium ion to react with sodium, for a separate experiment showed that trimethylammonium chloride reacts with sodium in liquid ammonia in just the same manner as ammonium chloride does.

of trimethylamine upon either borine carbonyl or diborane. The behavior of ammonia toward diborane and toward borine carbonyl is quite different from that of trimethylamine toward these reagents.

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, U. S. DEPARTMENT OF AGRICULTURE]

Principal Optical and Physical Properties of the Carbon Tetrachloride Solvate of Rotenone

BY ERNEST L. GOODEN AND CHARLES M. SMITH

For several years chemists and manufacturers working with rotenone have been familiar with the carbon tetrachloride solvate, in which one molecule of rotenone is combined with one molecule of carbon tetrachloride of crystallization ($C_{23}H_{22}O_6 \cdot CCl_4$).[1] Since this solvate is of great practical importance, especially in the analysis of derris and cubé, it was considered necessary to determine its principal optical and physical properties.

The material used for the study was a sample of rotenone that had been recrystallized several times and subjected to microdetermination of carbon and hydrogen to gain assurance of purity.[2] A portion of this analyzed sample was recrystallized from carbon tetrachloride to form the carbon tetrachloride solvate.

Optical Crystallographic Properties

The optical properties investigated were such as are determinable by the use of the petrographic microscope. The solvate crystals were colorless, with a typical elongated, somewhat flattened prismatic shape (Fig. 1). The crystals were found to be biaxial with the following refractive indices (white light): $\alpha = 1.563$, $\beta = 1.612$, $\gamma = 1.631$. The indication of negative optical character obtained by the selenite plate is fairly distinct, and the observed value of β is so much nearer γ than α as to allow no doubt that the character is truly negative. In all cases observed the elongation is negative, the long edges of the crystal lying in the vibration direction for α. Extinction is sensibly parallel at all stages of rotation about the axis of crystal length, which is the vibration direction for α. It is concluded that the crystal belongs in the orthorhombic system.

Density

The density of the crystals was measured with a pycnometer, with water as the displaced liquid. In view of the volatility of the solvate, the accuracy attainable under the conditions of the experiment is considered as extending to two decimal places only. The observed value is 1.40 g. per cc. at 30°. A comparison of the density of the solvate with the densities of rotenone and carbon tetrachloride indicates that practically no volume change accompanies the combination.

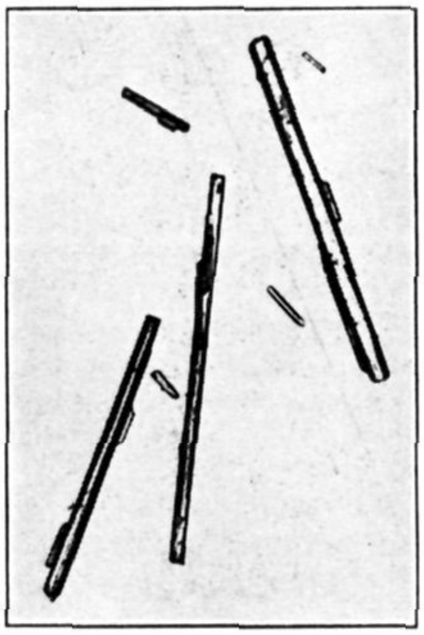

Fig. 1.—Carbon tetrachloride solvate of rotenone (× 175).

Dissociation Pressure

The dissociation pressure was investigated by the static method of vapor pressure measurement.[3] The source of controlled heating for the sample was the vapor above a boiling bath of a pure liquid, acetone, carbon tetrachloride and trichloroethylene being used separately for observations at their respective boiling points.

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(1) H. A. Jones, THIS JOURNAL, **53**, 2738 (1931).

(2) This is the sample referred to by Gooden and Smith, *ibid.*, **57**, 2116 (1935), as having been analyzed by J. R. Spies.

(3) The apparatus used was one constructed by O. A. Nelson, a modification of the apparatus described by Nelson and Senseman, *J. Ind. Eng. Chem.*, **14**, 58 (1922).