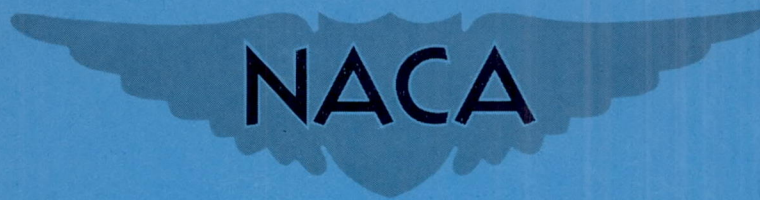


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RESEARCH MEMORANDUM

THERMAL REACTION OF DIBORANE WITH TRIMETHYLBORANE

By John H. Lamneck, Jr., and Samuel Kaye

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Cleveland, Ohio

NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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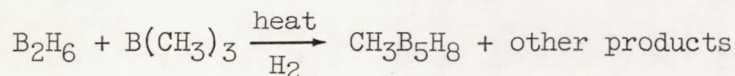
SUMMARY

Diborane and trimethylborane were reacted in a tube at 235° to 300° C in the presence of hydrogen. Methylpentaboranes were produced to the extent of 3 to 7 percent and separated in a specially designed vacuum fractionation column. Evidence was obtained to suggest that two isomers of monomethylpentaborane were isolated and that the one isomer obtained in largest quantity has not been previously reported. Impure samples of di- and trimethylpentaboranes were also obtained.

INTRODUCTION

Current aircraft require long ranges, high speeds, and high altitudes. To meet these requirements, fuels are needed that have high heats of combustion, high flame speeds, and wide flammability limits. Diborane, pentaborane, and decaborane satisfy these requirements but present problems because of unsatisfactory physical properties. Alkyl substitution of these hydrides is a possible method of overcoming these problems.

The pyrolysis of diborane to produce pentaborane is a well-known reaction (refs. 1 to 6). A mixture of diborane with trimethylborane will react to give the various substituted methylboranes (refs. 7 and 8). Simultaneously combining these two reactions could produce methyl-substituted pentaboranes;



A study was undertaken at the NACA Lewis laboratory to determine the extent of this reaction and the products obtained, if any.

Reaction conditions for an optimum conversion of diborane to pentaborane and of diborane and trimethylborane to monomethylborane were desired as the first step in the preparation of methylpentaboranes. Subsequently, conditions were varied from the experimental values

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(refs. 1 to 8) to increase the amount of the desired product and to study the effect of temperature. Crude products were fractionated and physical properties obtained from the purified fractions.

APPARATUS

A photograph of the pyrolysis apparatus is shown in figure 1, and a schematic drawing in figure 2. The charging tanks and receivers were of stainless-steel construction and of approximately 1-liter capacity. The first two receivers were fitted with large-bore 1/4-inch stainless-steel needle valves. All other valves were small 1/8-inch stainless-steel needle valves.

The flowmeters used were low flow-rate rotameters containing sapphire floats and having maximum capacities of 960 cubic centimeters of air per minute at a pressure of 14.7 pounds per square inch and 70° F. The reactor tube was 20 centimeters long and made of 19-millimeter inside-diameter Pyrex glass. An aluminum tube wrapped with Nichrome wire surrounded the glass tube over 16 centimeters of its length. Below the reactor were a water-cooled condenser and a 2-liter, two-neck round-bottom flask filled with steel wool to act as a solids trap. The temperature of the reactor was controlled by an automatic indicating potentiometer.

The hydrogen gas flowed through a catalytic purification unit and a dryer before being used. Product separation and purification apparatus included a low-temperature Hyd-robot Podbielniak fractionation column and a high-vacuum system built according to directions outlined in reference 9. The trap-to-trap distillations were found to be inadequate because they were limited to relatively small volumes, were time consuming, and the results approximated those of one-plate distillations. Therefore, an addition was made to the vacuum-system apparatus consisting of a 19-inch standard bubble-type condenser arranged vertically and filled with 5/16-inch glass helices. A schematic diagram of the condenser is shown in figure 3. One end of the condenser was fitted with a 50-milliliter bulb and the other was attached to the vacuum train through a Stock valve and a trap. Provision was made to circulate a refrigerated liquid through the jacket of the condenser to keep the operating pressure at, or near, 1 millimeter of mercury. This condenser column was designed to exploit the characteristics of the low-temperature molecular-type distillation and highly efficient fractionating columns. It has a large potential pot capacity but operates equally well on small samples since the hold-up in the column is minute. There is a continuous renewal of surface and a relatively long path from the pot through the condenser, which affords good contact between liquid and vapor.

Vapor pressures, molecular weights, and melting points were determined by methods outlined in reference 9. Infrared spectra were obtained in a gas cell with a double-beam recording spectrophotometer (ref. 10). Analyses were obtained by a high-temperature, high-pressure bomb method (ref. 11). Mass spectra were determined by the Chemistry Department of Western Reserve University on a Consolidated Engineering Analytical Mass Spectrometer that operated at an ionizing voltage of 70 volts and was equipped with a thermostated isotron and a metal analyzer tube. Gas chromatographic fractionation and separation was effected by a 4-foot, 1/4-inch copper tube filled with cetane on 100-mesh, or greater, Celite and maintained at 30° C. The carrier gas was helium and the temperature of the wires in the thermoconductivity cells was kept under 100° C.

The trimethylborane was synthesized in a 5-gallon reactor by reacting methyl magnesium bromide with boron trifluoride butyl etherate in butyl ether. The product was purified by fractionation through a 7-foot, 1-inch-diameter stainless-steel column packed with 3/16-inch Pyrex helices.

The diborane was transferred from a large commercial cylinder maintained at -78° C into a 1-liter stainless-steel tank by vaporization and condensation at -196° C. No further purification was effected.

Hydrogen from a commercial cylinder was purified by passing it through a catalytic purification tube and an alumina dehydrator tube.

Helium was used directly from the cylinder.

PROCEDURE

A flow of hydrogen at a ratio of 1 volume of hydrogen to 2 volumes of total gases was started through the apparatus after assembly, evacuation, and conditioning with the reactants. The reactor was brought to temperature and the receivers were cooled with dry ice and acetone, and liquid nitrogen. Flows of diborane and trimethylborane were then introduced at the ratio of 7 volumes of diborane to 1 of trimethylborane. An average residence time in the heated zone of the reactor was 3 seconds. Lengths of the runs were determined by the amount of product desired. Hydrogen was used to flush out the apparatus after a run was completed. All products were stored at -78° C.

RESULTS AND DISCUSSION

A summary of the cumulative data for the 12 runs is given in table I. Results of the Podbielniak fractionations of receivers 1 and 2 from runs 1 to 4 are listed in table II. The material in receiver 3 was

considered to be mostly diborane and was not fractionated. Analysis of the combined products of runs 5, 6, and 7 in the Podbielniak column was unsuccessful. In runs 8 to 11 the effect of temperature was investigated and vacuum-system analyses of runs 8, 9, and 11 are summarized in tables III, IV, and V. At 235° C 64 percent of the diborane passed through the reactor unchanged while at 265° C, the amount was 34 percent, and at 275° C it was 27 percent. Solid production increased from 1.5 percent by weight of the total charge at 235° C, to 24.2 percent at 265° C, and 39.3 percent at 275° C. At 235° C the amount of material produced that was in the volatility range of methylpentaborane amounted to 3.4 percent; at 265° C it was 4.5 percent; and at 275° C it was 6.8 percent based on the diborane introduced. Run 12 conducted at 270° C and lengthened to produce a large quantity of product for analysis gave comparable results. The diborane that passed through unreacted amounted to 22 percent, solids were 35 percent of total charge, and methylpentaboranes produced were 4.3 percent of the total based on charged diborane. No effort was made to analyze the product in the third receiver. The products in receivers 1 and 2 were evacuated at -78° C for 9 hours to remove the more volatile components such as diborane and methyldiborane. This procedure decreased the total product from 20.4 to 15.9 grams. The remaining material was introduced into the high-vacuum apparatus as two samples, and the volume was further reduced by a series of 10 trap-to-trap distillations at -78° C and 25 distillations at -68° C. In 11.3 grams removed there were small amounts of diborane and methyldiborane, larger amounts of dimethyldiborane and trimethyldiborane, and over 8 grams of pentaborane-9. The last fraction distilled had a vapor pressure of 52 millimeters of mercury at 0° C and would crystallize at 78° C, indicating that it was fairly pure pentaborane-9.

The remaining 4.6 grams of material from the total product of 15.9 grams consisted of some pentaborane-9 and compounds of higher molecular weight. Trap-to-trap distillations were performed 18 times at -64° C and six times at -51° C. However, separation was not adequate and each of the 24 fractions had a slightly reduced vapor pressure compared with the fraction immediately preceding it. Therefore, the 4.6 grams of product were recombined and charged to the pot of the condenser column described previously (fig. 3). Fuel alcohol was circulated through the column jacket at a temperature of -70° C, and the pot was left uncooled. Fractions were collected in a trap at -196° C for a period of time determined by the size of the sample desired. Table VI summarizes the fractions collected. Many of the fractions were combined on the basis of identical vapor pressures before other tests were made. Mass spectra were obtained on fractions 2 and 3, 22 to 29, 34, and 39 (all from run 12) and are listed in table VII. Fractions 2 and 3, 9 to 19, and 34, at first thought to be pure compounds, were analyzed by gas chromatographic techniques and separated into various components. The results obtained are summarized in table VIII.

Analysis of the runs indicates that the thermal reaction of diborane with trimethylborane produces many products, most of which are formed independently from the effect of heat on diborane and trimethylborane. However, interaction occurs to the extent of about 4 to 7 percent of the diborane introduced, resulting in the formation of alkylpentaboranes. The formation of both symmetrical and unsymmetrical dimethyldiborane was indicated by the boiling points of successive fractions from the Podbielniak distillations of runs 1 to 4 (table II). No tetraborane or pentaborane-11 was found in the analyses, but this was probably due to the decomposition of these compounds rather than a lack of formation. Very few of the fractions separated in runs 1 to 11 could be considered pure compounds because of the disadvantages of the standard low-temperature, low-pressure trap-to-trap distillations, which are described in reference 9.

From the components more volatile than methylpentaborane very little analytical data were obtained, except for vapor pressures and a few isolated molecular weights, elemental analyses, and infrared spectra. Much difficulty was encountered in obtaining the elemental analyses and, consequently, the data are not accurate in most cases but are presented for comparison purposes. Differences in the infrared spectra among the various fractions were slight, and this property could not be utilized to any great extent to differentiate among the various components. Three infrared spectra examples are included in figure 4 to illustrate the similarity. They are traces of the spectra for pentaborane, methylpentaborane, and dimethylpentaborane. Pure pentaborane-9 is distinguishable from the methyl-substituted compounds by the absence of a carbon-hydrogen bond absorption at 3.4 microns and by the presence of double peaks of absorption near 12.5 microns.

Purities of the four fractions analyzed by the mass spectrometer (fractions 2 and 3, 22 to 29, 34, and 39, all from run 12) were not known at the time of performing the analyses. The mass spectra of these four fractions are shown in figure 5. Precise numerical values for the relative peak heights are listed in table VII. Results from analyzing three of the same four samples (table VII) by gas chromatographic techniques are given in table VIII. Fraction 2 and 3 (run 12) seems to be a mixture of pentaborane-9 with methylpentaborane. Infrared spectra exhibited small double peaks at 12.5 microns and the gas chromatographic retention time of the first component coincided with that of a known sample of pentaborane-9. A study of peak heights from the mass spectrometer data (fig. 5(a)) indicates that material with a molecular weight corresponding to methylpentaborane-9 is the highest molecular weight compound present in an appreciable quantity and that it is the main component. Two separate references in the literature (refs. 12 and 13) list the vapor pressure of methylpentaborane-9 as 35 millimeters of mercury at 0° C. Assuming that the reported material was of high purity, this value corresponds

to the vapor pressure of the second component separated by the gas chromatographic fractionation of fraction 2 and 3 (run 12). If this is methylpentaborane-9, then the fourth and most prevalent component separated in this gas chromatographic fractionation must be another isomer of methylpentaborane-9 with a vapor pressure of 20 millimeters of mercury at 0° C.

Two isomers of monomethylpentaborane-9 are highly probable since there are two distinctly different boron-hydrogen bonds on the apex and base of pentaborane-9 that could be broken with the substitution of a methyl group for the hydrogen. However, in this experiment, a simple substitution was probably not involved but rather a synthesis of the pentaborane-9 structure with the methyl group already attached. Preparation in references 12 and 13 was by Friedel-Crafts substitution and did not yield any poly-substituted methylpentaboranes, whereas the method reported herein did produce the di- and trimethyl compounds. This would seem to indicate that Friedel-Crafts substitution involved the apex boron atom of pentaborane-9 and that in the present case the methyl group was attached to a base boron atom.

If two isomers have been formed, fractions 4 to 8 (run 12) would thus be mixtures of the two. A sample of the combination of fractions 9 to 19 (run 12) was fractionated by gas chromatography and found to be almost 99 percent of the isomer with a vapor pressure of 20 millimeters of mercury at 0° C. Molecular weight and elemental analysis on fractions 9 to 19 and mass spectra data on fraction 22 to 29 (fig. 5(b)) indicate that this material is methylpentaborane-9. The sample purified by gas chromatography has a vapor pressure of 20.2 millimeters of mercury at 0° C, a melting point of -63° C, and is more than 99 percent pure.

The fractions following fraction 29 (run 12) slowly decreased in vapor pressure. A mass spectral analysis was performed on fraction 34 (fig. 5(c)) and it indicated that dimethylpentaborane-9 was the main constituent. A gas chromatographic fractionation yielded four separate compounds; the latter two, amounting to 77 percent of the total amount, could be isomeric dimethylpentaborane-9.

A mass spectral analysis was also obtained for fraction 39 (run 12) (fig. 5(d)) in which a mixture was indicated with some trimethylpentaborane-9.

CONCLUDING REMARKS

Pentaborane-9 is the main product obtained from the passage of diborane and trimethylborane through a furnace at 235° to 300° C. Some methylpentaboranes are also formed along with methyldiboranes and solid boron hydrides.

A monomethylpentaborane-9 of lower volatility than that reported in the literature has been isolated.

An improved method of fractionation in a vacuum system has been demonstrated.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, May 14, 1958

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TABLE I. - DIBORANE AND TRIMETHYLBORANE REACTIONS

Run	^a 1 to 4	5	6	7	8	9	10	11	12
Temperature, °C	250	300	275	275	235	265	275	275	270
Diborane charge, g	^b 26.5	(c)	^b 1.01	^b 6.09	3.27	3.12	^b 3.27	3.16	88.6
Trimethylborane charge, g	^b 31.1	3.22	^b 1.17	4.96	1.03	1.005	^b 1.91	1.06	32.9
First receiver, g	15.9	1.50	0.19	2.41	0.86	1.055	0.88	0.92	15.2
Second receiver, g	3.6	0.13	0.07	1.03	0.35	0.46	0.44	0.22	5.2
Third receiver, g	14.7	1.33	0.39	2.46	2.87	1.39	0.94	1.13	25.3
Solids, g	Very little	6.62	0.11	3.49	0.06	1.005	1.86	1.66	42
Material lost, g	23.4		1.42	1.66	0.16	0.265	^d 1.06	0.29	33.8
Run time, min	-----	^e 80	^e 8	^e 35	12	12	12	12	^f 365

^aProducts of all four runs collected in same receivers.

^bDesired weight ratio of 3 of B₂H₆ to 1 of B(CH₃)₃ not achieved.

^cDiborane feed line leaked during run.

^dSome material lost accidentally.

^ePlugging occurred.

^fFour pluggings occurred during run.

TABLE II. - PODBIELNIAK FRACTIONATIONS OF PRODUCTS FROM RUNS 1 to 4

Compound	First receiver				Second receiver			
	^a Charged to column, ^b 5.9 g; percent recovered, 47.8				^c Charged to column, 3 g; percent recovered, 93.7			
	Boil- ing point, °C	Pres- sure, mm Hg	Recovered material, mole percent	Recov- ery, g	Boil- ing point, °C	Pres- sure, mm Hg	Recovered material, mole percent	Recov- ery, g
B ₂ H ₆					-93	752	40	0.73
CH ₃ B ₂ H ₅					-43	752	16	.44
B(CH ₃) ₃	-60	96	11.2	0.31	-21.5	752	19	.70
Unsymmetrical (CH ₃) ₂ B ₂ H ₄	-44	96						
	-3	737	45.6	1.27	-4	752	17	.65
Symmetrical (CH ₃) ₂ B ₂ H ₄	3	737	28.1	.77	4	752	8	.29
B ₅ H ₉	17	139	15.1	.47				

^aOperation was very erratic.

^bTotal sample was 10.6 grams, 5.3 grams having been removed by evacuation at -78° C.

^cOperation proceeded smoothly.

TABLE III. - VACUUM-SYSTEM ANALYSIS OF RUN 8

Frac- tion number	First receiver; charge, 0.775 g				Second receiver; charge, 0.32 g				Third receiver; charge, 2.74 g			
	Weight, g	Vapor pressure,		Probable main component	Weight, g	Vapor pressure,		Probable main component	Weight, g	Vapor pressure,		Probable main component
		mm Hg	at °C			mm Hg	at °C			mm Hg	at °C	
1	0.06	131	-78	CH ₃ B ₂ H ₅	0.03	--	---	CH ₃ B ₂ H ₅	1.34	298	-104	B ₂ H ₆
2	.04	88	-78	CH ₃ B ₂ H ₅	.03	12	-99	CH ₃ B ₂ H ₅	.06	591	-95	B ₂ H ₆
3	.07	73	-78	CH ₃ B ₂ H ₅	.07	12	-78	(CH ₃) ₂ B ₂ H ₄	.02	---	----	B ₂ H ₆
4	.22	13	-78	(CH ₃) ₂ B ₂ H ₄	.04	19 63	-56 0	(CH ₃) ₃ B ₂ H ₃	.19	57	-78	CH ₃ B ₂ H ₅
5	.10	2	-78	(CH ₃) ₃ B ₂ H ₃	.02	--	---	B ₅ H ₉	.46	12	-78	(CH ₃) ₂ B ₂ H ₄
6	.075	65 Solid	0 -78	B ₅ H ₉	.06	18 63	-23 0	B ₅ H ₉				
7	.10	53	0	B ₅ H ₉	.04	31 11	0 -23	CH ₃ B ₅ H ₈				
8	.07	4	-23	CH ₃ B ₅ H ₈								
Loss	.04	---	---	-----	.03	--	---	-----	.67	---	---	-----

TABLE IV. - VACUUM-SYSTEM ANALYSIS OF RUN 9

[First and second receivers; charge, 1.375 g]

Frac- tion number	Weight, g	Molec- ular weight	Vapor pressure,		Analysis, percent			Probable main component
			mm Hg	at °C	Carbon	Hydro- gen	Boron	
1	0.025	--	28	-131		-----		B ₂ H ₆
2	.09	--	70	-78		-----		CH ₃ B ₂ H ₅
3	.25	--	23	-78		-----		(CH ₃) ₂ B ₂ H ₄
4	.075	--	3.5	-78		-----		(CH ₃) ₃ B ₂ H ₃
5	.11	--	83	0		-----		(CH ₃) ₃ B ₂ H ₃
6	.225	67	63 206	0 23	8.9	14.84	76.2	B ₅ H ₉
7	.14	72	54 126	0 22.5		-----		B ₅ H ₉
8	.04	80	19 59	0 23.5				CH ₃ B ₅ H ₈
9	.10	--	-----	-----	16.55	14.48	66.19	CH ₃ B ₅ H ₈
Loss	.32							

TABLE V. - VACUUM-SYSTEM ANALYSIS OF RUN 11

[First and second receivers; charge, 1.14 g]

Frac- tion number	Weight, g	Molec- ular weight	Vapor pressure,		Analysis, percent			Probable main component
			mm Hg	at °C	Carbon	Hydro- gen	Boron	
1	0.02	---	-----	-----	-----	-----	-----	B_2H_6
2	.07	---	117	-78	-----	-----	-----	$CH_3B_2H_5$
3	.14	---	-----	-----	-----	-----	-----	$CH_3B_2H_5$
4	.008	---	-----	-----	-----	-----	-----	$CH_3B_2H_5$
5	.13	---	17 6	-78 -95	-----	-----	-----	$(CH_3)_2B_2H_4$
6	.18	67	8.5	-78	10.14	15.65	72.5	$(CH_3)_3B_2H_3$
7	.24	66	Solid 259	-78 33	5.44	17.7	76.5	B_5H_9
8	.06	71	51	0	23.4	16.2	61.6	B_5H_9
9	.045	78	38	0	-----	-----	-----	$CH_3B_5H_8$
10	.03	84	24	0	-----	-----	-----	$CH_3B_5H_8$
11	.07	87	20 58	0 24.5	18.8	16.7	62.2	$CH_3B_5H_8$
12	.03	104	-----	-----	-----	-----	-----	-----
13	.04	121	-----	-----	-----	-----	-----	-----
Loss	.08							

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TABLE VI. - VACUUM-SYSTEM ANALYSIS OF RUN 12

[Receivers 1 and 2, higher boiling part. Charge, 4.6 g.]

Fraction number	Weight, g	Melting point, °C	Molecular weight	Vapor pressure, mm Hg at 0° C	Analysis, percent			Probable main component
					Carbon	Hydrogen	Boron	
1	0.6158	-----	65.8	64	3.7	21.5	75.8	B ₅ H ₉
2,3	.2063	-98	78.1	39,40	----	----	----	CH ₃ B ₅ H ₈
4,5	.1184	-89	80.6	29.5,28	17.6	17.6	55.2	CH ₃ B ₅ H ₈
6,7	.0959	-83	87.5	24,23	18.5	18.0	59.5	CH ₃ B ₅ H ₈
8	.0673	-78.5	86.1	22.5	16.3	20.2	58.6	CH ₃ B ₅ H ₈
9 to 19	.7097	-68	77.6	20 to 21	17.1	14.3	61.6	CH ₃ B ₅ H ₈
20,21	.0681	-----	80.5	20	16.5	23.3	63.0	CH ₃ B ₅ H ₈
22 to 29	1.1155	-68	78.2	19 to 20	----	----	----	CH ₃ B ₅ H ₈
30,31	.5367	-----	87.7	18,17	----	----	----	CH ₃ B ₅ H ₈
32	.1145	-----	-----	14.5	----	----	----	CH ₃ B ₅ H ₈ and (CH ₃) ₂ B ₅ H ₇
33	.0330	-----	-----	13	----	----	----	(CH ₃) ₂ B ₅ H ₇
34	.0229	-----	-----	9	----	----	----	(CH ₃) ₂ B ₅ H ₇
35	.0669	-----	91.1	10	----	----	----	(CH ₃) ₂ B ₅ H ₇
36	.1507	-----	98.4	7	----	----	----	(CH ₃) ₂ B ₅ H ₇
37	.2808	-----	-----	8	----	----	----	(CH ₃) ₂ B ₅ H ₇
38	.1002	-----	113.1	6	----	----	----	(CH ₃) ₃ B ₅ H ₆
39	.0410	-----	126.8	4.5	----	----	----	(CH ₃) ₃ B ₅ H ₆
40	.0238	-----	114.9	3	----	----	----	(CH ₃) ₃ B ₅ H ₆
41	.0059	-----	-----	1-2	----	----	----	-----
Residue	.0041	-----	-----	-----	----	----	----	-----

TABLE VII. - MASS SPECTRA OF FRACTIONS FROM RUN 12

[Deflections in terms of scan number 3, most sensitive galvanometer, and 1-micron pressure.]

Mass number	Fraction				Mass number	Fraction				Mass number	Fraction			
	2 and 3	22 to 29	34	39		2 and 3	22 to 29	34	39		2 and 3	22 to 29	34	39
2	7.22	6.83	7.05	16.54	46	8.32	7.43	4.60	2.67	95	0.037	0.016	0.150	1.523
10	5.36	4.47	3.19	1.88	46.5	-----	-----	-----	.010	96	.077	.019	.131	1.092
11	20.3	16.88	12.08	4.25	47	11.42	11.08	7.78	4.57	97	.085	.022	.112	.471
12	1.69	2.14	1.51	1.06	48	9.47	9.16	8.04	5.74	98	.040	.025	.142	.727
13	5.51	4.53	3.73	2.70	49	4.22	4.81	6.09	5.12	99	.025	.031	.185	1.14
14	.332	.204	.213	.241	50	1.32	1.58	2.36	2.54	100	.020	.031	.219	1.41
15	1.29	.762	.800	1.05	51	.349	.498	2.42	3.66	101	.012	.031	.240	1.56
16	.085	.087	.094	.111	52	.463	.299	.610	.567	102	.005	.031	.283	2.06
17	.047	.019	.010	.013	53	1.34	.667	.949	.853	103	.005	.035	.407	3.11
18	.172	.045	.015	.033	54	3.21	1.63	.941	.572	104	.012	.050	.567	4.87
19	-----	-----	-----	.007	55	5.76	3.62	2.08	1.29	105	.017	.060	.619	5.53
20	.006	.011	.005	1.05	56	7.47	6.25	4.07	2.42	106	.017	.047	.511	4.92
21	.065	.045	.021	.013	57	9.81	8.53	6.46	3.85	107	-----	.006	.047	.586
22	.256	.183	.088	.046	58	11.73	10.14	8.50	5.65	108	.107	.006	.056	.577
23	.585	.457	.260	.156	59	14.20	10.36	9.19	5.78	109	1.27	.013	.077	.582
24	.969	.806	.529	.333	60	12.70	8.37	8.25	5.09	110	5.40	.038	.107	.451
25	1.03	.951	.936	.769	61	14.10	13.00	14.38	7.63	111	8.05	.047	.099	.205
25.5	-----	.019	.015	.033	62	15.28	14.08	16.32	8.32	112	.217	.009	.077	1.65
26	2.46	2.98	3.97	4.08	63	6.87	4.67	8.51	7.24	113	.052	.006	.086	1.70
27	4.91	7.54	9.97	11.78	64	5.68	3.85	7.13	6.30	114	-----	.006	.064	1.25
27.5	-----	-----	.010	-----	65	.563	.715	1.04	1.06	115	-----	.003	.009	.050
28	.336	1.51	.868	2.44	66	1.88	2.38	1.95	1.36	116	-----	.003	.009	.075
28.5	.015	-----	-----	-----	67	4.66	5.51	3.49	2.51	117	-----	.003	.013	1.45
29	.461	1.80	.876	2.95	68	8.20	7.81	5.07	3.31	118	-----	.003	.017	.250
29.5	.015	.008	-----	-----	69	8.84	7.62	5.68	3.75	119	-----	.003	.021	.356
30	.015	.049	.026	.085	70	6.92	8.37	6.10	3.95	120	-----	.003	.021	.286
31	.037	.026	.015	.013	71	10.63	13.29	7.37	4.71	121	-----	-----	.009	.065
32	.212	.151	.073	.052	72	14.30	18.00	7.19	4.07	122	.007	-----	.009	1.00
33	.670	.533	.254	.124	73	17.25	20.7	7.27	4.33	123	.020	-----	.013	1.50
33.5	.012	-----	.010	-----	74	17.75	21.5	7.45	4.18	124	.167	-----	.017	1.75
34	1.64	1.43	.768	.404	75	11.65	14.32	7.35	5.75	125	.627	.006	.021	1.50
34.5	.027	.023	.015	.013	76	13.82	16.90	8.26	8.82	126	.969	.006	.017	.080
35	2.94	2.72	1.96	1.24	77	11.72	14.23	6.07	10.30	127	.032	-----	.017	.065
35.5	-----	.026	.026	.020	78	9.64	11.27	6.03	10.78	128	.005	-----	.017	.035
36	4.01	4.00	5.43	2.41	79	.144	.204	1.32	2.42	129	-----	-----	-----	-----
36.5	-----	.045	.031	.013	80	.060	.113	1.70	2.46	130	-----	-----	-----	-----
37	4.93	5.56	9.37	8.07	81	.082	.120	1.75	2.83	131	-----	-----	-----	-----
38	.633	.645	.691	2.24	82	.080	.113	1.46	3.33	132	-----	-----	-----	.005
39	.807	1.24	1.29	2.30	83	.147	.167	2.13	4.84	133	-----	-----	-----	.005
40	.800	.617	5.67	6.48	84	.202	.233	3.17	5.44	134	-----	-----	-----	.010
41	1.67	2.72	23.4	28.2	85	.209	.353	5.47	6.09	135	-----	-----	-----	.010
41.5	-----	-----	.013	.015	86	.139	.435	7.39	6.18	136	-----	-----	-----	.010
42	.907	.661	.747	1.31	87	.139	.450	8.09	5.22	137	-----	-----	-----	.020
42.5	-----	-----	.004	.010	88	.139	.472	8.76	5.98	138	-----	-----	-----	.035
43	2.20	4.24	1.91	5.68	89	.134	.466	8.84	6.05	139	-----	-----	-----	.030
43.5	-----	-----	.009	.010	90	.162	.563	11.38	6.00	140	-----	-----	-----	.015
44	2.52	1.95	.813	.602	91	.142	.510	11.30	3.79	141	-----	-----	-----	.010
44.5	-----	-----	-----	.005	92	.117	.412	9.30	3.35	142	-----	-----	-----	.010
45	4.66	3.96	1.89	1.08	93	.012	.016	.275	.968					
45.5	-----	-----	-----	.010	94	.012	.013	.118	1.248					

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TABLE VIII. - GAS CHROMATOGRAPHIC FRACTIONATIONS OF RUN 12

Fraction	Retention time	Percent of total	Vapor pressure, mm Hg at 0° C	Probable compound	Melting point, °C	Weight, g
2 and 3	24.5	28.6	----	B ₅ H ₉		0.035
	44	8.5	35.7	More volatile CH ₃ B ₅ H ₈		0.0128
	55	2.3	----			-----
	84	60.6	20	Less volatile CH ₃ B ₅ H ₈		0.0911
9 to 19	44	1.2	----	More volatile CH ₃ B ₅ H ₈	---	0.0014
	88	98.8	20.2	Less volatile CH ₃ B ₅ H ₈	-63	0.1182
34	51	13.3	----			-----
	77.5	9.4	----	Less volatile CH ₃ B ₅ H ₈		0.0013
	104	11.1	----	More volatile (CH ₃) ₂ B ₅ H ₇		0.0017
	140	66.2	9.1	Less volatile (CH ₃) ₂ B ₅ H ₇		0.0104

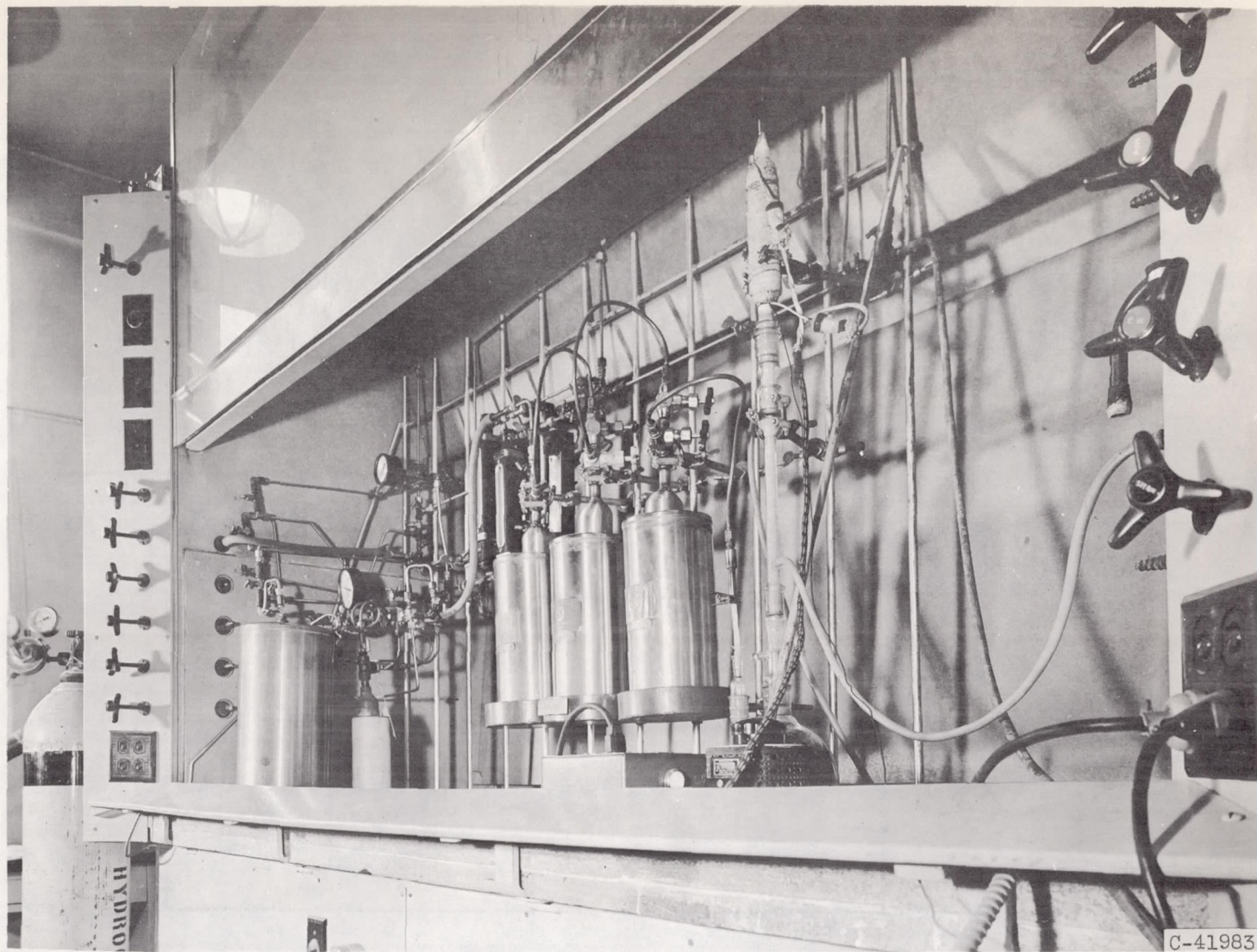
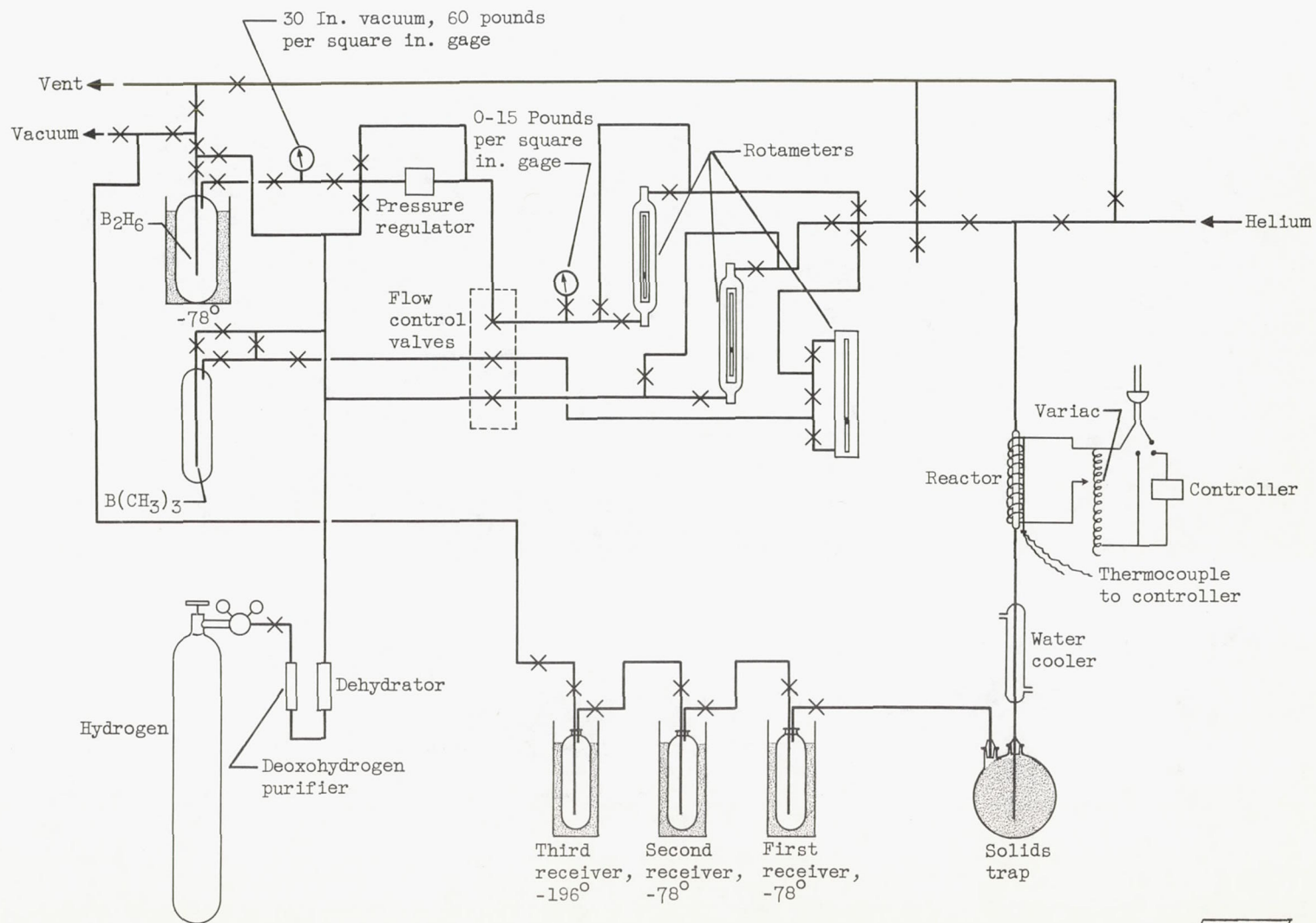
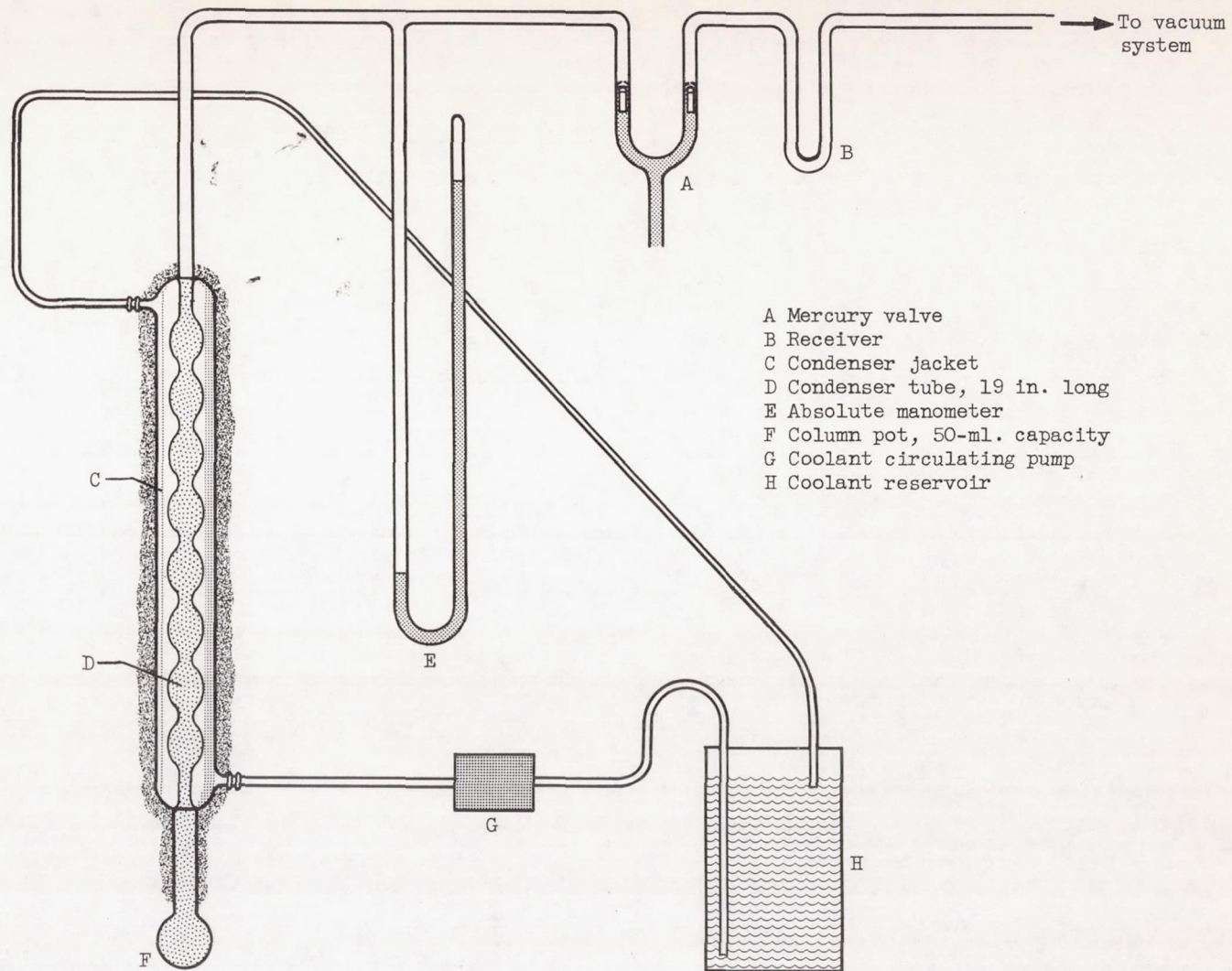


Figure 1. - Apparatus for the thermal reaction of diborane with trimethylborane.



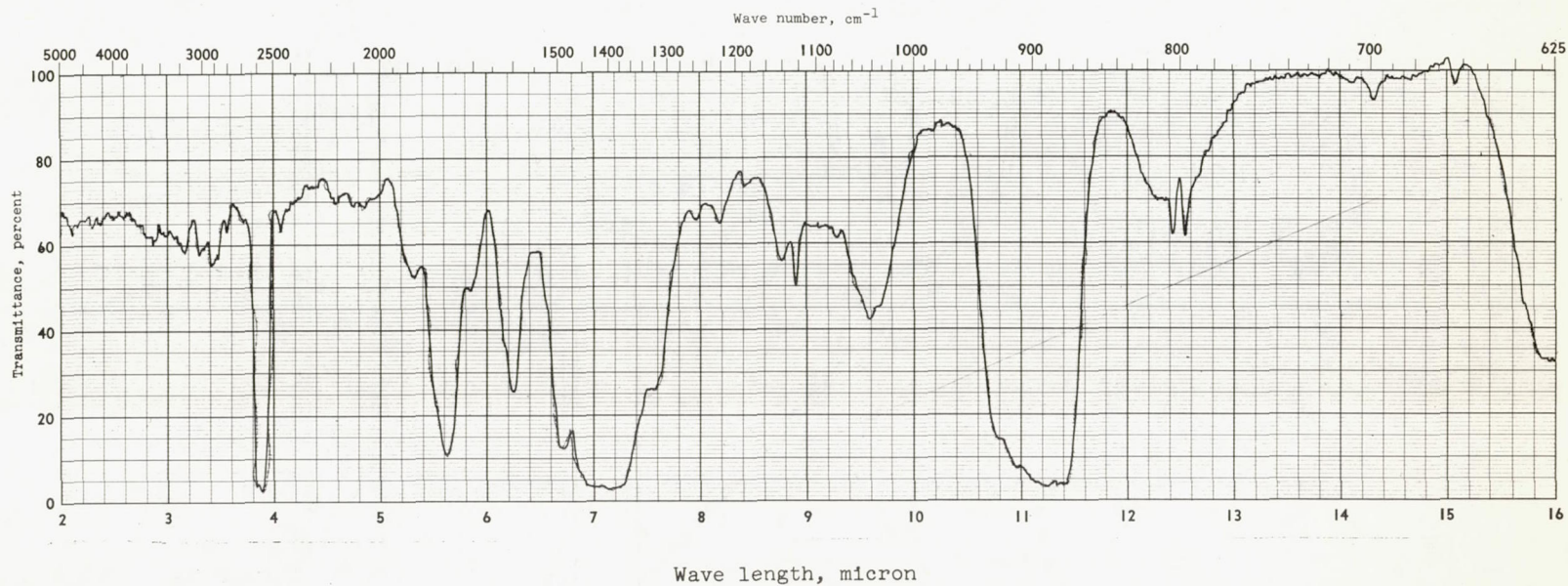
CD-5171

Figure 2. - Apparatus for the thermal reaction of diborane with trimethylborane.



CD-5174

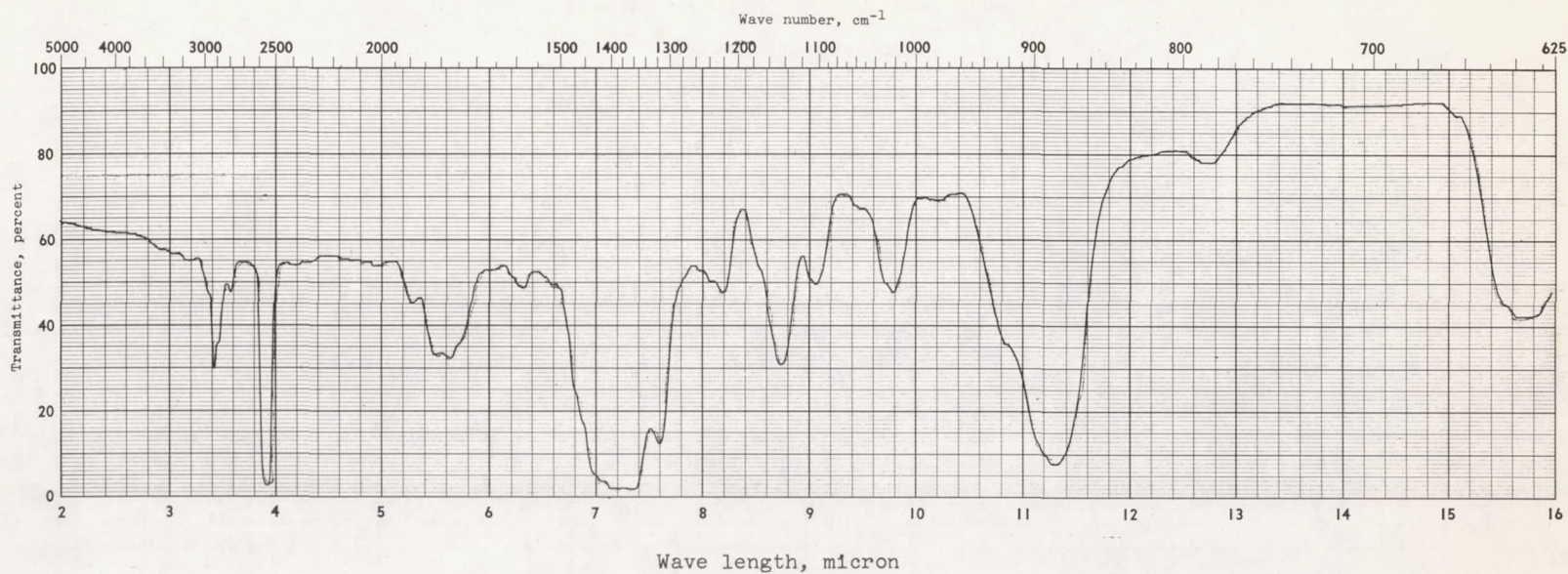
Figure 3. - Condenser fractionating column.



Wave length, micron

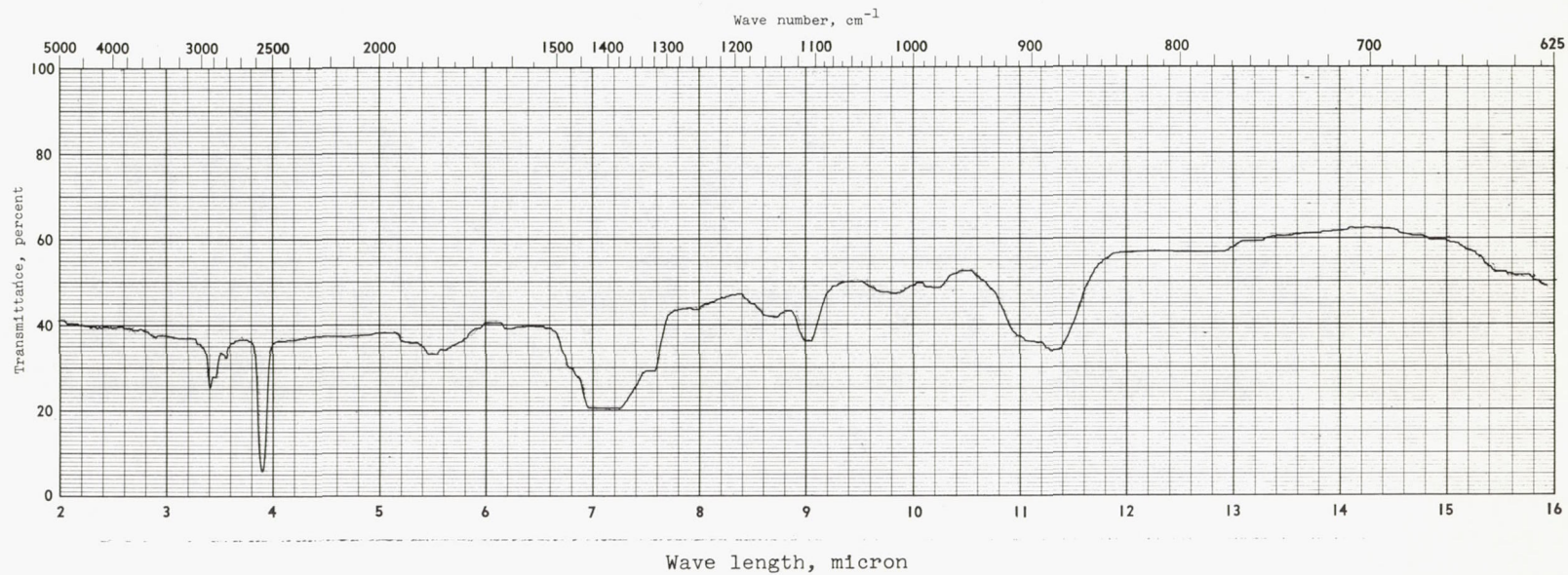
(a) Pentaborane.

Figure 4. - Infrared spectra.



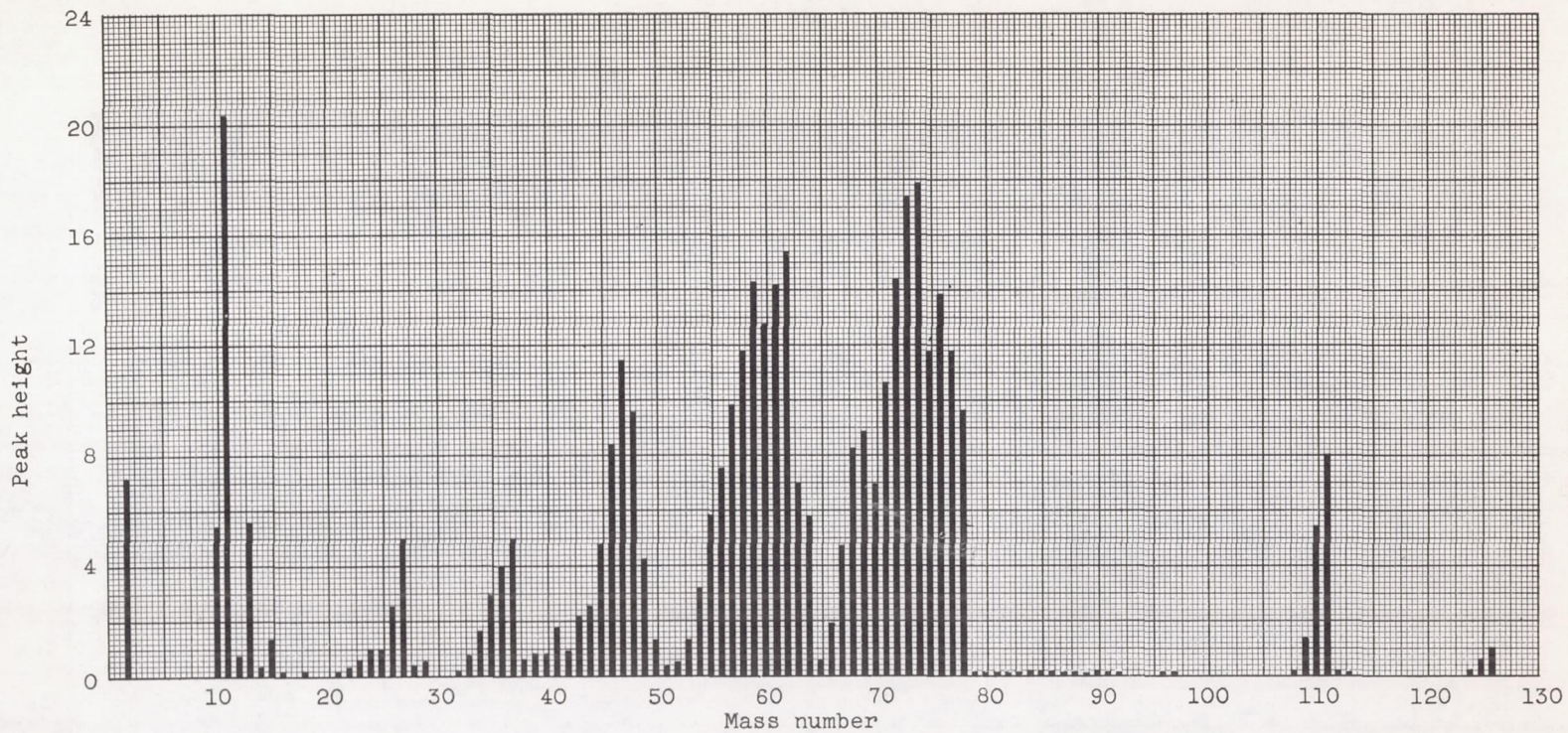
(b) Methylpentaborane (less volatile).

Figure 4. - Continued. Infrared spectra.



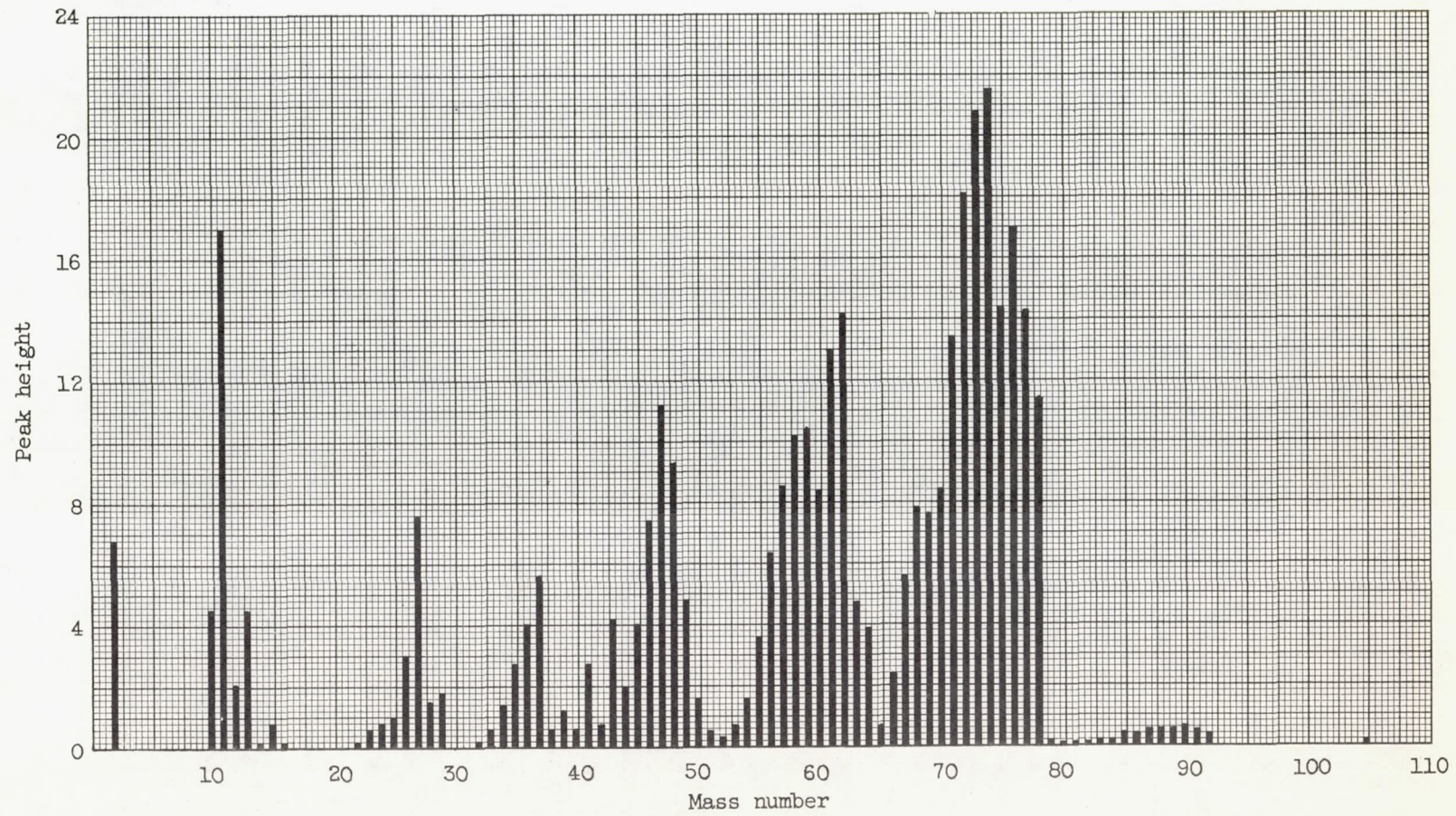
(c) Dimethylpentaborane.

Figure 4. - Concluded. Infrared spectra.



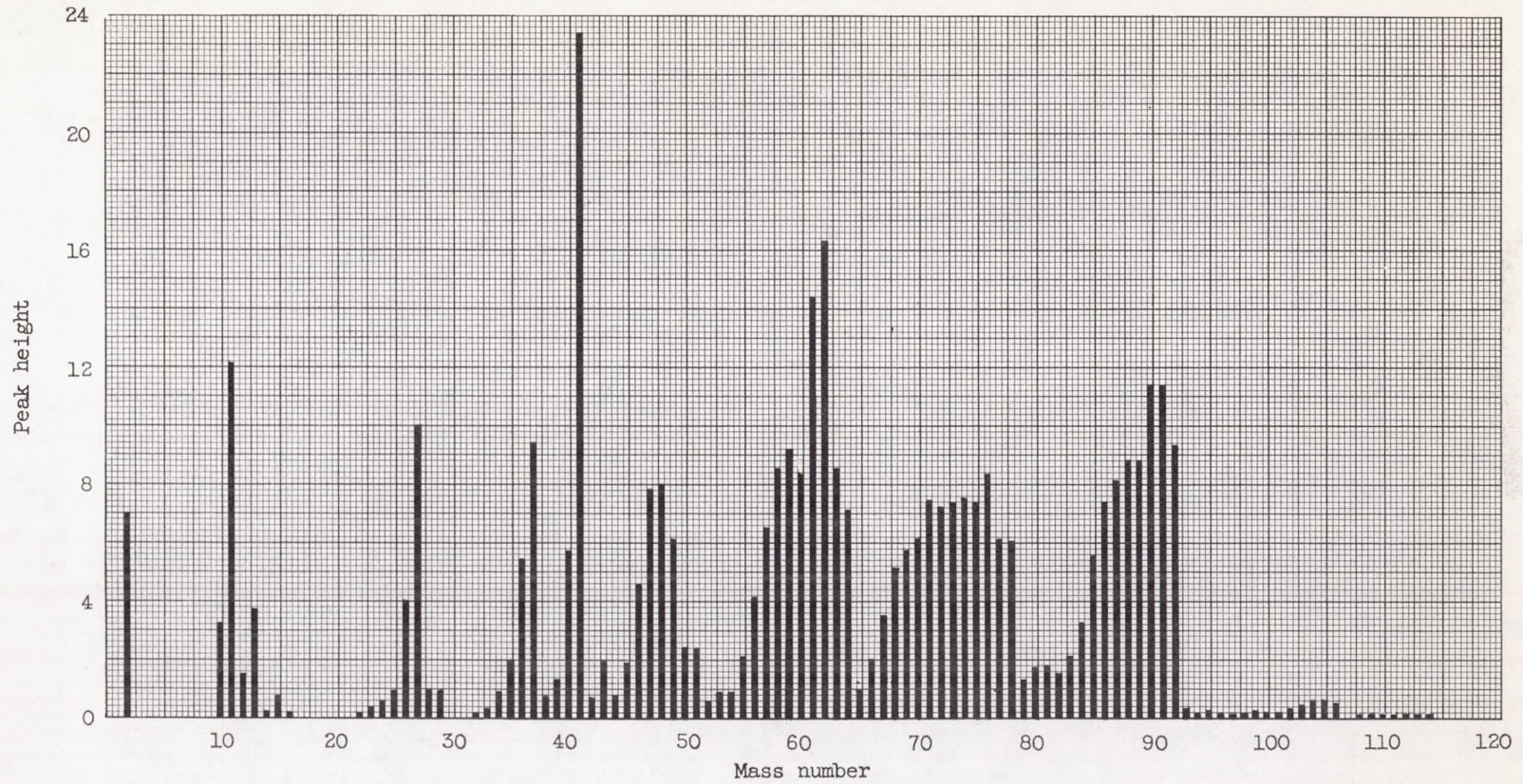
(a) Fraction 2 and 3.

Figure 5. - Mass spectra of fractions from run 12.



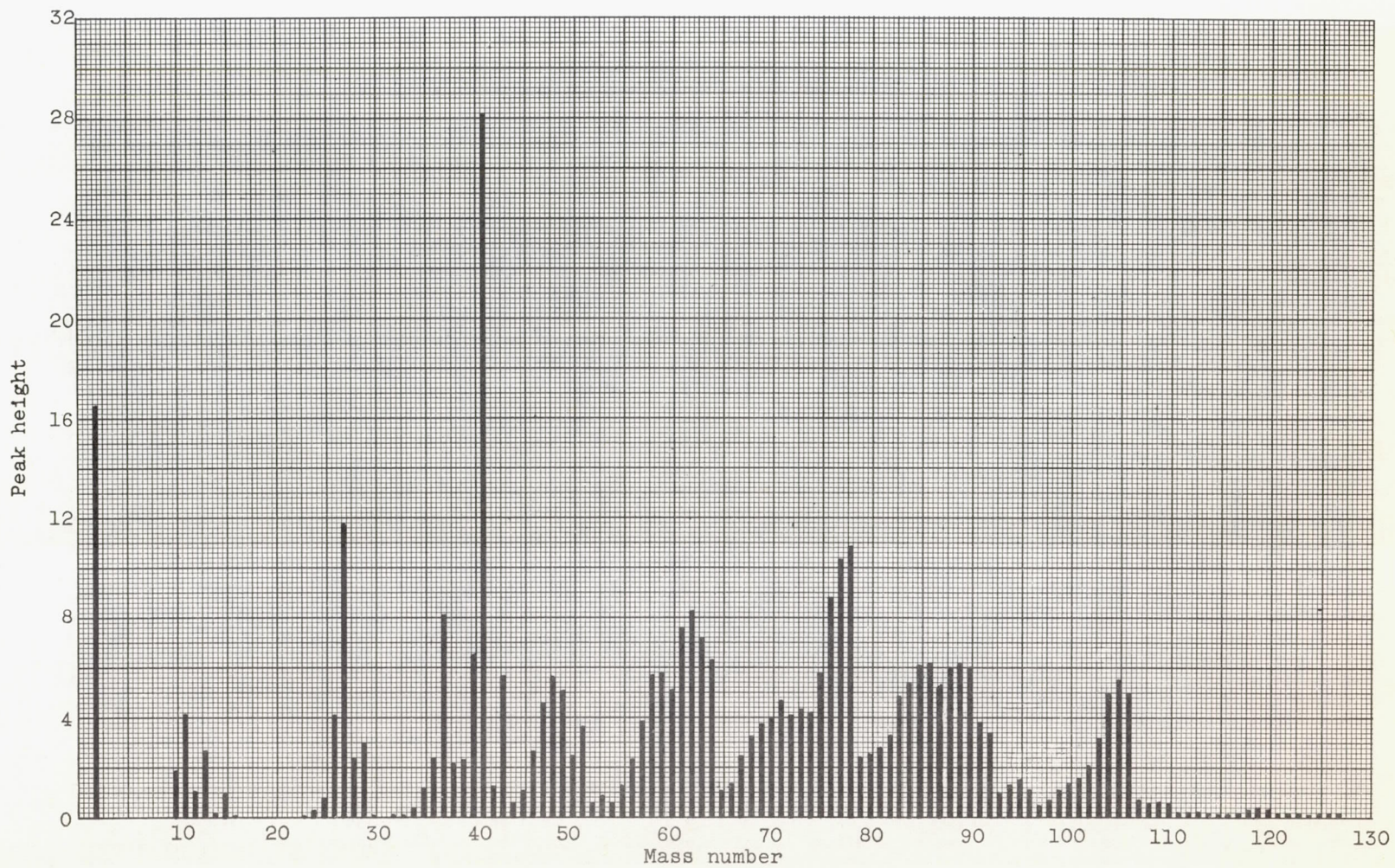
(b) Fraction 22 to 29.

Figure 5. - Continued. Mass spectra of fractions from run 12.



(c) Fraction 34.

Figure 5. - Continued. Mass spectra of fractions from run 12.



(d) Fraction 39.

Figure 5. - Concluded. Mass spectra of fractions from run 12.