NACA

RESEARCH MEMORANDUM

THERMAL DECOMPOSITION OF ETHYLPENTABORANE IN GAS PHASE

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THERMAL DECOMPOSITION OF ETHYLPENTABORANE IN GAS PHASE

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SUMMARY

The thermal stability of gaseous ethylpentaborane was investigated at temperatures from 185° to 244° C. The products of the decomposition were hydrogen, methane, a nonvolatile boron hydride, and traces of decaborane. From experiments at various concentrations it was determined that the reaction was approximately 1.5-order. Reaction-rate constants were determined for the initial reaction at each temperature investigated. A linear correlation was found for the effect of temperature on the initial rate of decomposition. Measurements were made of the rate of decomposition of pentaborane under conditions similar to those used with ethylpentaborane. It was determined that the ethylpentaborane had a greater rate of decomposition than pentaborane.

Using the following equation yields the 1.5-order-rate constant for ethylpentaborane at temperatures intermediate between those measured:

$$\log k = -\frac{1.0 \times 10^4}{T} + 14.9$$

where k is the reaction constant (sec^{-1} $cm^{-0.5}$ Hg), and T is the temperature (°K).

INTRODUCTION

As a continuation of the study of the thermal stability of boron hydrides, the previous investigation of the stability of pentaborane (ref. 1) has now been extended to ethylpentaborane. The alkylboranes are of interest in aircraft propulsion because of the possibility that their chemical properties, such as inflammability and toxicity, and their physical properties, such as volatility and melting point, would be more desirable than those of the boranes. The work was initiated on ethylpentaborane, because this was the first alkylborane other than the alkyldiboranes that was available in purified form.

In the present work the thermal decomposition of ethylpentaborane
has been measured at temperatures from 185° to 244° C. The order of the
reaction has been determined, and the rate of thermal decomposition of
the ethylpentaborane has been compared with that of pentaborane.

APPARATUS AND PROCEDURE

The ethylpentaborane after degassing was distilled into an evacuated
reaction vessel 15 centimeters long and 4.5 centimeters in diameter, and
then sealed off. The reaction vessel was open to a capillary-bore mercury
manometer. The manometer was wound with resistance wire and heated to
avoid condensation of ethylpentaborane. The reaction vessel was immersed
in an oil bath equipped with thermostat, which was electrically heated.
Temperatures were measured with a thermocouple, and decomposition was
measured by noting the change in pressure indicated by the mercury manom-
eter. A diagrammatic sketch of the apparatus is shown in figure 1.

RESULTS AND DISCUSSION

The rate of pyrolysis of ethylpentaborane was measured as a function
of time at the temperatures 185°, 196°, 218°, and 244° C. For purposes
of comparison the rate of pyrolysis of pentaborane was measured at the
temperatures of 218° and 244° C. The results for these decompositions
are shown in figures 2 to 4 where the total pressure is plotted against
time. At several temperatures the reaction was carried until near com-
pletion. The results indicate a smooth reaction without a pronounced in-
duction period or an autocatalytic effect.

In order to determine the characteristics of the reaction, each ex-
periment at each temperature was plotted as a first-order reaction as
shown in figure 5 where the log of the ratio of the initial pressure to
the pressure of the remaining ethylpentaborane $\log \frac{P^o_{EP}}{P^t_{EP}}$ is plotted against
time. The symbols in figure 5 correspond to the symbols used in figures
2 to 4. The pressure of the remaining ethylpentaborane is calculated
from the following equation:

$$P = P^o_{EP} - P^t_{EP} + 2.5\ P^t_{EP}$$

where P is the total pressure, P^o_{EP} is the initial total pressure of
ethylpentaborane, and P^t_{EP} is the pressure at any time during the decom-
position of ethylpentaborane. It was determined from experiments, which
approached complete decomposition, that the final pressure was approximate-
ly 2.5 times the initial pressure. At least the initial portion of such

plots may be approximated by a straight line, except at a temperature of 244° C where the deviation from a first-order plot starts at a low percentage of decomposition. The slope of the line gives a rate constant for the reaction; this pseudo-constant is expressed in first-order terms and is designated by k'.

From separate calculations, based on the dependence of the rate of total-pressure increase $\log \frac{dP^O}{dt}$, on the initial pressure of ethylpentaborane $\log P^O$, it was determined that the initial reaction was approximately a 1.5 order. Therefore, the pseudo-constants k' were converted to 1.5-order constants by dividing them by the square root of the initial pressure of ethylpentaborane. The values of these derived rate constants, designated by k, at various temperatures are shown in table I. The correlation of these values of k with the temperature is shown in figure 6 where the reciprocal of the temperature is plotted against the average of the logs of the rate constants, $\log k$.

In order to compare the rate of decomposition of ethylpentaborane with the decomposition of pentaborane, the decomposition of the pentaborane was measured at 244° and 218° C. The plots of the total pressures of pentaborane against time are shown in figures 3, 4(a), and 4(b). The plots of the reactions as first-order reactions are shown in figures 5(c) and 5(d).

The values for the 1.5-order reaction-rate constants for pentaborane, which are obtained by conversion of the pseudo-first-order constants, are shown in table I. The variation with temperature is shown in figure 6.

When the results for ethylpentaborane and pentaborane are compared, it appears that at any temperature, within the range of this investigation, the rate of decomposition of ethylpentaborane is greater than the rate of decomposition of pentaborane. Moreover, the rate of decomposition of ethylpentaborane increases more slowly with an increase in temperature than the rate of decomposition of pentaborane.

From the slope of the line in figure 6 an activation energy of 45.5 kilocalories per mole was calculated for the ethylpentaborane decomposition. From the following expression, the 1.5-order reaction-rate constant may be estimated at other temperatures:

$$\log k = -\frac{1.0 \times 10^4}{T} + 14.9$$

where k, the reaction-rate constant, is expressed in sec^{-1} $cm^{-0.5}$ of mercury and T is expressed in degrees Kelvin.

The products of the reaction consisted of hydrogen, methane, high-molecular-weight boron hydrides, and traces of decaborane. Infrared analysis of the gaseous products showed only methane. Vapor-pressure measurements also indicated the presence of methane. Ethane, which might be expected as a decomposition product, was not detected in the infrared analysis. The high-molecular-weight boron hydrides were light yellow, nonvolatile solids that decomposed before they melted. A small amount of decaborane could be isolated by careful distillation of the reaction products.

CONCLUSIONS

The results indicate that the ethylpentaborane gas-phase pyrolysis proceeds as a 1.5-order reaction that has an over-all activation energy of 45.5 kilocalories per mole.

The over-all reaction may be formulated as follows: ethylpentaborane $\rightarrow$ high-molecular-weight hydrides $+ H_2 + CH_4 +$ traces of $B_{10}H_{14}$. The sum of the hydrogen and methane pressures is about 2.5 times greater than the initial pressure of ethylpentaborane. The results indicate that, over the ranges of temperature and concentration investigated, ethylpentaborane is less stable than pentaborane.

Lewis Flight Propulsion Laboratory
    National Advisory Committee for Aeronautics
        Cleveland, Ohio, April 26, 1956

REFERENCES

1. McDonald, Glen E.: The Rate of Decomposition of Liquid Pentaborane from 85° to 202° C. NACA RM E55H01, 1955.

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TABLE I. - RATE CONSTANTS OF ETHYLPENTABORANE AND PENTABORANE

AT VARIOUS TEMPERATURES

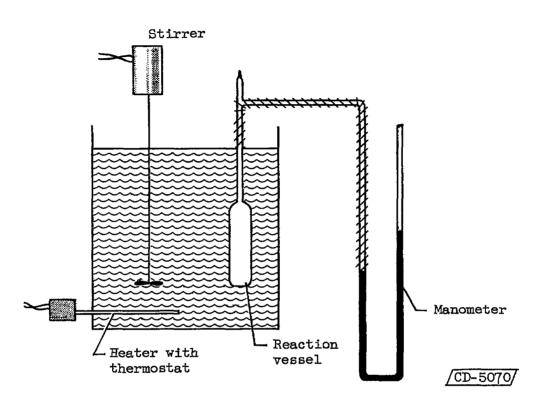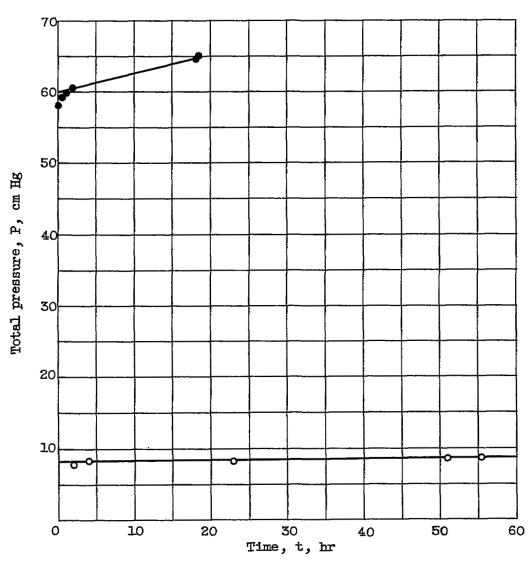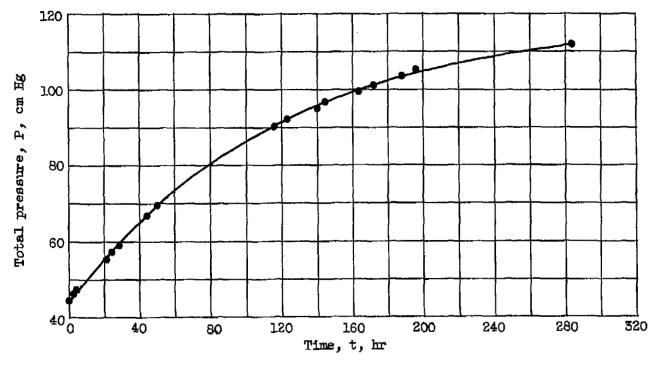| Temperature, T, $^{\circ}C$	Reciprocal of temperature, $(1/T)$, $^{\circ}K^{-1}$	Pressure, cm	Pseudo-constants, k', sec^{-1}	Reaction constant, k, $sec^{-1}\ cm^{-0.5}\ Hg$	Log of rate constants, $\log k$
Ethylpentaborane					
185	2.18×10^{-3}	7.9	3.3×10^{-7}	1.2×10^{-7}	-6.92
		59.5	9.6×10^{-7}	1.2×10^{-7}	-6.92
196	2.13	24.3	2.2×10^{-6}	4.5×10^{-7}	-6.35
		45.0	2.6×10^{-6}	3.9×10^{-7}	-6.41
		98.0	3.2×10^{-6}	3.2×10^{-7}	-6.49
218	2.04	18.0	9.2×10^{-6}	2.2×10^{-6}	-5.72
		46.0	1.5×10^{-5}	2.2×10^{-6}	-5.66
		65.0	1.8×10^{-5}	2.2×10^{-6}	-5.66
		80.9	2.1×10^{-5}	2.3×10^{-6}	-5.64
244	1.94	35.0	1.8×10^{-4}	3.0×10^{-5}	-4.52
		70.0	2.4×10^{-4}	2.9×10^{-5}	-4.54
Pentaborane					
218	2.04×10^{-3}	139.1	4.6×10^{-6}	3.9×10^{-7}	-6.41
244	1.94	37.0	6.5×10^{-5}	1.1×10^{-5}	-4.95
		118.6	1.3×10^{-4}	1.2×10^{-5}	-4.92

Figure 1. - Apparatus.

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(a) Temperature, 185° C.

Figure 2. - Variation of total pressure of ethylpentaborane
with time at various temperatures.

(b) Temperature, 196° C.

Figure 2. - Continued. Variation of total pressure of ethylpentaborane
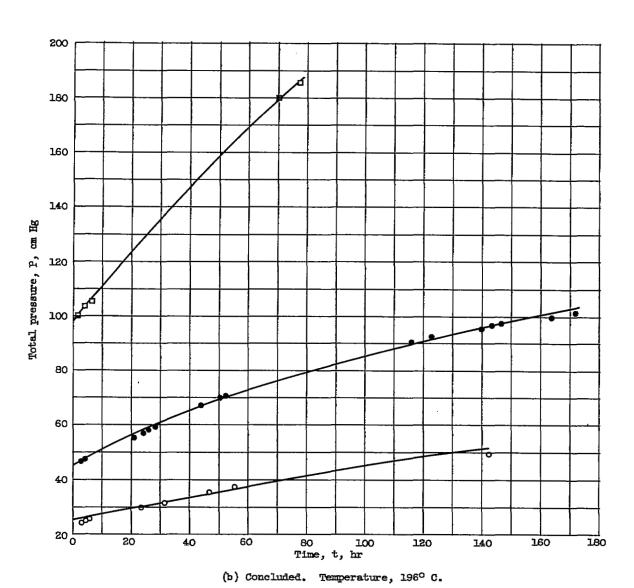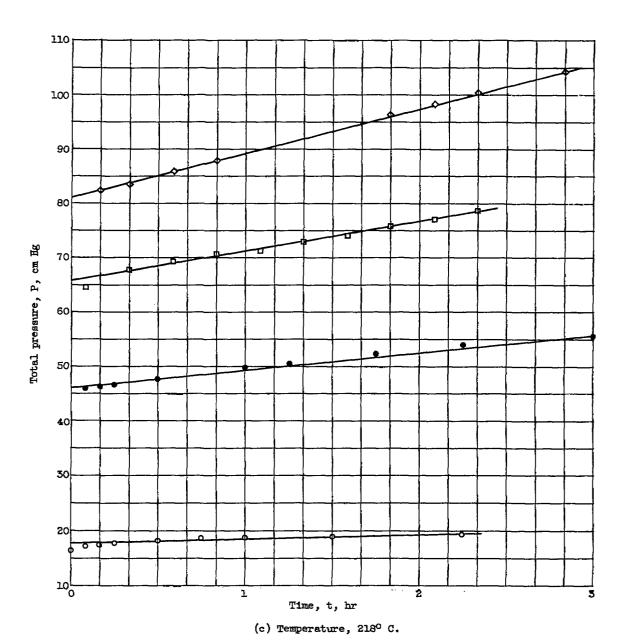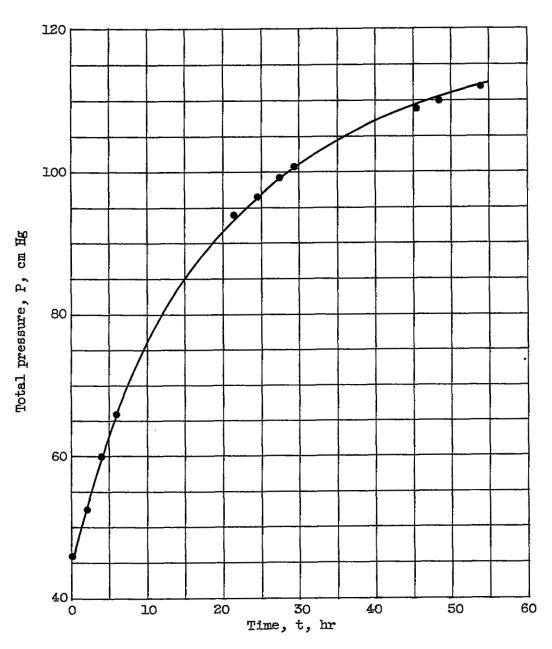with time at various temperatures.

(b) Concluded. Temperature, 196° C.

Figure 2. - Continued. Variation of total pressure of ethylpentaborane with time at various temperatures.
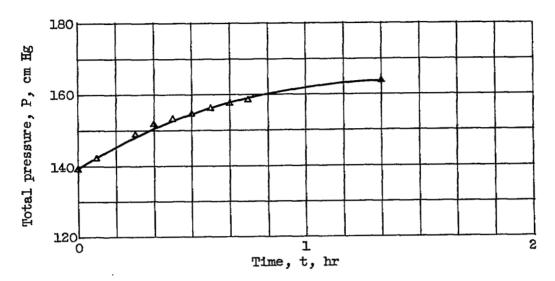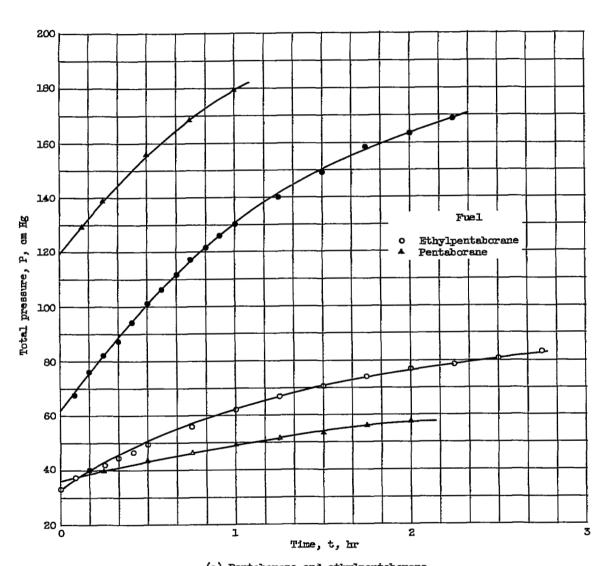
(c) Temperature, 218° C.

Figure 2. - Continued. Variation of total pressure of ethylpentaborane with time at
   various temperatures.

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(c) Concluded.   Temperature 218° C.

Figure 2. - Concluded. Variation of total pressure of
ethylpentaborane with time at various temperatures.

Figure 3. - Variation of total pressure of pentaborane
with time at temperature of 218° C.

(a) Pentaborane and ethylpentaborane.

Figure 4. - Variation of total pressure with time at a temperature of 244° C.

(b) Pentaborane.
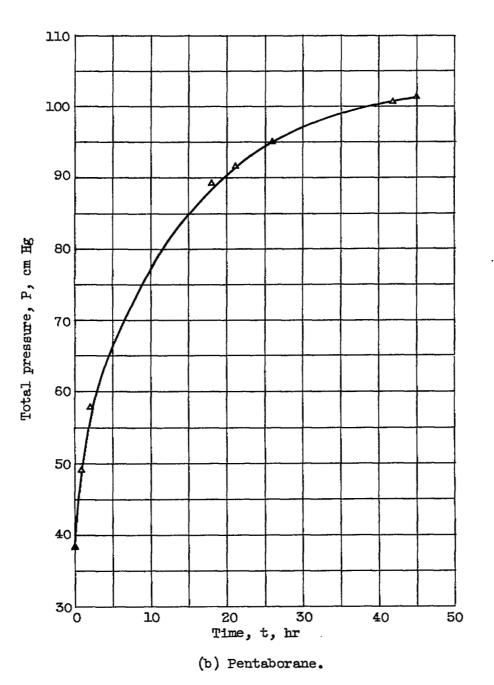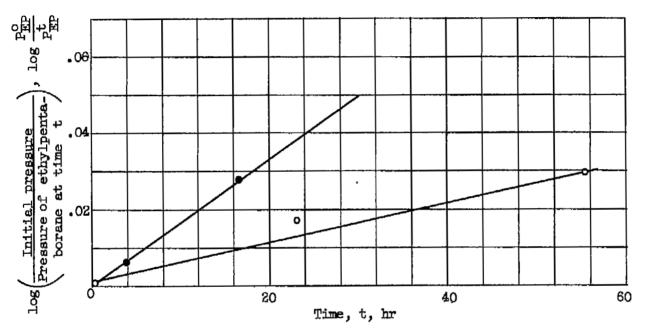
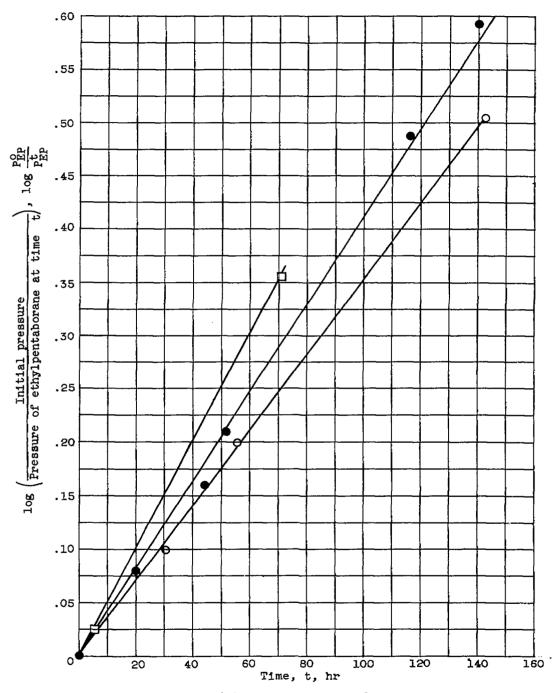Figure 4. - Concluded.   Variation of total pressure with time at a temperature of 244° C.

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(a) Temperature, 185° C.

Figure 5. - Log of reciprocal of remaining ethylpentaborane fraction plotted against time at various temperatures.

(b) Temperature, 196° C.

Figure 5. - Continued. Log of reciprocal of remaining ethyl-
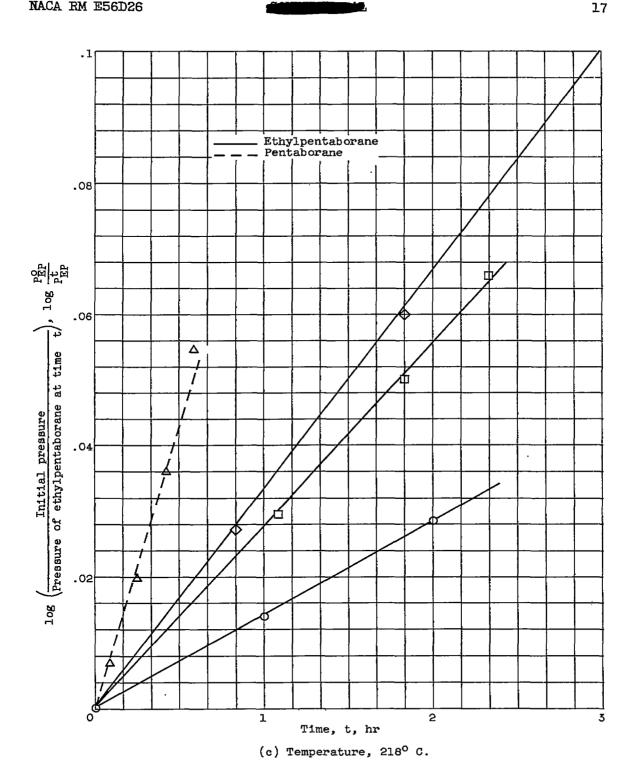pentaborane fraction plotted against time at various
temperatures.

(c) Temperature, 218° C.

Figure 5. - Continued. Log of reciprocal of remaining ethylpentaborane fraction plotted against time at various temperatures.

(c) Concluded. Temperature, 218° C.
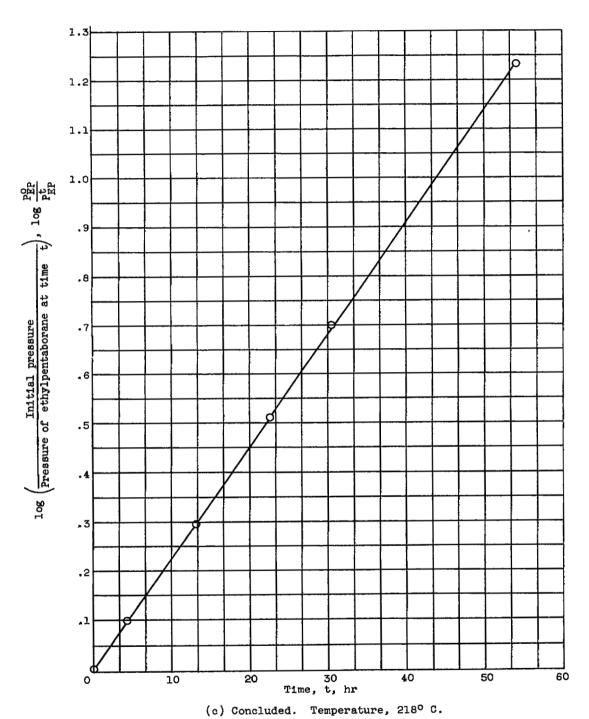
Figure 5. – Continued. Log of reciprocal of remaining ethylpentaborane
fraction plotted against time at various temperatures.
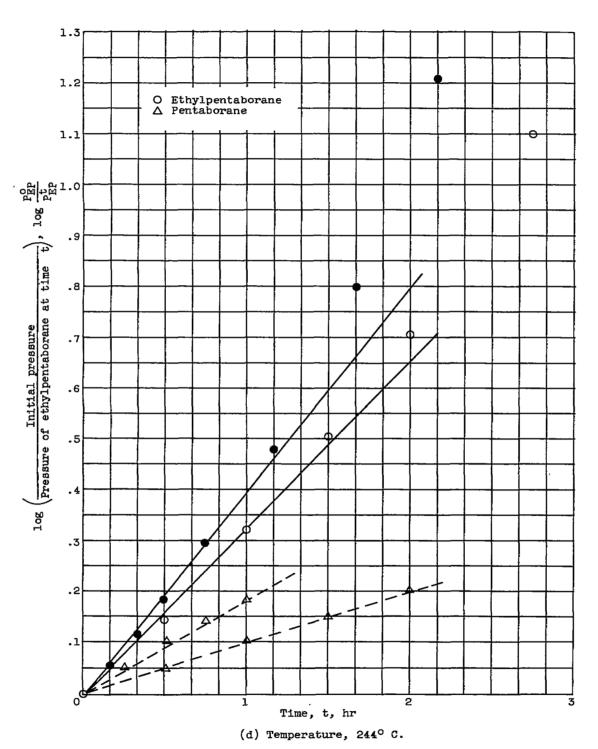
(d) Temperature, 244° C.

Figure 5. - Concluded. Log of reciprocal of remaining ethylpentaborane
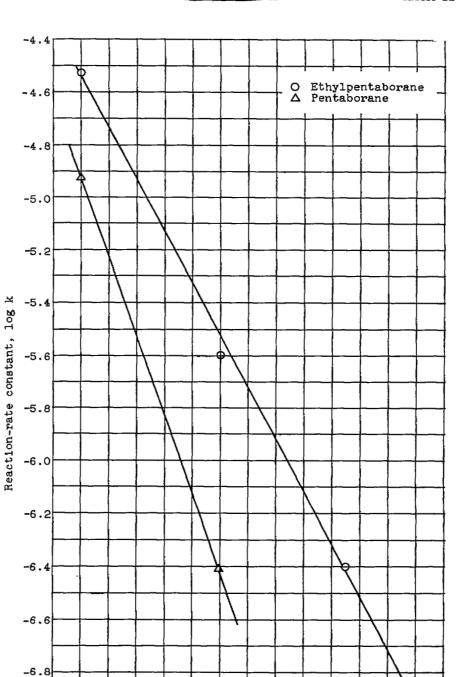fraction plotted against time at various temperatures.

Figure 6. - Correlation of rate constant with temperature.