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SYNTHESIS AND HYDROLYSIS-RATE STUDIES OF DECABORANE DERIVATIVES

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RESEARCH MEMORANDUM

SYNTHESIS AND HYDROLYSIS-RATE STUDIES OF DECABORANE DERIVATIVES

By D. Lucas and A. Lipschitz

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SUMMARY

A series of experiments involving the reaction of water with decaborane and HEF-3, a boron fuel consisting mainly of ethyldecaborane, was performed. The results show that the presence of one alkyl group on the decaborane nucleus inhibits the hydrolysis reaction significantly and that the hydrolysis rate can be increased by using an acidic hydrolysis mixture. Two diiododecaborane isomers were prepared for use as intermediates in proposed dimethyldecaborane syntheses, and their melting points, molecular weights, and solubilities in certain solvents were determined. No dimethyldecaborane resulted from the reaction between these iodo isomers and methyl magnesium bromide, methyl lithium, or methyl bromide.

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INTRODUCTION

One of the problems in using boron-containing fuels is that of storage and handling. Since most boron hydrides hydrolyze on exposure to water, specific knowledge of the hydrolysis reaction of a boron-containing fuel is desirable. Therefore, a series of hydrolysis experiments was performed at the NACA Lewis laboratory on HEF-3, a high-energy fuel consisting mostly of ethyldecaborane with some di- and triethyldecaborane. These experiments involved the reaction of HEF-3, or decaborane, and water in either dioxane or ethyl alcohol and were varied by the addition of sodium hydroxide and ferric chloride. In all cases, the volume of gas evolved with time was measured. It was concluded that more information could be obtained by repeating the hydrolysis with an alkylated decaborane in a more highly purified form than that of HEF-3.

The present methods of preparing alkyldecaboranes are such that the products are mixtures of mono-, di-, and trialkyldecaboranes with physical and chemical properties similar enough to make a complete separation difficult. This difficulty possibly might be avoided by using a halogenated decaborane as an intermediate. A compound such as diiododecaborane could be purified by recrystallization and then might react with an alkylating agent that would replace the halogens on the decaborane nucleus with alkyl groups.

Halogenated boranes have been known since Alfred Stock's original work on the boron hydrides in the 1920's. A diiododecaborane was first prepared in 1929 (ref. 1, p. 98). This preparation was repeated in 1955 by Gale and Wagner (ref. 2), and the structure and the melting point of the diiododecaborane were determined.

Since dimethyldecaborane is of interest not only for its hydrolysis reaction but also as a possible high-energy fuel, it was decided to attempt its synthesis by using diiododecaborane as an intermediate. Because boron hydrides have certain similarities to organic compounds in their reactions, the organic methylating agents methyl magnesium bromide, methyl lithium, and methyl bromide were selected as compounds that might be effective in preparing dimethyldecaborane.

HYDROLYSIS OF DECABORANE DERIVATIVES

Apparatus and Procedure

The apparatus used in all the hydrolysis experiments is shown in figure 1. The constant-temperature water bath was maintained at $35.8^{\circ} \pm 0.3^{\circ}$ C. The homogeneous hydrolyzing medium, which was varied as shown in table I, was introduced into the reaction flask, and 0.3 milliliter of HEF-3 (NACA fuel 55Z8) was added. In one experiment, 0.1806 gram of decaborane recrystallized from ethyl acetate was used instead of HEF-3. If HEF-3 is assumed to be 100 percent ethyldecaborane, this is comparing the reaction of 1.64×10^{-3} moles of HEF-3 with 1.476×10^{-3} moles of decaborane. The progress of the reaction was observed by measuring the volume of gas collected in the gas burette as a function of time. Corrections were made for the vapor pressure of the hydrolyzing mixture, and the data were reduced to standard temperature and pressure.

Results and Discussion

Table I lists the moles of gas per mole of boron hydride that were evolved in each of the hydrolysis reactions during running time and also gives an idea of the completeness of the reaction by comparing these results with the expected number of moles of gas. Analyses of the gas evolved during the hydrolyses of HEF-3 and decaborane have shown the presence of hydrogen only. The equation for the complete hydrolysis of decaborane may be written as follows:

$$B_{10}H_{14} + 30\ H_2O \rightarrow 10\ B(OH)_3 + 22\ H_2$$

If HEF-3 is assumed to be 100 percent ethyldecaborane, a similar equation may be written for its hydrolysis:

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$$C_2H_5B_{10}H_{13} + 29\ H_2O \rightarrow C_2H_5B(OH)_2 + 9\ B(OH)_3 + 21\ H_2$$

The rate of the hydrolysis reactions is shown by the slopes of the curves in figure 2(a), where the volume of gas evolved is plotted against time. Figure 2(b), which shows an expanded view of part of figure 2(a), may be used more readily to determine the initial rates. It will be noted that, in all the reactions, the rate reaches a break point after the first few hours and then decreases to a more gradual rate.

Hydrolysis of boron hydrides has been described as the addition of the nucleophilic portion of the water molecule to boron and the subsequent release of a hydrogen (ref. 3). The present data show that the rate of hydrolysis depends on the pH of the hydrolytic medium. The pH of each of the hydrolytic solutions is given in table I. In figure 3, the logarithms of the initial rates, taken as the initial slopes of the lines of figure 2, are plotted against pH. This plot may be expressed as

$$\text{Rate of hydrolysis} \propto (H^+)^k \qquad (1)$$

where the exponent k has a value of about 0.2.

The initial hydrolysis rate seems to be constant, since gas is evolved at a fairly constant rate during the initial reaction. Therefore, the rate apparently is independent of HEF-3 concentration and, if the hydrogen ion takes part only as a catalyst, its concentration does not change. This interpretation may be used to explain the occurrence of breaks in the lines of figure 2; the hydrolysis continues at a constant rate fixed by the hydrogen-ion concentration until all the HEF-3 is converted to a less reactive form. The less reactive form may result from attack and replacement at the single active-hydrogen site that probably remains in monoalkylated decaborane. (Decaborane itself has two especially active hydrogens (ref. 4), one of which is probably replaced by the ethyl group in ethyldecaborane.)

The curve for decaborane exhibits two break points, one at about 2 hours and the other at about $7\frac{1}{2}$ hours (fig. 2(a)). Since the decaborane molecule has two especially reactive hydrogens, the two break points may be due to the replacement of one of these, followed by attack on the second at a reduced rate.

This explanation of HEF-3 hydrolysis, which postulates the formation of a less reactive form of ethyldecaborane, also would seem to predict that equivalent amounts of gas would have evolved by the time the break point in the hydrolysis occurred; figure 2 shows that this is not the case. However, it may be significant that the extent of reaction, as shown in table I, roughly follows the same order of pH for the various hydrolytic media used in HEF-3 hydrolysis. It is evident that more work is required before the hydrolysis of decaborane derivatives can be fully understood.

Since the presence of one alkyl group on the decaborane nucleus inhibits the hydrolysis reaction, the preparation of a dialkyldecaborane was believed to be worthwhile in order to see if this resistance to hydrolysis increased with the number of alkyl groups. A pure alkylated boron hydride was also desired for such studies, inasmuch as the effects of impurities in HEF-3 on the hydrolysis rate were not known. Attempts accordingly were made to prepare dimethyldecaborane, as described in the following section.

BORON HYDRIDE SYNTHESIS

Preparation of Diiododecaborane

This synthesis of diiododecaborane is a repetition of Stock's original preparation (ref. 1, p. 98). A 2.1-gram (0.0171 mole) sample of decaborane was heated in a sealed 500-milliliter flask with 9.3 gram (0.0360 mole) of iodine for $19\frac{1}{2}$ hours at 110° C until only a small amount of iodine vapor was visible in the flask. The flask was opened, and the solid reaction product was extracted with 200 milliliters of carbon disulfide, treated with mercury to remove any unreacted iodine, and filtered to remove insoluble higher iodination products. The carbon disulfide was removed under vacuum, and the 5.9 grams of yellow solid residue was recrystallized from benzene to yield 0.3 gram of a yellow crystalline material that melted at 234° to 237° C. n-Heptane was added to the benzene solution, and 3.4 grams of yellow crystals melting at 135° to 140° C was obtained. Analysis of both samples for percent iodine agreed with that calculated for diiododecaborane, as shown in table II. Only the higher melting-point isomer has been reported previously (refs. 1 (p. 98) and 2).

Reactions of Diiododecaborane Isomers

With methyl magnesium bromide. - To a solution containing 7.1 grams of diiododecaborane (0.0190 moles; m.p., 135° to 140° C) in 200 milliliters of anhydrous ethyl ether, 21 milliliters of an ether solution of methyl magnesium bromide (0.0380 mole) were added gradually over a 1/2-hour period. During this time, gas steadily evolved from the solution. At first a finely divided white precipitate that settled to the bottom of the flask appeared, and the yellow color of the solution faded; a viscous yellow-brown mass gradually accumulated in the bottom of the flask. At the end of 1/2 hour, the contents of the flask were poured into a mixture of 100 milliliters of 6N HCl and 50 grams of ice; the viscous yellow-brown mass dissolved at this point. The ether layer, a slightly cloudy yellow-orange solution, was separated and dried over anhydrous calcium sulfate. The ether was evaporated under reduced pressure, and a flaky yellow solid remained. A carbon tetrachloride extraction of this solid showed that only a small amount of the solid was soluble in carbon tetrachloride.

This experiment was repeated with 2.7 grams of diiododecaborane (0.0072 mole; m.p., 234° to 237° C) and 8 milliliters of an ether solution of methyl magnesium bromide (0.0152 mole). The reaction and the results observed were the same as those described for the low-melting-point isomer; only a yellow solid was recovered from the reaction mixture on evaporation of the solvent.

With methyl lithium. - A solution containing 5.5 grams of diiododecaborane (0.0015 mole; m.p., 135° to 140° C) in 200 milliliters of anhydrous ethyl ether was prepared, and an ether solution of methyl lithium was made from methyl bromide and lithium according to the method of Gilman and Jones (ref. 5, ch. 7). Then 22.0 milliliters of this methyl lithium solution (0.00294 mole) were added to the diiododecaborane solution over a period of 20 minutes, and the resulting solution was refluxed for 1 hour. A white precipitate formed during the addition of the methyl lithium solution, and gas evolved steadily. The ether was distilled off under reduced pressure and a solid pale yellow residue was left. No liquid product was obtained.

This experiment was repeated with 0.2 gram of diiododecaborane (m.p., 234° to 237° C) and 2 milliliters of the methyl lithium solution. This reaction followed the same pattern as that of the low-melting-point isomer but resulted in the formation of a colorless reaction mixture and a white residue.

With methyl bromide. - No visible reaction occurred when 1.9 grams of diiododecaborane (0.00508 mole; m.p., 135° to 140° C) and 1.5 grams of methyl bromide (0.0158 mole) were heated in a 520-milliliter flask at 110° C for a total time of 46 hours.

Results and Discussion

No difficulty arose during the preparation of diiododecaborane. The results of the melting-point, molecular-weight, and percent-iodine determinations made on the two diiododecaborane isomers are given in table II, and the results of certain solubility determinations are presented in table III. The lower melting-point isomer was much more soluble in all the solvents tried than the high melting-point isomer.

Dimethyldecaborane is a colorless liquid with the consistency of a light oil at room temperature (ref. 6). No liquid product was isolated in any of the reactions between the diiododecaborane isomers and methyl magnesium bromide, methyl lithium, or methyl bromide. Since the synthesis of dimethyldecaborane was the principal interest, no organized efforts were made to determine what the solid reaction products were.

CONCLUDING REMARKS

Hydrolysis-rate experiments conducted on decaborane and HEF-3 showed that the rate of HEF-3 hydrolysis varies with the pH of the hydrolytic medium and is the highest in ferric chloride and water, somewhat less in water, and least in a sodium hydroxide solution.

Two diiododecaborane isomers are formed when iodine and decaborane are reacted together, one melting at 135° to 140° C, and the other at 234° to 237° C. The higher melting-point isomer is the only one previously reported.

Under the conditions used, dimethyldecaborane cannot be prepared by a reaction between either of the diiododecaborane isomers and methyl magnesium bromide, methyl lithium, or methyl bromide.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, August 8, 1957

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TABLE I. - EXTENT OF HYDROLYSIS OF BORON HYDRIDE FUELS IN VARIOUS HYDROLYTIC MEDIUMS

Fuel	Hydrolytic medium		pH Of hydrolytic medium	Duration of experiment, hr	Moles gas per mole fuel	Extent of reaction, percent
0.3 ml HEF-3	5 ml 5N NaOH	25 ml ethyl alcohol	11.2	25	0.242	1.2
	5 ml H_2O	25 ml dioxane	5.7	48	1.35	6.2
	5 ml H_2O	25 ml ethyl alcohol	7.6	40	1.353	6.5
	5 ml H_2O,0.5g $FeCl_3 \cdot 6H_2O$	25 ml dioxane	2.2	72	5.28	25.2
0.1806g $B_{10}H_{14}$	5 ml H_2O	25 ml dioxane	2.2	40.7	14.91	68.2

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TABLE II. - PROPERTIES OF DIIODODECABORANE ISOMERS

Property	Low-melting-point isomer	High-melting-point isomer	Calculated value
Melting point	135°-140° C	234°-237° C	-----
Molecular weight	[a]305	382	374.1
Percent iodine	70.5	68.5	67.8

[a] Probably low because of decomposition of sample.

TABLE III. - ORDER OF SOLUBILITY OF DIIODODECABORANE ISOMERS IN VARIOUS SOLVENTS

Solvent	Remarks
Acetone	Soluble with decomposition
95 Percent ethanol	Soluble with decomposition
Benzene	
Ether	
Carbon disulfide	
Chloroform	
Carbon tetrachloride	
n-Heptane	

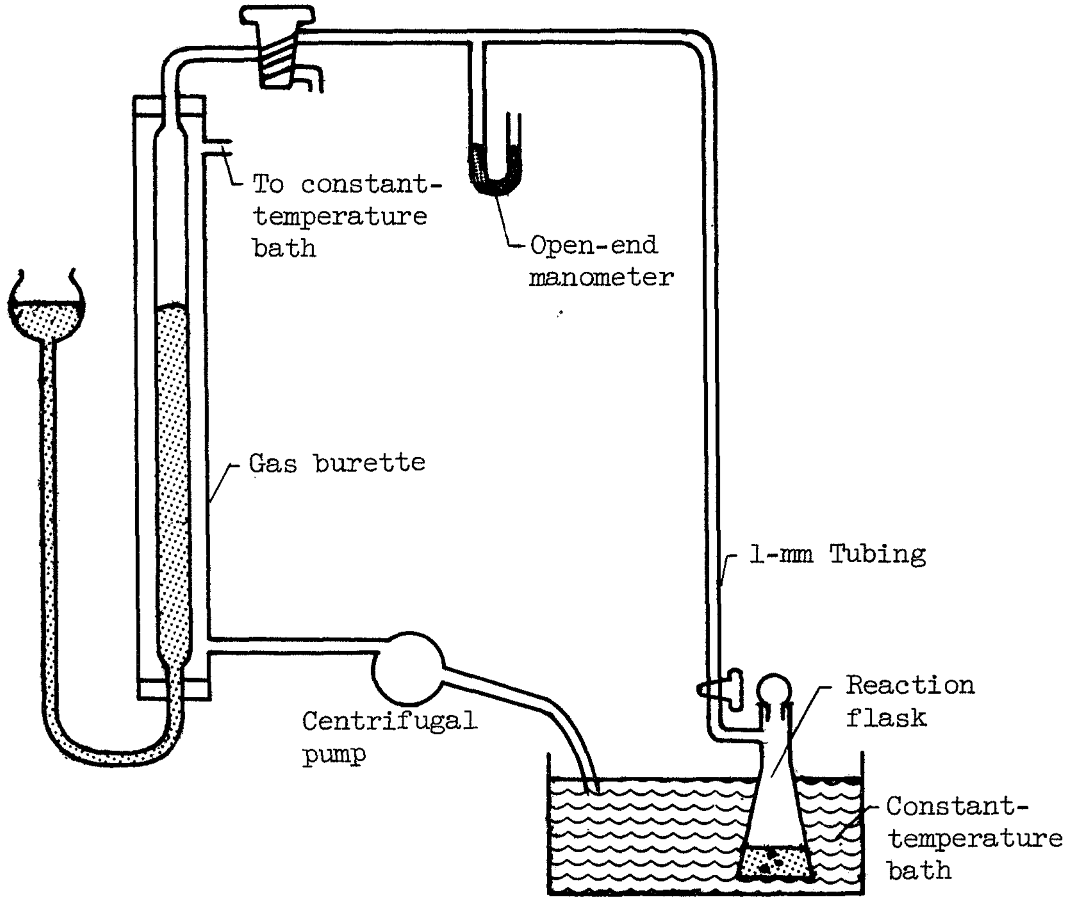

Figure 1. - Hydrolysis apparatus.

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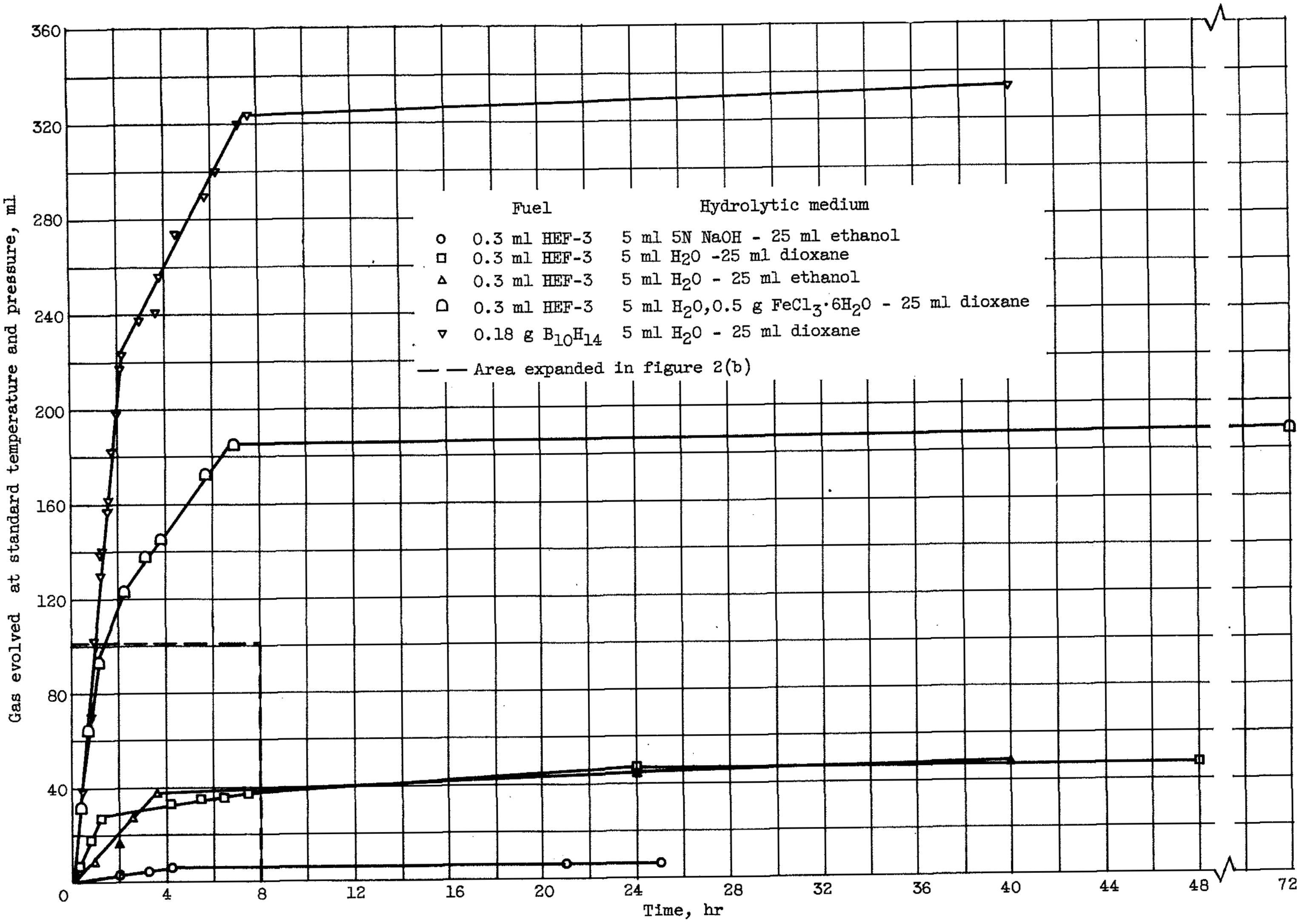

(a) Complete plot of data.

Figure 2. - HEF-3 and decaborane hydrolysis.

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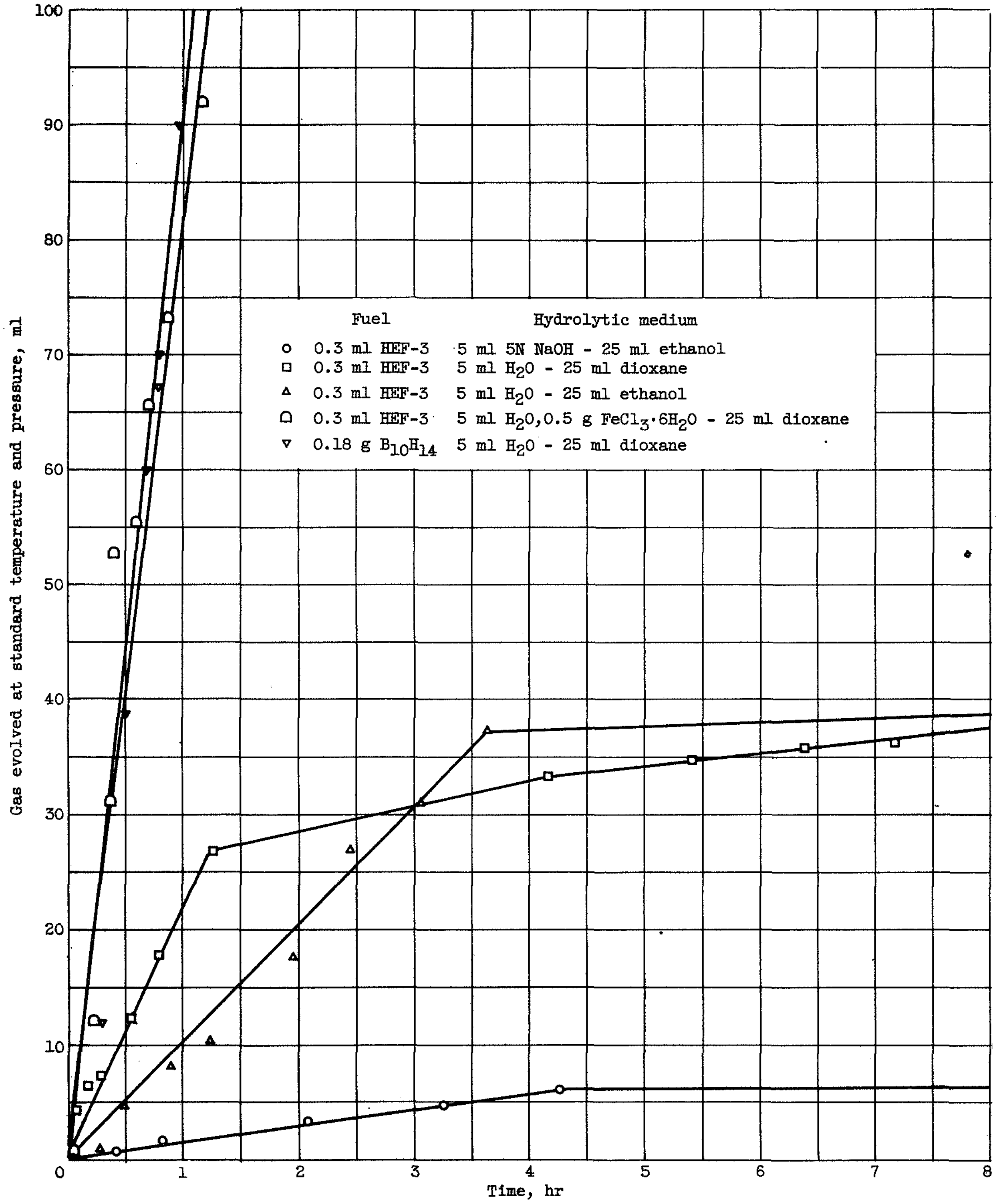

(b) Expansion of dotted-line area, figure 2(a).

Figure 2. - Concluded. HEF-3 and decaborane hydrolysis.

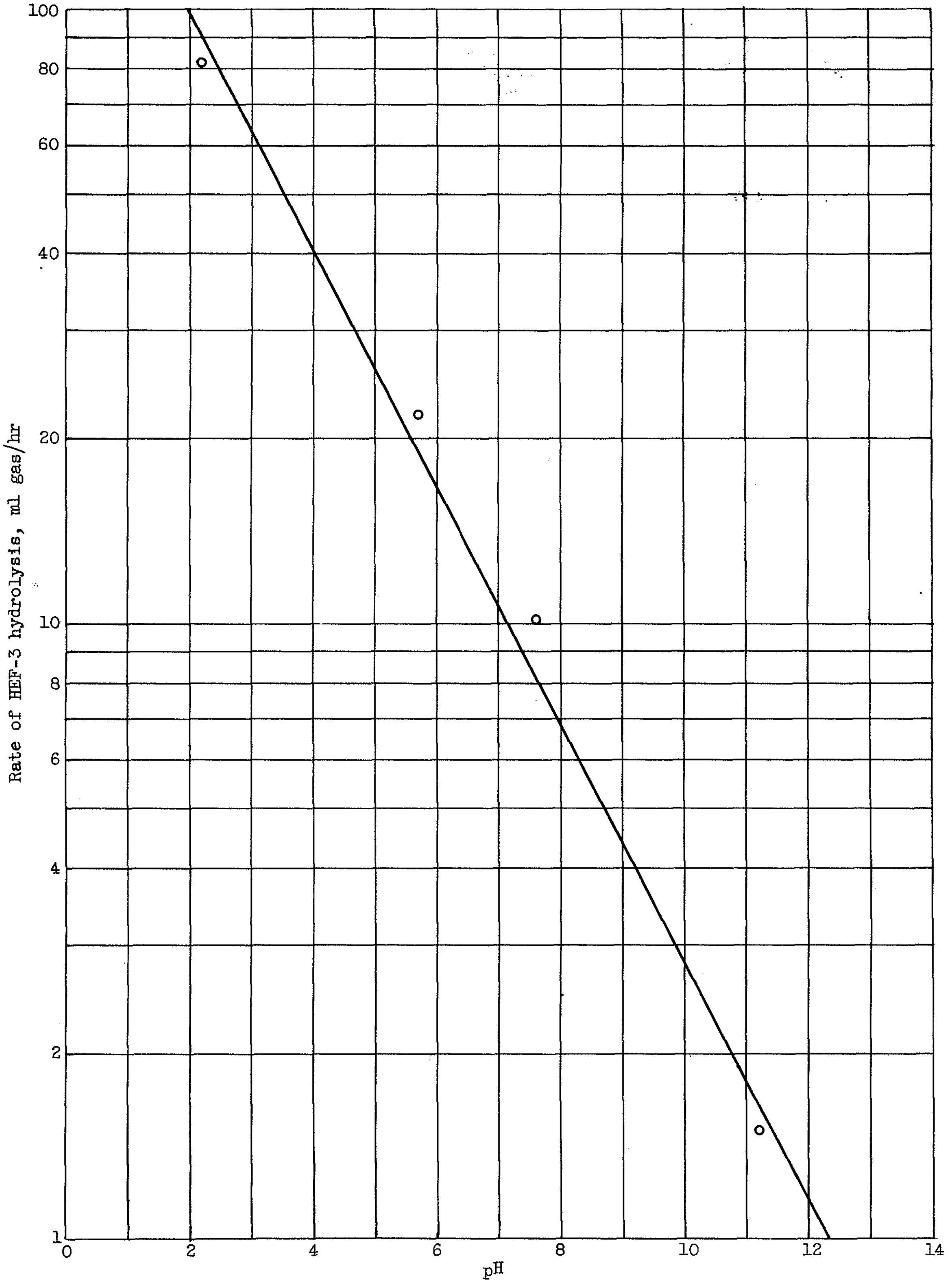

Figure 3. - Variation of rate of HEF-3 hydrolysis with pH.

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