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A RESEARCH PROGRAM FOR UNDERSTANDING THE MECHANISMS OF FLAME INHIBITION

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By Monsanto Research Corporation, Dayton, Ohio
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FOREWORD

This report was prepared under Contract AF 33(657)-10304, "A Research Program for Understanding the Mechanisms of Flame Inhibition." The contract was initiated under Project No. 6075, Task No. 607505, by the Aeropropulsion Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with B. P. Botteri as project engineer.

The work was performed during the period 15 November 1962 - 15 January 1964 at the Dayton Laboratory of Monsanto Research Corporation. Dr. G. B. Skinner was project leader, and Drs. A. D. Snyder and G. H. Ringrose have worked with him.

The assistance of G. A. Clienhens, D. L. Zanders, J. F. Moon, and J. V. Pustinger is gratefully acknowledged.

ABSTRACT

The effects of inhibitors on the diborane-air and pentaborane-air reactions were studied by measuring flame speeds of borane-air-inhibitor mixtures at low pressures, and by the shock tube technique. The best flame inhibitors were the hydrocarbons and halogenated hydrocarbons which had been found earlier to inhibit hydrogen-air flames. Some of these inhibitors were ineffective in lengthening ignition delays in the shock tube, indicating that a different mechanism may apply in flame propagation than in shock ignition.

Detailed kinetic calculations of the effects of CH_4, C_2H_4, CF_3Br and $C_2F_4Br_2$ on the hydrogen-oxygen reaction have yielded values for the rate constants of the reactions whereby these inhibitors remove H atoms from the reacting system.

PUBLICATION REVIEW

This report has been reviewed and is approved.

For the Commander:

Ross J. Gafvert

ROSS J. GAFVERT, Chief
Support Techniques Branch
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A RESEARCH PROGRAM FOR UNDERSTANDING THE MECHANISMS OF FLAME INHIBITION

1. SUMMARY

The aim of the major part of this research has been to obtain fundamental understanding of combustion and extinguishment for the diborane-air and pentaborane-air reactions. Chemical agents that extinguish the flames by inhibiting the combustion process were considered. Since the elementary steps in uninhibited combustion are not well known for these flame systems, a considerable part of the overall effort was devoted to studying uninhibited combustion.

Pyrolysis of diborane and pentaborane were studied in the shock tube. For both compounds the overall reaction was first-order. Pentaborane was the more stable of the two. The activation energy for diborane pyrolysis was 25,000 cal., about the same as was found in experiments at lower temperatures by other workers, suggesting that the same mechanism may apply. The activation energy for pentaborane pyrolysis was 13,600 cal.

Ignition induction times for diborane- and pentaborane-oxygen-argon mixtures were measured. Since the induction times were independent of oxygen concentration, and the activation energies close to those for pyrolysis, it appears that pyrolysis is the rate-controlling step in ignition. Shock tube ignition of pentaborane-oxygen-argon mixtures required slightly higher temperatures than those containing diborane, although static bulb experiments have previously indicated that pentaborane is more flammable than diborane.

Three additives, methane, butadiene and 1, 2-dibromotetrafluoroethane did not inhibit combustion of diborane in the shock tube. Butadiene and toluene inhibited combustion of pentaborane, while 1, 2-dibrometetrafluoroethane did not.

Diborane- and pentaborane-air flames were studied at low pressures, both with and without inhibitors. The maximum flame speeds at 10 mm pressure occurred at equivalence ratios just over one (a slight excess of borane in the flame).

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Maximum speeds were 1000 cm/sec for diborane-air and 700 cm/sec for pentaborane-air. These values decreased to about half at atmospheric pressure. Of some 30 gaseous and vaporized liquids tested as inhibitors, butadiene and toluene were the most effective in both boranes, 2% of additive in the fastest-burning borane-air mixture decreasing the flame speed to one-third of the uninhibited value. Several other additives had significant but somewhat smaller effects on the flame speeds. The fact that the most effective additives are also effective in inhibiting the hydrogen-oxygen reaction by removing hydrogen atoms suggests that diborane-air flames are propagated by a mechanism somewhat like that of the hydrogen-oxygen reaction, although shock tube ignition appears to occur by a different mechanism.

The spectrum of the diborane-air flame showed the presence of BH, BO and B_2O_3, all products of the later stages of combustion. Emission spectroscopy has not proved useful in our inhibition studies, since it does not reveal the intermediates present in the early stages of the combustion process, that are responsible for flame propagation.

Computer calculations relating the ignition induction times of hydrogen-oxygen-inhibitor mixtures, observed in an earlier phase of the inhibition programs, to elementary free-radical reactions have been completed. These calculations show how these inhibitors interact with the combustion mechanism to slow the overall combustion process.

A survey of the literature on the combustion of boranes is included as an appendix.

2. INTRODUCTION

The major portion of the research described here was undertaken to discover what chemicals inhibit the diborane- and pentaborane-oxygen reactions, and to study the mechanisms of the inhibition processes. We have been chiefly interested in gas phase inhibition, and therefore have used experimental techniques (shock tube and burner flames) in which the effects of solid surfaces are at a minimum.

In a smaller portion of the research, quantitative kinetic calculations were carried out to correlate data obtained earlier on the inhibition of the hydrogen-oxygen reaction by several additives. Although such calculations are time-consuming, they are important in establishing inhibition mechanisms.

3. APPARATUS

3.1 Shock Tube The shock tube (Figure 1) is of the single-pulse type, first described by Glick, Squire and Hertzberg (Ref. 1). The reaction and driver sections were made from 3-inch stainless steel pipe, the former being 12 feet long and the latter variable between 6 and 28 feet. The expansion tank was 3 feet in diameter and 8 feet long. Thin plastic diaphragms (f, Figure 1) separated the sections, while "O" ring seals were used throughout, so the sections could be individually evacuated or pressurized.

For measuring the shock speed, SLM pressure transducers (a and b) spaced 4 feet apart near the downstream end of the reaction section were used. Two identical trigger circuits amplified the transducer signals, while thyratron elements with manual reset assured that only one signal was emitted from each amplifier in an experiment. The amplifier signals were used to start and stop a timer accurate to one microsecond (Hewlett-Packard, type 523-B), and also to start two oscilloscopes. One recorded the pressure as indicated by SLM pressure transducer (c), while the other recorded the output from a photomultiplier tube in spectroscopic experiments. A quartz window (d), also 3 inches from the end, was used for these measurements. A small tube directly below SLM gage (c) led to a quick opening valve from which gas samples could be drawn for analysis.

Gas mixtures to be studied were made up beforehand by pressure. Argon and oxygen (Air Reduction Co.), diborane (Callery Chemical Co.), and other gases (Matheson Co.) were used

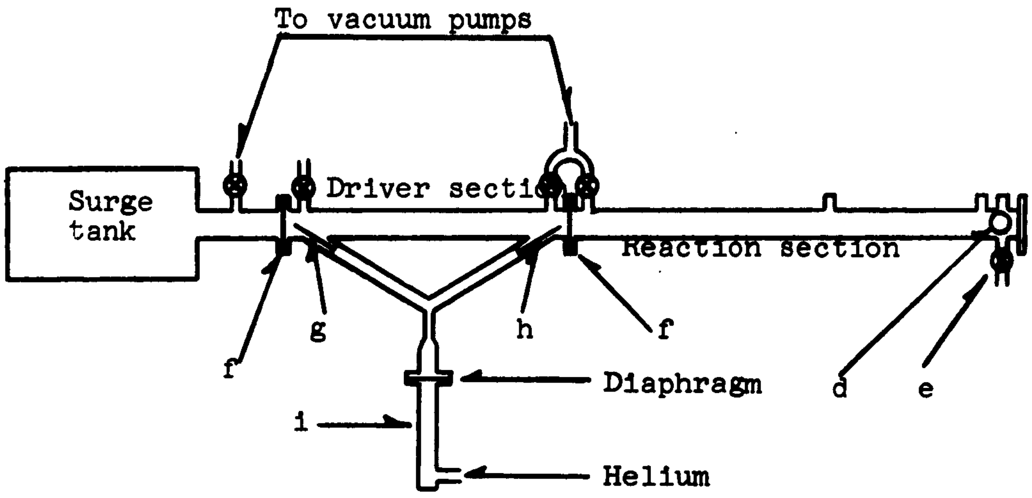


Figure 1. Schematic drawing of shock tube

without further purification. Gas samples were analyzed for hydrogen and helium by a vapor chromatograph of Monsanto design, which had a detection limit of about 30 ppm. Even though the driver gas was in direct contact with the sample gas during the experiment, never more than 2%, usually less than 1%, driver gas was found in the sample after the run. A Beckman Model IR-4 spectrophotometer was used for the analysis of the diborane, the sample being contained in a 10-cm cell with sodium chloride windows.

In a typical run, all sections of the shock tube were first evacuated, and then the sample and driver gases were added. Since the "tailored-interface" technique was used, to give a heating pulse of uniform temperature, small amounts of nitrogen were usually added to the helium driver gas to match it with the sample and pressure ratio. The two diaphragms were then ruptured at the proper time by plungers (g and h). The plungers were activated pneumatically by use of the auxiliary shock tube (i), in which the diaphragm was burst by the pressure of its driver gas. A sample of gas was taken for analysis within a few seconds after the experiment. The oscilloscope traces were recorded by Polaroid camera.

For each experiment, the shock speed, pressure record and photo-cell record were obtained. From the shock speed, the temperature (T_3) and pressure (P_3) behind the reflected shock wave were calculated, using the known thermal functions of the components of the gas mixtures, assuming the gases behaved ideally and that no chemical reaction occurred ahead of the reflected shock wave. The pressure record showed that the pressure during a run varied somewhat, but was generally in the neighborhood (± 10-20%) of P_3. It was assumed that T_3 and P_3 were actually realized just behind the reflected shock wave, and that subsequent pressure changes caused change in temperature given by the isentropic equation.

$$\frac{T}{T_3} = \left(\frac{P}{P_3}\right)^{\frac{\gamma-1}{\gamma}}$$

This is reasonable since small changes of 10-20% in pressure have negligible entropy changes. T versus time was plotted for each run, and the arithmetic average temperature was taken as the temperature of the run. Usually this average temperature was within 50° of T_3.

One difficulty in reflected shock wave studies is that the gas sample in the tube is heated, not all at once, but over a period of up to a few milliseconds as the shock wave moves through the gas. In our experiments, this difficulty is avoided because, after being heated, the gas is brought nearly to rest (ideally, completely to rest) and the pressure transducer (c), windows (d), and sampling tube (3) are all at the same point along the tube, and near the closed end. Under these conditions, it seems safe to assume that the pressure and spectroscopic measurements are both made on the sample of hot, stationary gas, and that the gas taken for analysis is representative of that same gas after cooling.

A photograph of the shock tube apparatus is shown in Figure 2.

3.2 Low-Pressure Burner Parker and Wolfhard (Ref. 2) had shown earlier that premixed diborane-air flames can be burned, but that stable flames useful for study can only be obtained at low pressures (i.e., in the range of a few millimeters). The high flame speed and small quenching diameter of diborane-air flames require that small nozzles be used to prevent flash-back of the flames at atmospheric pressure, and the solid reaction products (B_2O_3 being the final one) soon plug the nozzles. At lower pressures larger burner tubes, which plug more slowly, can be used.

Our low-pressure burner, shown in Figure 3, resembles the one built earlier by Vanpee, Wolfhard and Clark (Ref. 3). The main glass sections are of 6-inch Pyrex pipe, the lower section being a 6 x 3-inch cross, with fused quartz observation windows on the 3-inch flanges. A 2-inch line from the top leads to a 130 cfm vacuum pump. The operating pressure can be varied from a few millimeters to an atmosphere by adjusting a valve in the 2-inch line, with a smaller valve in parallel for finer control. Gases are metered to the burner through calibrated rotameters operating at 7 psig, while gas flow rates are controlled by needle valves just downstream of the rotameters. The gases can be mixed soon after they leave the metering valves or, if a minimum time for reaction after mixing is desired, they can be mixed in the burner tube itself. The arrangement for the former type of mixing is shown in Figure 3.

For inhibitor screening with the low-pressure burner, inhibitors were added to the air stream while the latter was still above atmospheric pressure. The diborane was added, at low pressure,

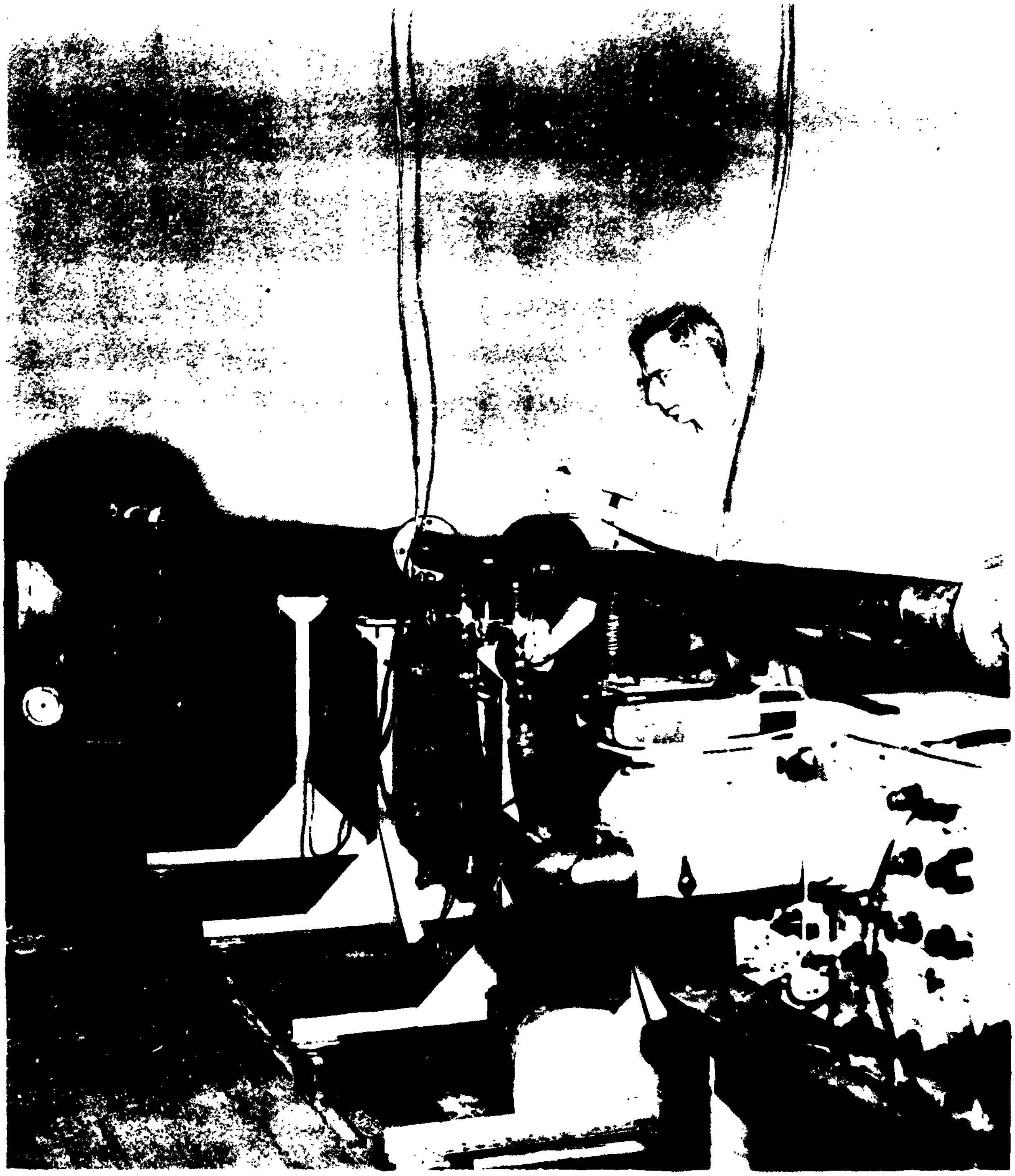


Figure 2. General view of shock tube

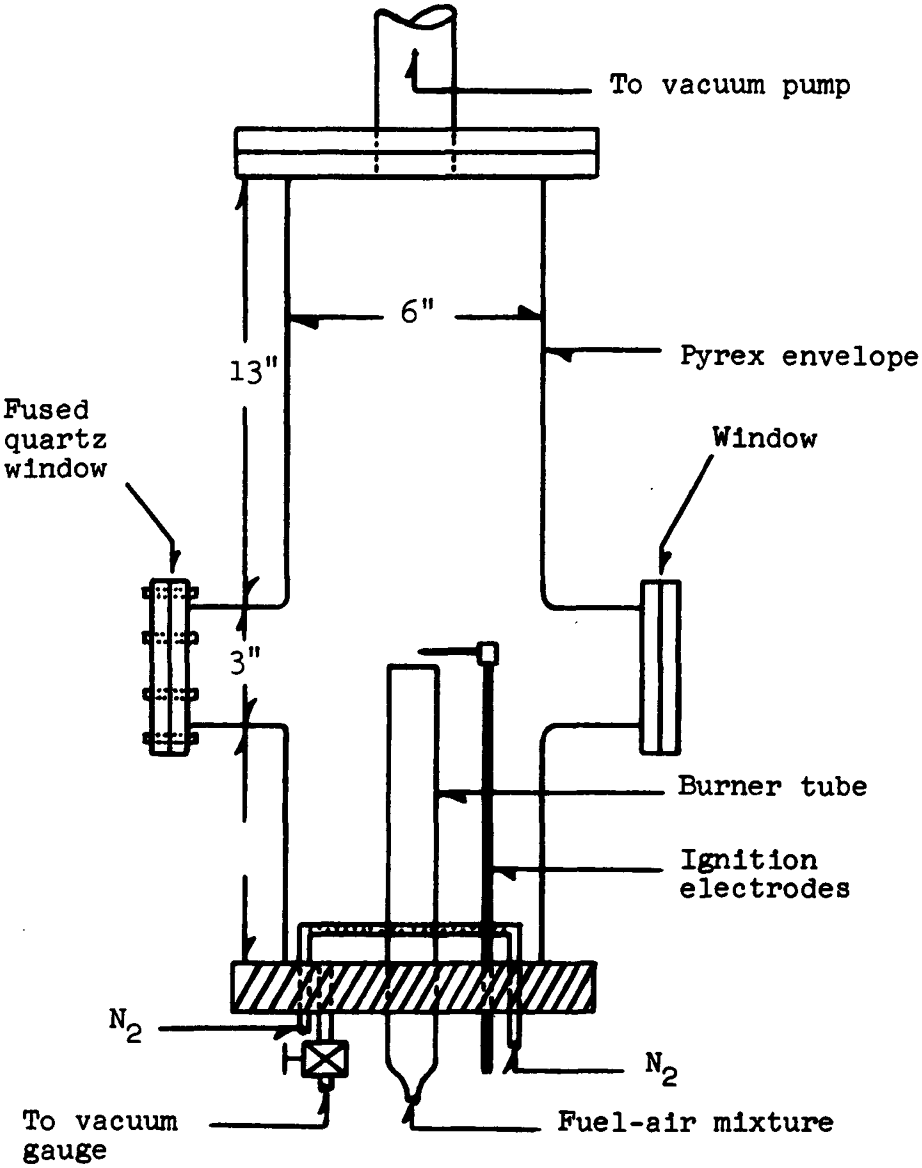


Figure 3. Schematic drawing of low pressure burner

at the bottom of the burner tube. Liquid inhibitors were metered by a motor-driven syringe into a heated section of the air line immediately ahead of the let-down valve. The line beyond the let-down valve did not have to be heated, since the liquids all had sufficient vapor pressure that, at the 2% concentration used, there was no danger of condensation at room temperature once the total gas pressure had dropped to the 9 mm value used in most of the experiments.

All measurements were made on conical flames on glass burner tubes, a one-inch tube being most commonly used. Attempts to study flat flames on a porous metal burner were unsuccessful due to rapid accumulation of solids on the burner, which wrinkled the flame. For flame speed measurements, direct photographs of the flames were taken using a Model 100 Polaroid 4-S light reducing filter. Polaline Type 146-L transparency film was employed with Polaroid Dippit #646 to harden the image. The photographs were 2/5 actual size,and were magnified 12 times on a microfilm reader for measuring. In making the measurements, the objective was to obtain the dimensions of the inside of the luminous cone. Best results were obtained from slightly underexposed films on which the light from the flat surface of the flame facing the camera was too faint to register. Direct rather than schlieren photography was used because of the very small density gradients in the low-pressure flames.

Measurements of flame spectra were made with a Jarrell-Ash Model 82000 grating spectrometer covering the range 2500 to 6000A.

Photographs of the burner are shown in Figures 4 and 5.

3.3 Pentaborane Metering System Because of the low vapor pressure of pentaborane at ambient conditions and its low thermal stability, it was deemed unwise to meter the fuels at elevated pressure as in the case of diborane. The possibility of delivering the fuel to the burner via the motor driven syringe was not considered due to the toxic and pyrophoric nature of B_5H_9.

A system was devised whereby B_5H_9 could be metered employing rotameters at reduced pressures. The B_5H_9 was delivered to the rotameter at a constant pressure of either 100 or 150 mm

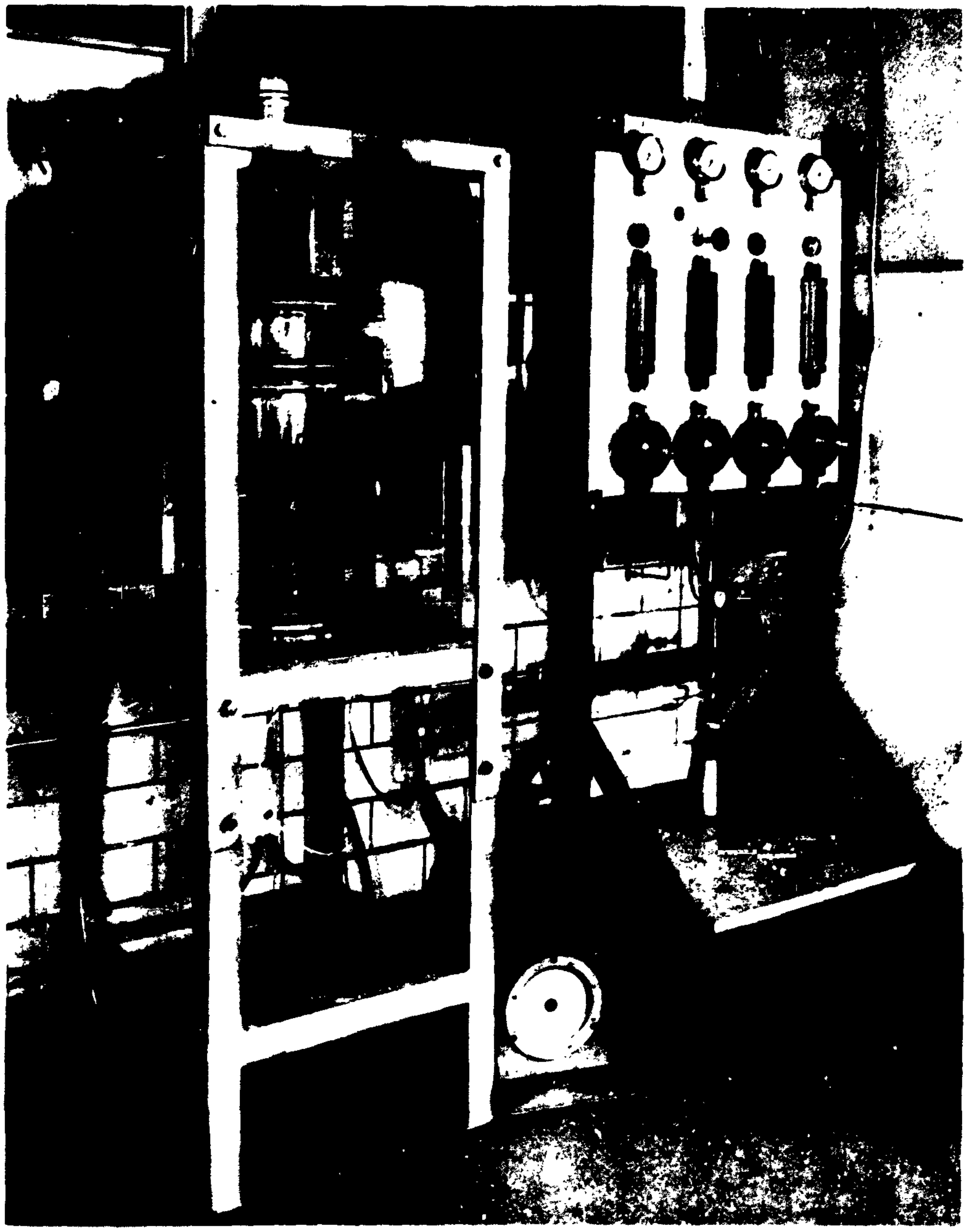


Figure 4. General view of low-pressure burner

Figure 5. Conical flame in low-pressure burner

absolute. The pressure was adjusted by means of a variation in the temperature of the fuel resevoir. The flow rate to the burner was controlled by a needle valve down stream of the rotameter, at which point the pressure dropped to that maintained in the burner. This arrangement obviated heating the fuel resevoir, the transfer lines, and the rotameter which would be required for metering above atmospheric pressure.

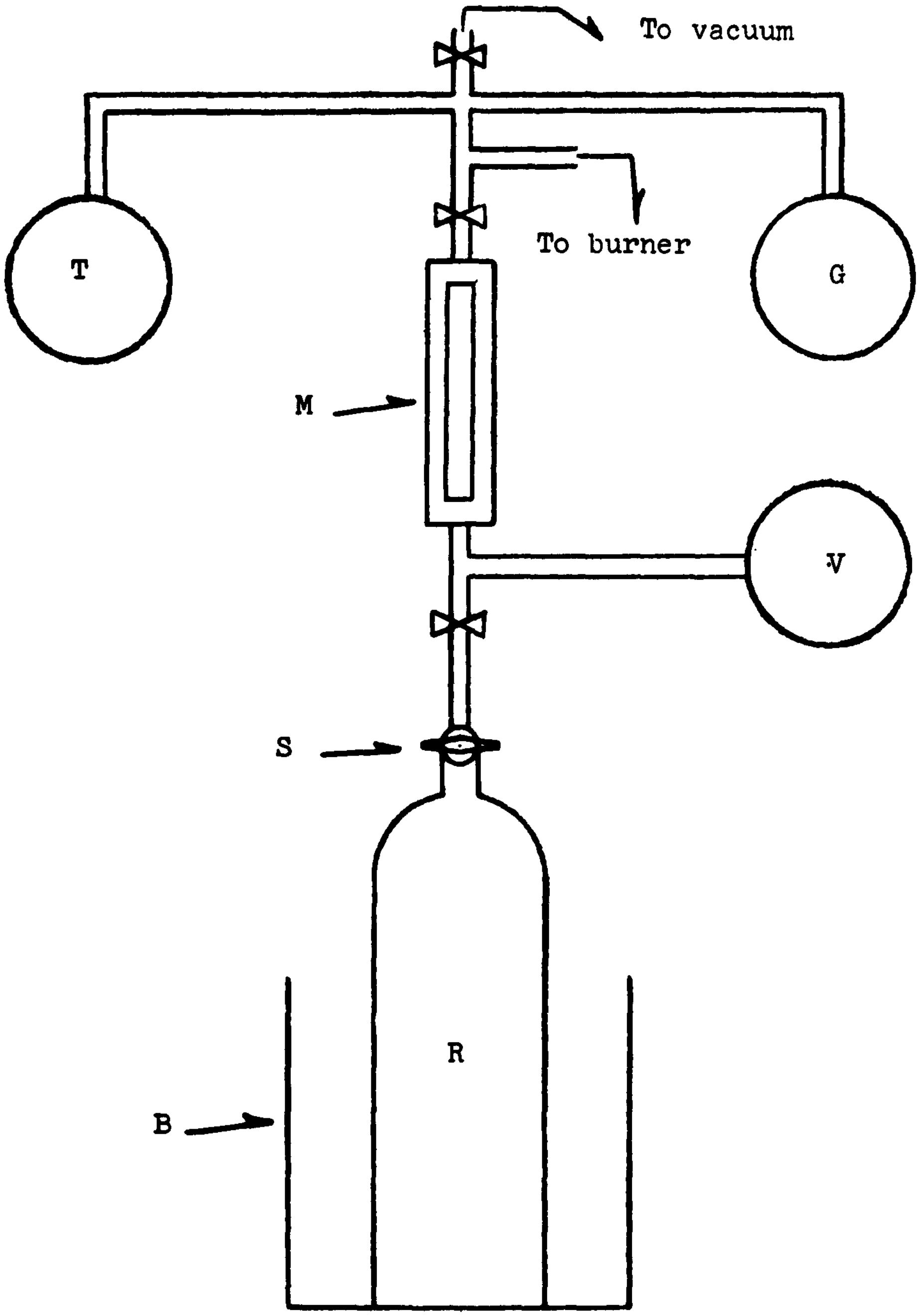
Before operation with pentaborane, the system was tested employing acetone vapor, since its physical properties (vapor pressure, density, molecular weight, viscosity) approach those of B_5H_9. The rotameters were calibrated with acetone and later with B_5H_9. The calibrations were accomplished by passing vapor through the rotameter at a known inlet pressure and over a known period of time at a given rotameter setting. The effluent stream was frozen in a liquid nitrogen trap of calibrated volume. Measurement of the pressure and temperature of the vaporized pantaborane yielded the flow rate in standard cc/sec of gas. The system is shown schematically in Figure 6.

4. RESULTS AND DISCUSSION

4.1 Inhibition of Diborane Oxidation

4.1.1 Pyrolysis of Diborane

4.1.1.1 Experimental Procedure Three gas mixtures containing nominally 0.25, 1 and 3% diborane by volume in argon were made up using accurate pressure gauges, and pyrolyzed in the shock tube. Chromatographic analysis showed that the gas mixtures contained small amounts of hydrogen (0.03, 0.11 and 0.16% by volume respectively), part of which was probably produced from slow decomposition of the diborane, and part from reaction of diborane with water absorbed on apparatus walls. In subsequent work, diborane was allowed to stand in all the apparatus prior to actual experimental work, to act as a desiccant. The decomposition and reaction of the diborane undoubtedly changed the compositions of the experimental mixtures slightly from the nominal values, but since, as it turned out, the pyrolysis reaction was of



⋈ - Valves
S - Stopcock
M - Rotameter
T - Liquid N_2 trap

R - B_5H_9 liquid reservoir
B - Variable temp. bath
V - Vacuum gauge - low press.
G - Accurate low pressure gauge

Figure 6. Schematic drawing of pentaborane handling system first order, this was not considered important.

The total pressure of the heated gas behind the reflected shock wave was 5 atmospheres, and the reaction time 19 milliseconds. After cooling, the products were analyzed for B_2H_6 by infrared and for hydrogen by gas chromatography. Pentaborane (B_5H_9) was qualitatively detected by infrared in some of the pyrolyzed samples, while $B_{10}H_{14}$ was identified by its characteristic odor and its appearance as a white condensate in the sample collection bulb. A yellow-to-brown solid obtained in higher-temperature runs was probably a boron-hydrogen polymer containing less than one hydrogen atom per boron atom. The yield of more than two atoms of hydrogen per atom of boron is further evidence, other than appearance, for the production of this polymer.

Temperatures have been corrected for the relatively small heat of reaction. Although the quantities of each reaction product were not known, it was assumed for calculating the correction that when less than 1.6 moles H_2 were produced per mole B_2H_6 decomposed, the reaction products were B_5H_9 and $B_{10}H_{14}$, and when more than 1.6 moles H_2 were produced the products were $B_{10}H_{14}$ and polymer. The latter was assumed to have zero heat of formation. A considerable error in this calculation could be tolerated since the maximum correction was only 12°.

<u>4.1.1.2 Experimental Results</u> The experimental results are given in Tables 1 to 3.

Confirmation of the first-order rate dependence is shown in Figure 7, where all of the rate constants of Tables 1 to 3 are plotted. A least-squares equation was obtained for all the data points, the points for 0.25% diborane being weighted at half those for 1% and 3% because the experimental error in analysis was greater for the lowest concentration. The least-squares equation is

$$\log k = 10.10 - 5{,}520/T$$

where k is the rate constant in $\sec^{-1}$
T is the absolute temperature, °K

The experimental activation energy (2.303R x 5,520) is 25.3 Kcal.

Table 1

Results for Pyrolysis of Gas Mixture Containing 0.25% Diborane in Argon

Temp., °K	Moles H_2 Produced/ Mole B_2H_6 Originally Present	B_2H_6 Unreacted, %	First Order Rate Const., sec^{-1}
593	0.01	92	4.0
607	0.10	83	9.4
607	0.43	81	11.5
612	0.08	79	13
640	0.70	58	30
647	1.41	30	60
677	2.00	16	101
679	1.31	24	80

Table 2

Results for Pyrolysis of Gas Mixture Containing 1% Diborane in Argon

Temp., °K	Moles H_2 Produced/ Mole B_2H_6 Originally Present	B_2H_6 Unreacted, %	First Order Rate Const., sec^{-1}
609	0.33	81	11
638	0.61	61	25
666	1.20	34	57
683	1.61	14	103
698	1.87	6.5	152
786	2.38	5	-
918	2.65	5	-

Table 3

Results for Pyrolysis of Gas Mixture Containing 3% Diborane in Argon

Temp., °K	Moles H_2 Produced/ Mole B_2H_6 Originally Present	B_2H_6 Unreacted, %	First Order Rate Const., sec^{-1}
595	0.19	87	7
616	0.37	76	15
639	0.66	57	29
660	1.46	29	65
687	1.81	15	106

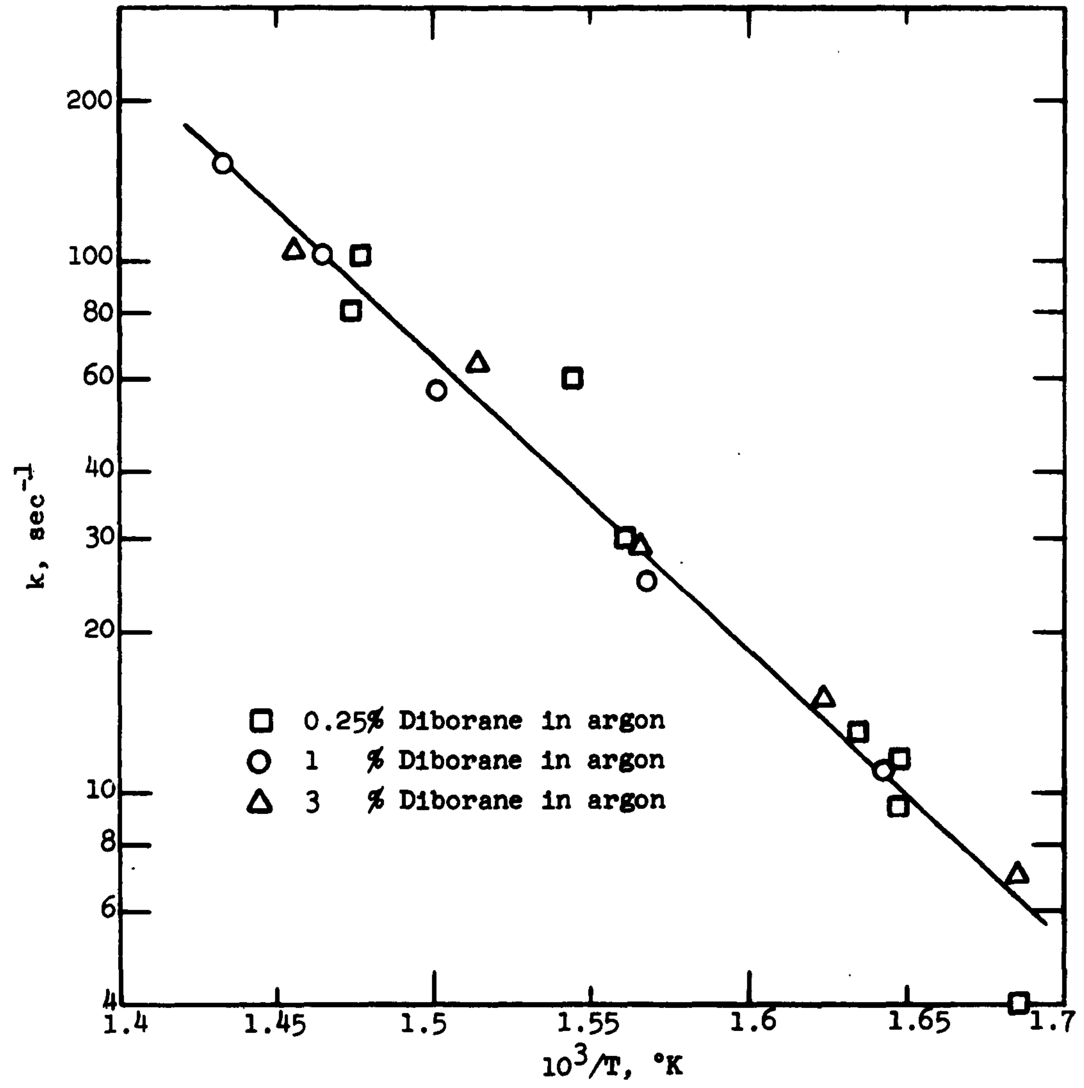


Figure 7. Rate constants for pyrolysis of diborane

4.1.1.3 Pyrolysis Mechanism Although there are no other experimental data available in this temperature range, it would be worthwhile to compare our data with literature values at lower temperatures. Those who had done this earlier work agreed that the rate of diborane decomposition appeared to depend on the 3/2 power of the diborane composition, and calculated rate constants accordingly. To make an approximate comparison with our data, we have recalculated their data as first-order rate constants which, as would be expected, are not too "constant" for differing initial diborane pressures and fractions reacted. The recalculated rate constants are listed below, where only the average of several experimental values at each temperature are given.

From Table I of the paper of Clarke and Pease (Ref. 4) the following rate constants are obtained:

Temp., °C	k, sec^{-1}
85	6.2×10^{-6}
103	1.6×10^{-5}
122	7.5×10^{-5}
140	2.7×10^{-4}
164	1.0×10^{-3}

From Table IX of Bragg, McCarty and Norton's paper (Ref. 5) we obtain the following data:

Temp., °C	k, sec^{-1}
100	1.5×10^{-5}
110	2.6×10^{-5}
120	5.8×10^{-5}

Two experiments by Morrey, Johnson, Fu and Hill (Ref. 6) give values of $k = 1.9 \times 10^{-4}$ sec^{-1} at 138°C. All of these low-temperature data are plotted in Figure 8, while the range of the experimental data of Figure 7 is shown as a rectangle. A straight line through all the data has the equation

$$\log k \ (sec^{-1}) = 10.32 - 5{,}690/T$$

with an activation energy of 26.0 Kcal. The close agreement between this over-all value, our value at high temperatures of 25.3 Kcal, and the values of 26.0 Kcal given

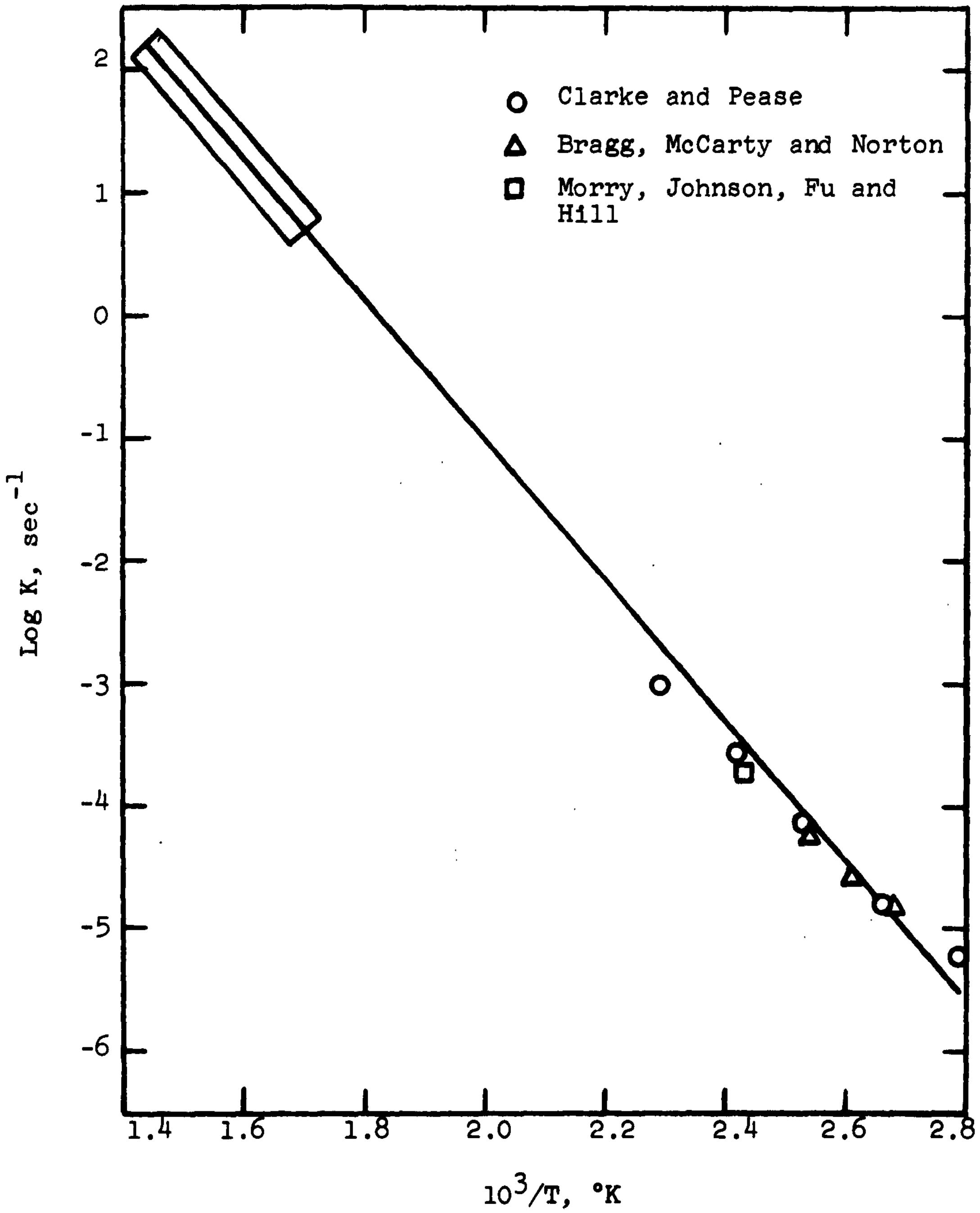


Figure 8. Comparison with literature data on diborane pyrolysis

by Clarke and Pease (Ref. 4) and 27.4 Kcal by Bragg, McCarty and Norton at low temperatures, suggest that the same reaction mechanism is operative over the whole temperature range. However, if this were so, the reaction order would also remain constant over the range.

In his review paper of 1958, Bauer (Ref. 7) has summarized the all but conclusive evidence that borine, BH_3, is the first intermediate produced in pyrolysis of diborane in the temperature range 80-150°C. The reaction

$$B_2H_6 \rightleftharpoons 2\ BH_3 \qquad (1)$$

is very rapid, so that this reaction remains at equilibrium during the pyrolysis reaction. That is, when a sample of diborane is heated, reaction (1) proceeds rapidly, before any other significant changes occur, to produce the amount of BH_3 that is in equilibrium with diborane at the new temperature (and pressure). Therefore, if K_1 is the equilibrium constant of reaction (1), then

$$K_1 = \frac{[p\ (BH_3)\ ]^2}{p(B_2H_6)}$$

where p (BH_3) and $p(B_2H_6)$ are the partial pressures of BH_3 and B_2H_6, respectively, and

$$p(BH_3) = \sqrt{K_1 p(B_2H_6)}$$

The equilibrium constant is given by the expression

$$\log K_1\ (\text{atm.}) = 7.478 - 6205/T$$

Bauer also presents evidence that the next step in the pyrolysis reaction is

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2 \qquad (2)$$

These steps are included in a more elaborate reaction scheme recently advanced by Clapper (Ref. 8). He considers that B_3H_7 reacts with B_2H_6 to produce the observed (though relatively unstable) B_4H_{10} and B_5H_{11} by the reactions

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3 \qquad (3)$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_{11} + H_2 \qquad (4)$$

Accordingly, for each molecule of diborane that reacts by (2), additional molecules react by (3) or (4). Considering, also, that B_4H_{10} and B_5H_{11} are not stable products, and their decomposition products can also react with B_2H_6, several molecules of B_2H_6 decompose for each one that reacts by (2).

Because the concentration of BH_3 is proportional to the square root of the B_2H_6 concentration, the disappearance of B_2H_6 by reaction (2) is 1.5 order with respect to B_2H_6 as was observed in the low temperature pyrolysis experiments.

However, because of the additional reactions such as (3) and (4), the over-all rate of disappearance of B_2H_6 need not follow the 1.5 order dependence, although experimentally it does in the 80-150°C range. The change to the first-order dependence which we observed at higher temperatures could be accounted for by changes in the relative importance of reactions (3), (4) and others as the temperature increases. Since the experimental activation energies determined at lower and higher temperatures are nearly the same, and since a common curve can be drawn through both high and low temperature data when the low-temperature data are recalculated as first-order constants, it now seems that Bauer's mechanism could apply to our high-temperature data as well as to the earlier data.

4.1.2 Ignition of B_2H_6-O_2-Argon Mixtures

4.1.2.1 Experimental Procedures Three uninhibited B_2H_6-O_2-Argon mixtures were studied. All contained 0.25% B_2H_6 by volume, while the oxygen contents were 0.375%, 0.75% and 1.5%, corresponding to equivalence ratios of 2, 1 and 0.5 based on the over-all reaction.

$$B_2H_6 + 2O_2 \longrightarrow B_2O_3 + 3H_2O$$

The total gas pressure during the heating period was 5 atmospheres.

Ignition induction times for these mixtures were measured from oscilloscope records of the light outputs as functions of time. The onset of combustion is signalled by a rapid increase in light output, and the ignition point was taken as that when the light output reached 10% of its maximum value. The total light output in the range of 6000-2200 A was detected.

4.1.2.2 Experimental Results The reaction, or at least the light-emitting phase, was completed rapidly, and no light was emitted by the reaction products. This is not surprising, since the calculated temperature rise due to heat of reaction was no more than 200°C (because of the argon dilution) so the temperature of the reaction products would be only about 500°C, too low to emit a significant amount of light radiation of thermal origin.

The rapid increase in reaction rate at the end of the induction period, as evidenced by the light output record, was confirmed by spectroscopic analysis for diborane in two experiments carried out with the stoichiometric mixture.

In the first experiment the gas mixture was heated to 515°K for 29 milliseconds. No light output was observed, indicating that the heating time was less than the induction period. However, a slight extrapolation of the average curve of Figure 9 indicates that the induction time could not have been much greater than 35 milliseconds. The diborane content of the cooled sample was 97% of the original amount, clearly indicating that very little diborane is used up during most of the induction period.

In the second experiment, at 533°K, the induction time was found to be 18.5 milliseconds. The sample was quenched (by lowering the pressure to produce adiabatic cooling) immediately after the end of the induction period, expansion of the sample starting within a millisecond after the light intensity reached 10% of its maximum value. In spite of this immediate and rapid cooling, all but 18% of the diborane disappeared in the experiment.

These results are similar to those obtained with hydrogen-oxygen-argon mixtures, and are typical of a branching-chain free radical mechanism. They also demonstrate that the kinetics of the oxidation process cannot be determined by quenching shock-heated samples, since the transition from no measurable reaction just prior to the end of the induction period to almost complete reaction just following is too sharp. That is, analysis would only serve to detect the end of the induction period, and this can be done more easily by measuring the light output.

The experimental induction times are given in Table 4 to 6.

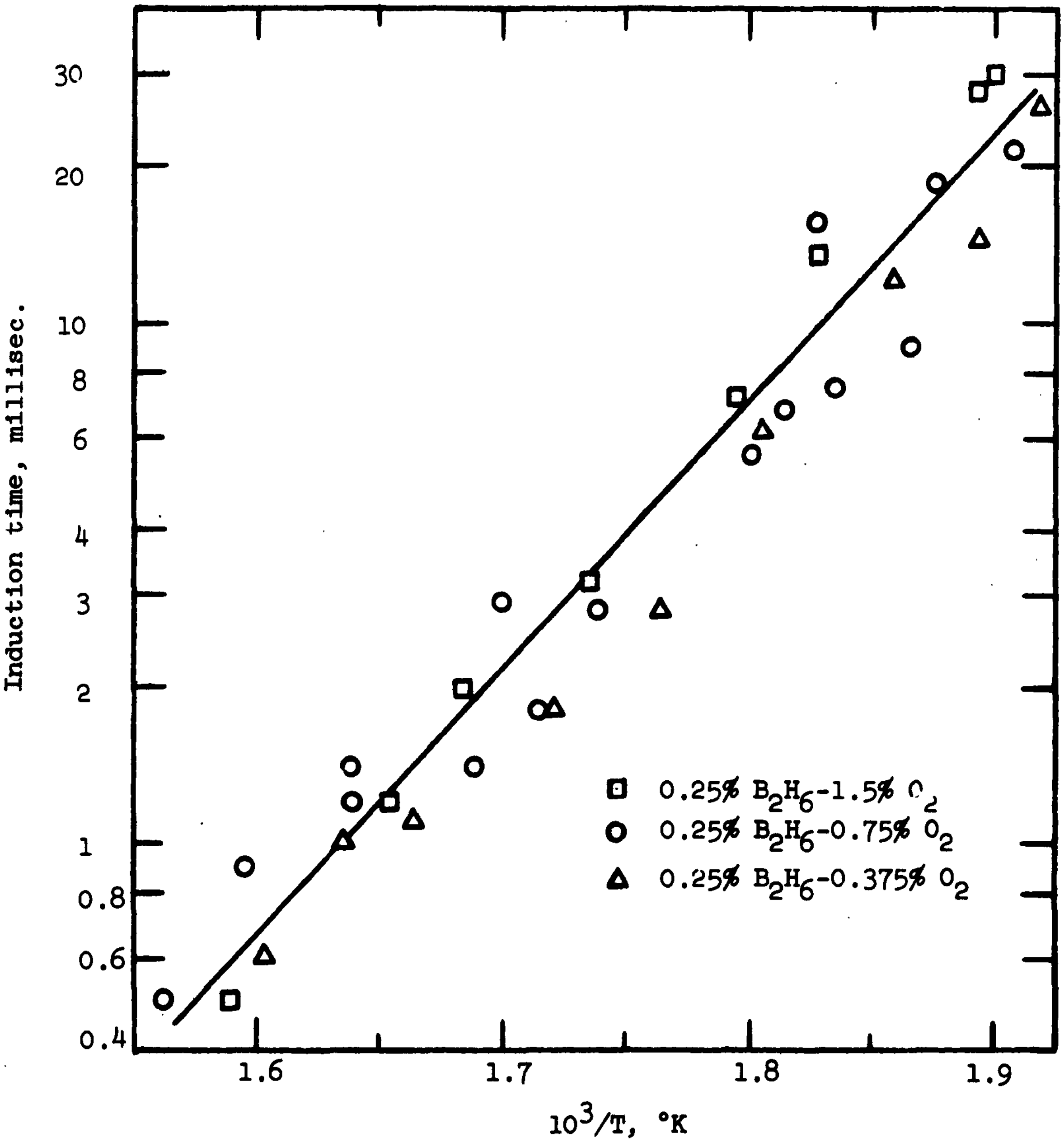


Figure 9. Ignition induction times for diborane-oxygen-argon mixtures

Table 4

Ignition Induction Times for Gas Mixture Containing 0.25% B_2H_6, 0.375% O_2 and 99.375% Argon (Equivalence Ratio 2.0)

T, °K	Induction Time, milliseconds
521	26.0
528	14.5
538	12.0
554	6.2
567	2.8
581	1.8
601	1.1
616	1.0
624	0.6

Table 5

Ignition Induction Times for Gas Mixture Containing 0.25% B_2H_6, 0.75% O_2, and 99.0% Argon (Equivalence Ratio 1.0)

T, °K	Induction Time, milliseconds
524	21.5
533	18.5
536	9.0
545	7.5
547	15.5
551	6.8
555	5.6
575	2.8
583	1.8
588	2.9
592	1.4
610	1.2
610	1.4
627	0.9
640	0.5

Table 6

Ignition Induction Times for Gas Mixture Containing 0.25% B_2H_6, 1.50% O_2 and 98.25% Argon (Equivalence Ratio 0.5)

T, °K	Induction Time, milliseconds
526	30.0
528	28.0
547	13.5
557	7.2
576	3.2
594	2.0
604	1.2
630	0.5

Least-squares curves were calculated for each equivalence ratio, in the form

$$\log t_1 = A + B/T$$

where t_1 is the induction time in milliseconds
T is the temperature in °K
A and B are constants

The "activation energy" for ignition is obtained by taking 4.576 B. The calculated values for each equivalence ratio are given below, along with the temperature at which the induction time was 5 milliseconds (a value in the middle of the experimental range).

Equivalence Ratio	A	B	ΔH, Kcal	T, °K for t_1=5
2.0	-8.143	4,940	22.6	559
1.0	-7.511	4,620	21.1	563
0.5	-9.361	5,710	26.1	568

The differences among the three sets of data are small and lie within the range of experimental error, as is seen when the data are plotted together (Figure 9).

4.1.2.3 Ignition Mechanism The independence of the induction times on oxygen concentration is in striking contrast to the situation in the hydrogen-oxygen reaction, where the induction times are approximately inversely proportional to the oxygen concentration (Ref. 9). In the hydrogen-oxygen reaction, the rate-controlling step at low temperature is

$$H + O_2 \longrightarrow OH + O$$

so that doubling the oxygen concentration will double the rate of reaction and halve the induction time. The implication is that oxygen is not involved in the rate-controlling step in diborane oxidation. What, then, is the rate-controlling step?

Based on evidence now available, decomposition of diborane is the most likely candidate. If this is the slow step in the oxidation process, then varying the oxygen concentration should not affect the induction time, since further reaction would be limited by the pyrolysis intermediates available, not the O_2. The similarity of the activation energies found for pyrolysis and oxidation also points to this conclusion.

Goldstein (Ref. 10) has shown that in slow (nonexplosive) oxidation experiments carried out near 150°C, diborane actually disappears more slowly in the presence than in the absence of oxygen. That is, oxygen inhibits diborane pyrolysis. He has supposed that O_2 reacts with BH_3,

$$BH_3 + O_2 \longrightarrow BH_3OO \qquad (5)$$

followed by

$$BH_3OO + B_2H_6 \longrightarrow B_3H_7O_2 + H_2 \qquad (6)$$

However, these reactions do not reduce the rate of pyrolysis, since the BH_3 concentration, being determined by equilibrium rather than kinetic considerations, is not reduced by reaction (5). The pyrolysis rate would be reduced if O_2 reacts with B_3H_7,

$$B_3H_7 + O_2 \longrightarrow B_3H_7O_2 \qquad (7)$$

and this is a more likely initial reaction than (5).

Since it is known that diborane can react explosively with oxygen, in qualitatively the same manner as hydrogen can, branching chain reactions are involved in the oxidation. The explosive mechanism has been shown by Roth (Ref. 11) to include a bimolecular chain branching reaction and a termolecular chain breaking reaction. Since the O atom in the chain is indicated by the striking effects of $Fe(CO)_5$ in inhibiting diborane-oxygen explosion at the second explosion limit, and by the sensitizing effect of NO_2 (Ref. 12) at this limit, a likely chain branching reaction is

$$B_3H_7 + O_2 \longrightarrow B_3H_7O + O \qquad (8)$$

following which many more reactions are possible. The further steps in the oxidation process are now unknown, although the molecules $B_2H_2O_3$ (Ref. 13), $B_3H_3O_3$ (Ref. 14) as well as the spectroscopically observed BO and BH are known to take part.

4.1.3 Shock Tube Inhibition Studies The effects of adding small amounts of CH_4, CF_3Br and 1, 3-butadiene to the stoichiometric diborane-oxygen-argon mixture studied above were measured. In each case 0.07% of additive (by volume) was added to the basic 0.25% B_2H_6, 0.75% O_2 mixture.

There was some question that CF_3Br and C_4H_6 might react with B_2H_6 on mixing at room temperature, and that it might therefore be impossible to premix the reaction mixture as must be done for shock tube work. However, B_2H_6 additive mixtures made up in an infrared cell showed no measurable change in concentrations over a three-day period, so premixing the reactants presented no problems.

There was no significant difference between the induction times with and without the inhibitors, so these inhibitors are ineffective under shock tube conditions. The least-squares constants for these data, corresponding to those given above for the uninhibited mixtures, are:

Inhibitor	A	B	H, Kcal	T, °K, for ti=5
CH_4	-9.238	5,530	25.3	558
CF_3Br	-9.564	5,810	26.6	566
1, 3-C_4H_6	-7.882	4,849	22.2	565

The failure of these additives to inhibit is not entirely due to their lack of reactivity at the relatively low ignition temperatures used. Two experiments were run with CF_3Br added in which the samples were quenched as soon as possible after ignition occurred. The two quenched samples contained, respectively, 64 and 15% of the original B_2H_6, and 76 and 28% of the original CF_3Br. Most of the CF_3Br was converted to COF_2. Therefore the CF_3Br was reacting, although somewhat more slowly than B_2H_6, but apparently its reactions were not interfering with the ignition process.

4.1.4 Low Pressure Burner Studies - Uninhibited Flames

4.1.4.1 Stability Regions

The stability of diborane-air flames in the low pressure burner were determined as a function of equivalence ratios from 0.4 to 1.6. An equivalence ratio of 1 corresponds to a 1:3 diborane-oxygen ratio, which could react completely accordingly to the equation

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$$

The regions are presented in Figure 10. The 0.39, 0.80 and 1.56 equivalence ratio mixtures were studied in detail, while the stable limits for the 0.48 and 0.92 mixtures were roughly defined. These data were obtained by stabilizing a flame on the 2.6 cm diameter burner at a given mass flow rate and pressure. By adjustment of the needle valve to the vacuum pump, the pressure was increased until flashback occurred. The pressure was then decreased until the blow-off point was reached.

4.1.4.2 Effect of Equivalence Ratio on Flame Speeds

The flame speeds of uninhibited diborane-air mixtures were studied as a function of equivalence ratio at a pressure of 9.2 mm. This value was selected, since the higher flame speed mixtures (0.5 to 2.0 equivalence ratio) would be stable at this pressure on the 2.6 cm burner. The resulting data are presented in Table 7 and average values are plotted in Figure 11. The results of Table 7 are not quite as accurate as those obtained later since the photographic technique was under development during this work. However, the reproducibility of the results is within ± 10%.

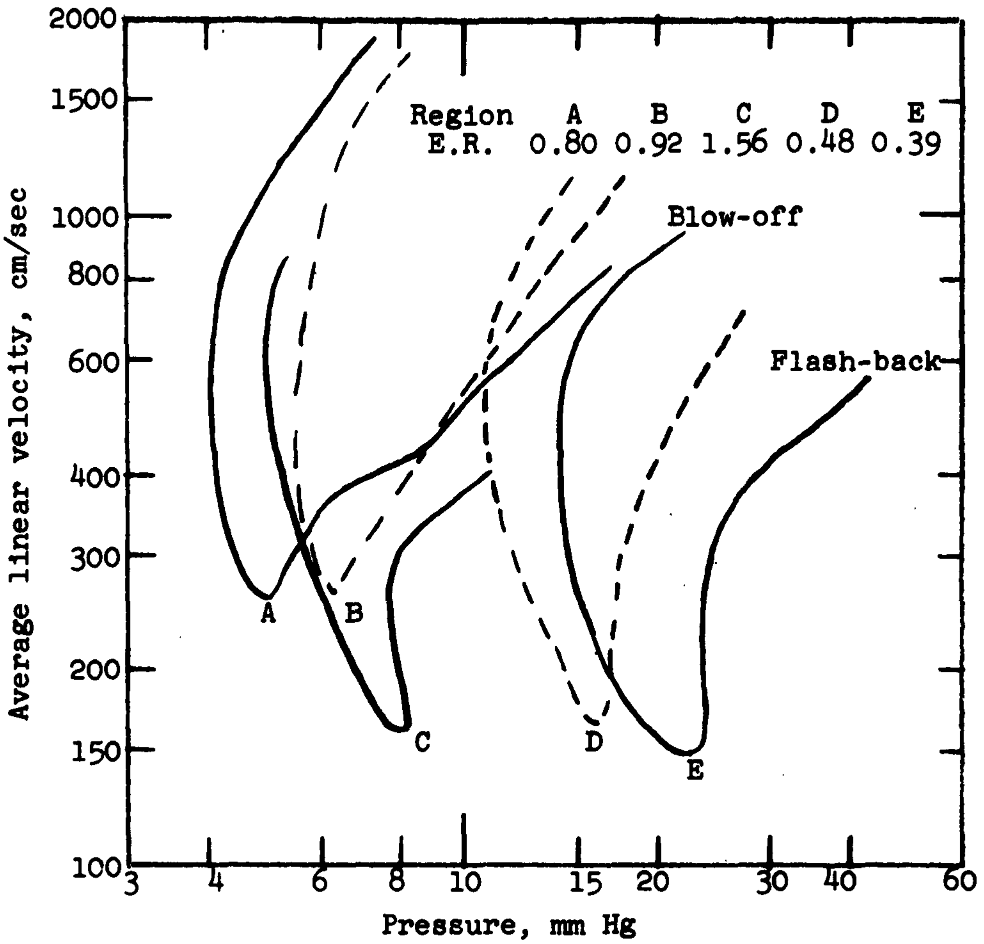


Figure 10. Stable regions of B_2H_6-air flames in low pressure burner (2.6 cm diameter) for several equivalence ratios

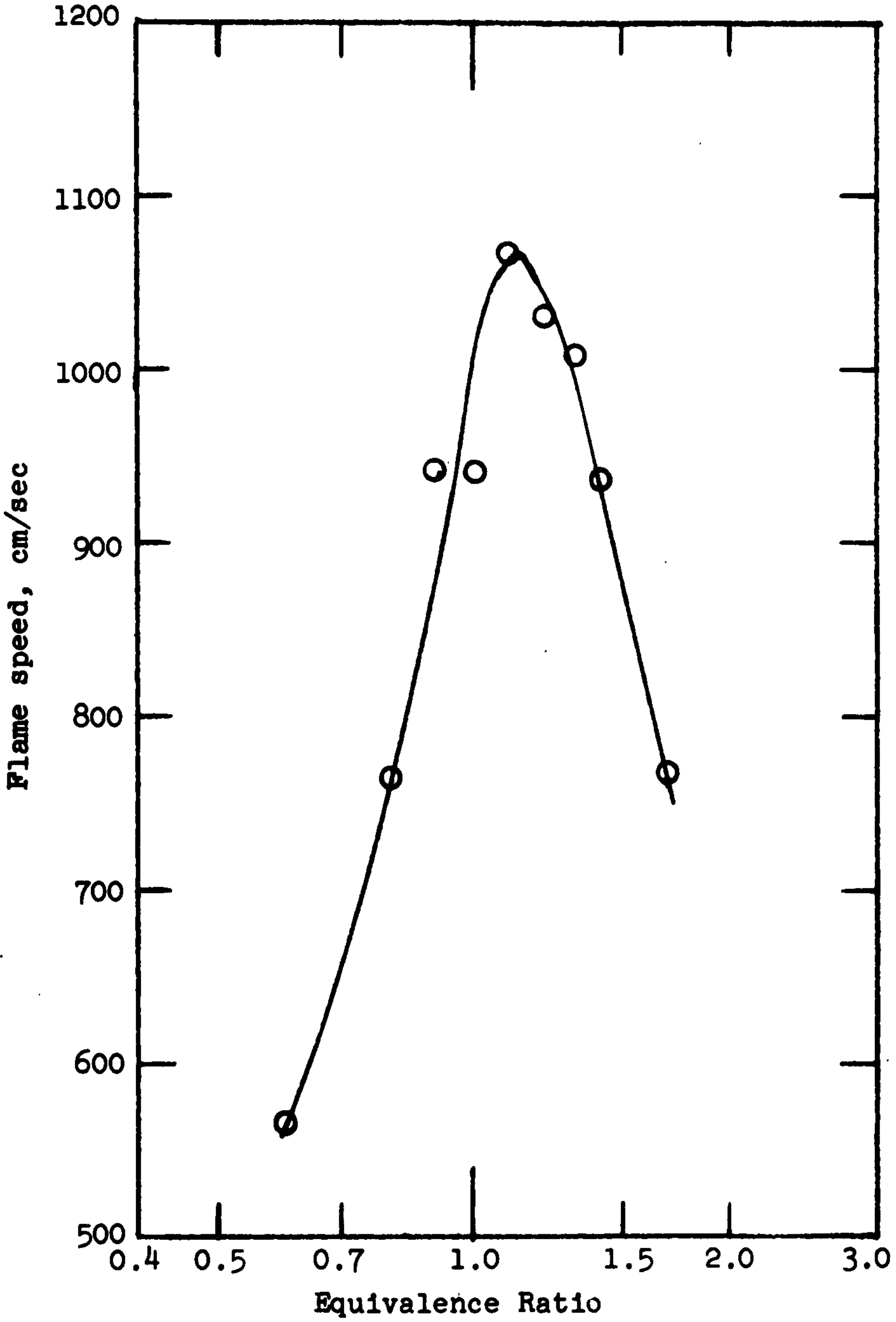


Figure 11. Flame speeds of uninhibited diborane-air mixtures at 9.2 mm Hg on 2.6 cm burner

Table 7

Flame Speeds of Uninhibited Diborane-Air Mixtures at 9.2 mm on 2.6 cm burner

Equivalence Ratio	Flame Speed, cm/sec	Av. Flame Speed cm/sec
.60	560	560
.80	760	760
.90	940	940
1.00	980* 900	940
1.09	1040 1090 1070 1050	1060
1.21	1010 1070 1010	1030
1.31	1020 1090 960 960*	1010
1.40	940*	940
1.68	730* 810	770

*Pressure = 8.8 mm

4.1.4.3 Effect of Pressure on Flame Speeds

The pressure dependence of the flame speed of the fastest-burning diborane-air mixture (1.16 equivalence ratio) was studied. Flame speeds at several pressures were obtained by using burner tubes of several diameters, so that the tube diameter was held inversely proportional to the pressure. The experimental results are given in Table 8, and plotted in Figure 12. Parker and Wolfhard's value (Ref. 2) at 760 mm is also shown in Figure 12.

Table 8

Pressure Dependence of Diborane-Air Flame Speed (Equivalence Ratio 1.16)

Pressure, mm	Tube Diameter, cm	Flame Speed, cm/sec	Average, cm/sec
9.2	2.61	980 1040	1010
13	1.76	860 910	880
30	0.76	780 710 900 820	800
58	0.38	640 700 630	660

4.1.4.4 Effect of Flame Temperature on Flame Speeds Flame speeds of stoichiometric diborane-oxygen mixtures with argon diluent were studied. The mole per cent argon varied from 84 to 97, corresponding to calculated adiabatic flame temperatures (assuming complete reaction to B_2O_3 and H_2O) of 2750° to 990°K. The 97% argon flame was stabilized at atmospheric pressure on a 3/4-inch diameter burner and photographed by the schlieren technique. The other compositions were burned in the low-pressure burner at various pressures.

The data are given in Table 9. Since it is difficult to visualize the effect of changing composition when the pressure is also changing, the flame speeds were "normalized" to 50 mm pressure using Figure 12, with the assumption that a given change of pressure would make the same fractional change of flame speed for all the flames. These values calculated for 50 mm are given in the last column of Table 9.

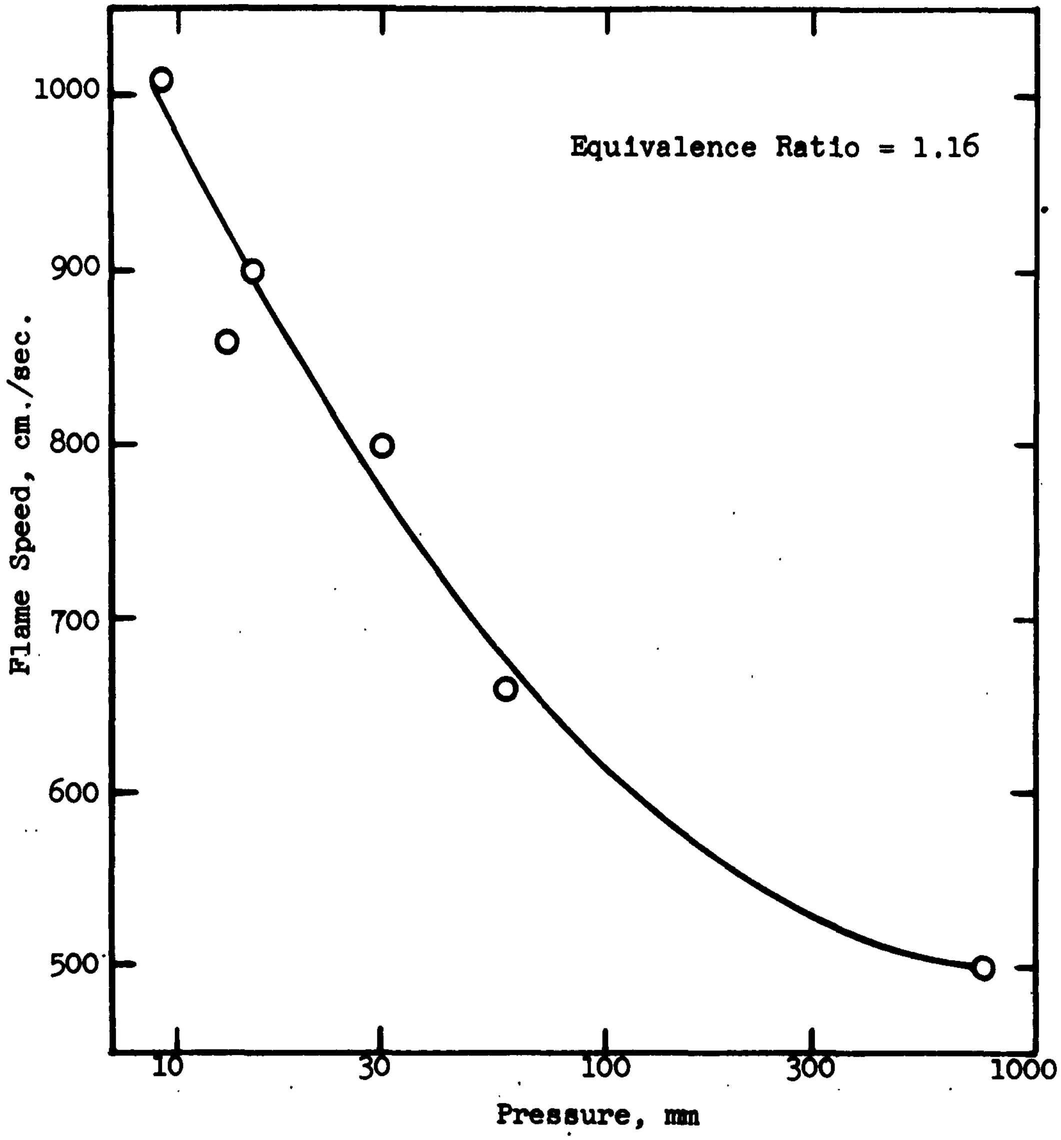


Figure 12. Effect of pressure on B_2H_6-air flame speed

Table 9

Flame Speeds of Argon-Diluted, Stoichiometric Diborane-Oxygen Mixtures

% Argon	Pressure, mm	Flame Speed, cm/sec	Flame Speed Calc., 50 mm cm/sec
84	15	570	440
86	20	590	410
88	24	350	300
90	29	260	230
92	28	210	190
96	741	20.7	29
97	750	9.5	13

4.1.4.5 Flame Spectra Emission spectra of argon-diluted stoichiometric diborane-oxygen flames were recorded using the Jarrell-Ash Model 82000 spectrometer. Attempts to study flat flames on a 2-inch porous metal burner mounted in the low-pressure burner envelope were unsuccessful due to rapid clogging and the build-up of solid combustion products on the burner rim. Therefore, conical flames on the 2.6 cm burner tube were studied.

The main spectral features observed were the BO α system resulting from the $A^2\Pi \longrightarrow X^2\Sigma^+$ transition (from 3400 to 4400A) and the BH $^1\Pi - ^1\Sigma$ bands with band head at 4332A. In addition the B_2O_3 "fluctuation" bands were observed, but they appeared to be emitted from the burned gas rather than from the primary reaction zone of the flame. Weak emission from boron was tentatively identified from 2800 to 3260A. A typical spectrum is shown in Figure 13.

Spectra were recorded for flames with from 84 to 96 per cent argon, with corresponding flame temperatures between 2750 and 1190°K. Measurements of the intensity of the (0,0) BH band at 4332A relative to the average of the intensities of the (2,0) and (1,2) BO bands at 3849, 4038 and 4747A indicate that the BH intensity increases about twofold over that of BO as the flame temperature is increased from 1600 to 2750°K. This is illustrated in Figure 14.

The main spectral features observed here are in agreement with those found earlier by Parker and Wolfhard (Ref. 2). The absence of the $^2\Sigma-^2\Pi$ band of OH at 3064A is also in agreement with this work and with that of Berl and co-workers (Ref. 15) and Wolfhard et al (Ref. 16).

4.1.5 Inhibition of Diborane-Air Flames

4.1.5.1 Inhibitor Screening The effects on the flame speed produced by adding 2 per cent by volume of 32 gases and vaporized liquids were observed, using the 1.16 equivalence ratio flame as a standard. The results are given in Table 10.

The order of effectiveness of the inhibitors was not that which had been expected from the shock tube work. There the rate of oxidation seemed to depend primarily on the rate of diborane pyrolysis, so it had been expected that molecules such as ammonia, methyl amine and carbon monoxide, which would be likely to combine with pyrolysis intermediates would be the best inhibitors. In fact, they were not. The order of inhibitor effectiveness actually bears a close resemblance to that for the hydrogen-air reaction (Ref. 17), indicating that flame propagation in the diborane-air flames proceeds by a mechanism resembling, in some respects at least, that of the hydrogen-oxygen reaction.

Apparently there is a difference between the ignition processes in the shock tube, where temperatures were in the range 525-640°K, and in the flames, where presumably the ignition temperatures could be higher. If flame propagation occurs via species such as hydrogen atoms, at temperatures in the range of 1000°K, then butadiene, bromotrifluoromethane and toluene would be expected to inhibit flames. However, if BH_3 formation or other related pyrolysis reactions control ignition at lower temperatures, where no high temperature flame front or other ignition source is present, then these same additives would be ineffective as inhibitors at the low temperature conditions. This is probably the reason for the different results obtained by the two experimental techniques.

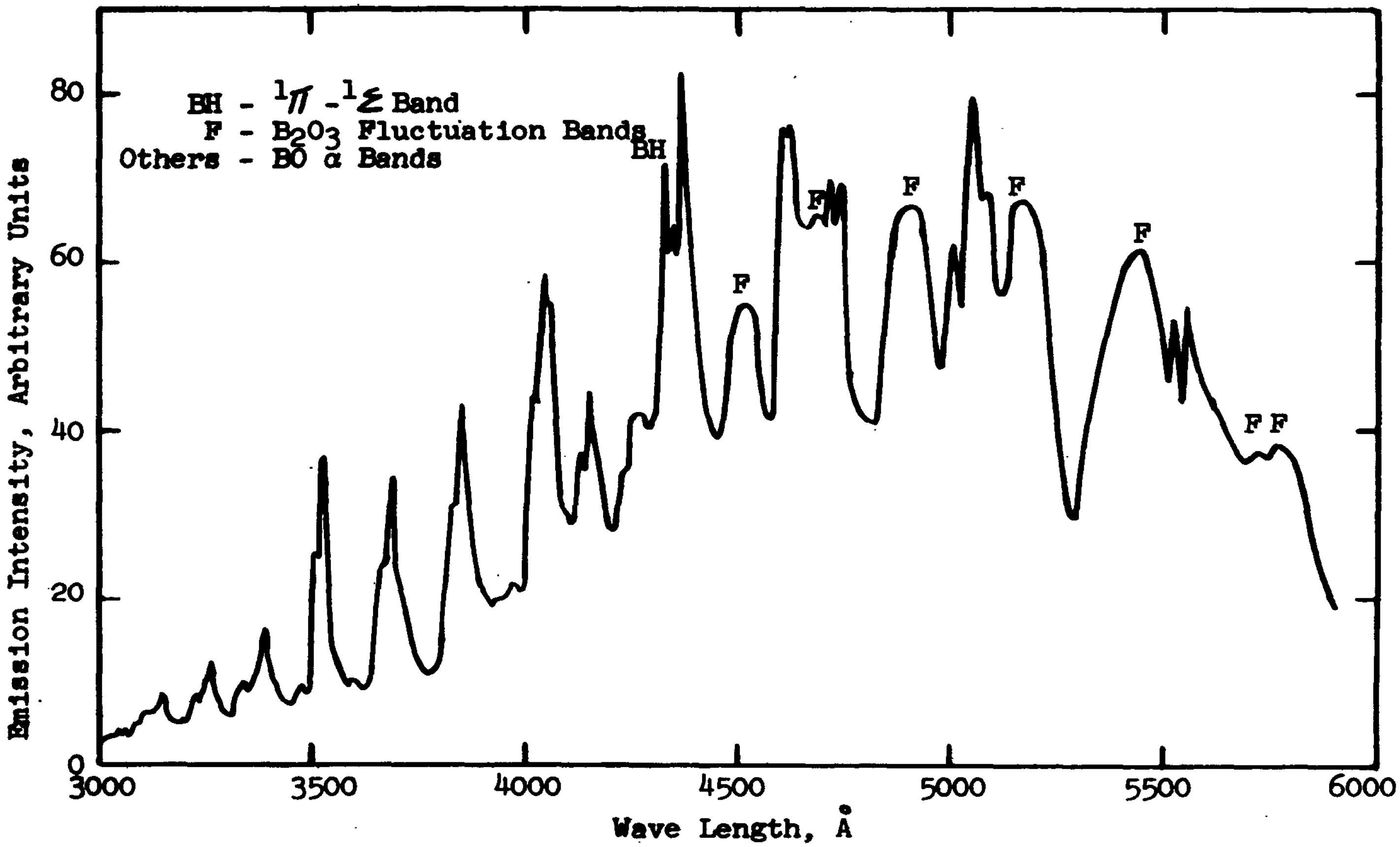


Figure 13. Emission spectrum of stoichiometric B_2H_6-O_2 flame 94 mole per cent argon

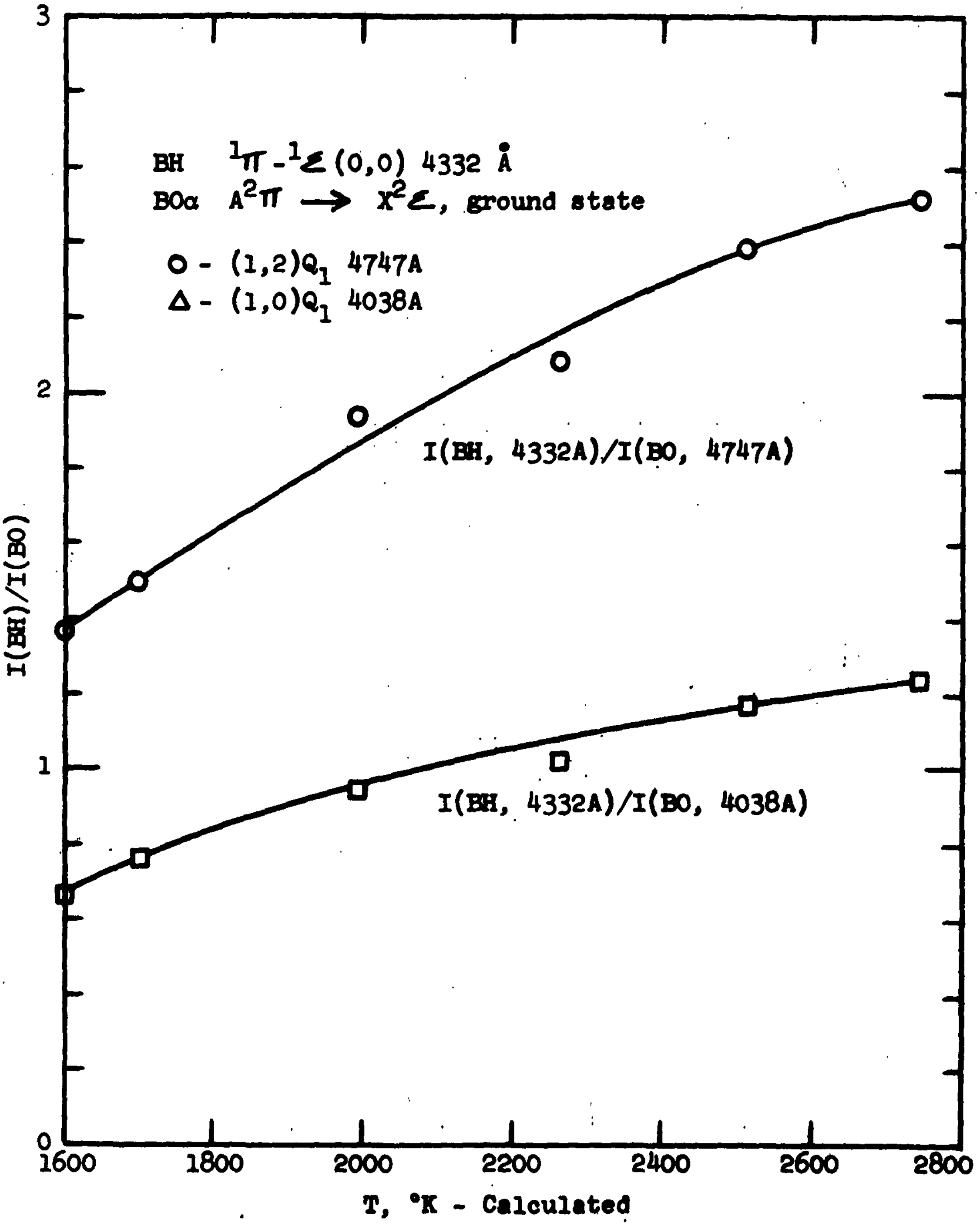


Figure 14. Changes in BH/BO intensity ratio with temperature

Table 10

Flame Speeds of Diborane-Air-Inhibitor Mixtures at 9 mm Pressure

Diborane: 7.5 parts by volume
Air: 92.5 " " "
Inhibitor: 2.0 " " "
Equivalence Ratio: 1.16

Inhibitor	Flame Speed, cm/sec	% of Uninhibited Flame Speed
A. Gaseous Inhibitors		
Butadiene	240*	26*
Ethyl chloride	590	60
Bromotrifluoromethane	640	65
Methyl bromide	680	69
Phosgene	730	75
Methane	740	75
Acetylene	760	78
Vinyl chloride	790	81
Ammonia	800	82
Ethylene oxide	810	83
Hydrogen sulfide	810	83
Monomethyl amine	820	83
Ethylene	850	87
Sulfur dioxide	870	89
Nitric oxide	920	94
Carbon monoxide	970	99
B. Vaporized Liquids		
Toluene	260**	28*
Benzene	370	38
Ethyl iodide	380	39
Diethyl ether	430	44
Dimethyl sulfide	440	45
Stannic chloride	450	46
Dibromotetrafluoroethane	510	53
Acetone	540	55
Carbon disulfide	650	67
Carbon tetrachloride	700	71
Bromochloromethane	710	73
Methanol	740	76
Chloroform	750	76
Phosphorus trichloride	800	82
Nitromethane	830	85
Water	920	94
None	980	100

*At pressure of run, uninhibited flame speed was 930 cm/sec.

**At pressure of run, uninhibited flame speed was 920 cm/sec.

4.1.5.2 Inhibition of Argon-Diluted Flames

The effect of a small amount of butadiene on the stoichiometric diborane-oxygen-argon flames described above was studied. The diborane-oxygen-butadiene ratios were 3:9:1, maintaining the stoichiometric ratio of diborane to oxygen. Above 90% argon the flames could not be stabilized at low pressure with the butadiene present. Experimental flame speeds, and values "normalized" to 50 mm, are listed in Table 11.

Table 11

Flame Speeds of Argon-Diluted,
Stoichiometric Diborane-Oxygen-Butadiene
Mixtures

% Argon	Pressure, mm	Flame Speed, cm/sec	Flame Speed, Calc., 50 mm
84	32	160	150
86	50	140	140
88	50	120	120
90	50	130	130
96	741	13.4	18.8

Figure 15 illustrates the inhibitory effect of added butadiene as a function of calculated adiabatic flame temperature, employing the data of Tables 9 and 11. The butadiene is more effective in the higher temperature flames (lower argon content), although the difficulty of stabilizing the low-temperature butadiene-containing flames indicates qualitatively that it was inhibiting them also.

Extrapolation of the results of Figure 15 to a temperature of 600°K would indeed predict that, under the shock tube conditions, little or no inhibitory effect would be observed with the best flame inhibitor identified.

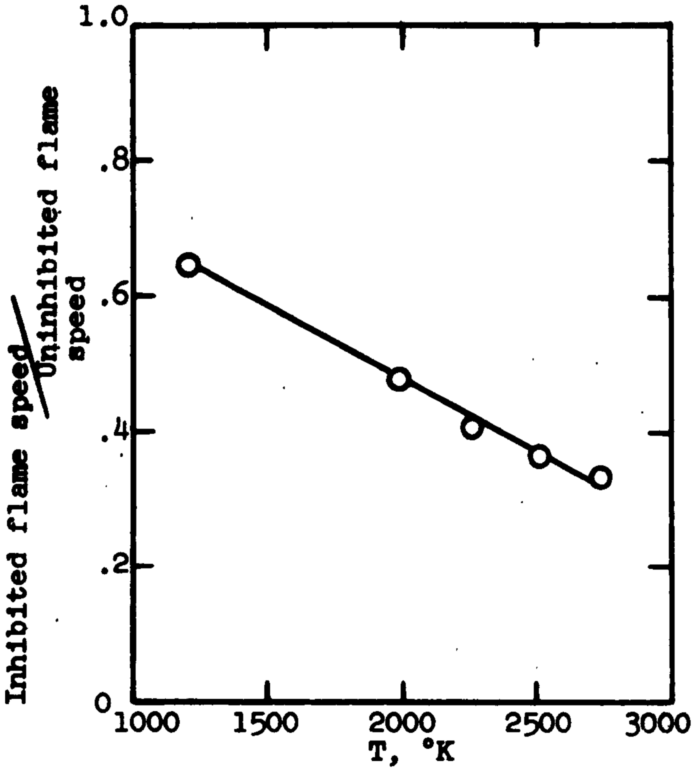


Figure 15. Effect of temperature on butadiene inhibition of diborane-oxygen-argon flames.

$O_2:B_2H_6:C_4H_6 = 9:3:1$

4.2 Inhibition of Pentaborane Oxidation

4.2.1 Pyrolysis of Pentaborane

4.2.1.1 Experimental Procedure Two gas mixtures, containing 0.25% and 1% pentaborane by volume in argon were made up by using accurate pressure gauges and pyrolyzed in the shock tube. The vapor pressure of pentaborane was high enough to permit handling of these dilute mixtures without heating the apparatus.

The total pressure of the heated gas behind the reflected shock wave was 5 atmospheres, and the reaction times between 14 and 20 milliseconds. After cooling, the products were analyzed for pentaborane by infrared absorption. No temperature correction for the heat of reaction was made, the heat effects being too small to be significant.

4.2.1.2 Experimental Results The results are given in Tables 12 and 13. Confirmation of the first-order rate dependence is shown in Figure 16, where all the rate constants of Tables 12 and 13 are plotted. A least-squares equation was obtained, in which all of the points were weighted equally. The least-squares equation is

$$\log k = 5.573 - 2,970/T$$

where k is the rate constant in $\sec^{-1}$
T is the absolute temperature, °K

The experimental activation energy (4.576 x 2,970/1000) is 13.6 Kcal/mole.

Table 12

Results for Pyrolysis of Gas Mixture Containing 0.25% Pentaborane in Argon

Temp., °K	Time, Millisec.	B_5H_9 Unreacted, %	First Order Rate Const., $\sec^{-1}$
652	17	80	14
676	17	77	15
714	16	56	36
749	15	62	32
766	16	49	44
785	15	48	46
832	14	12	157

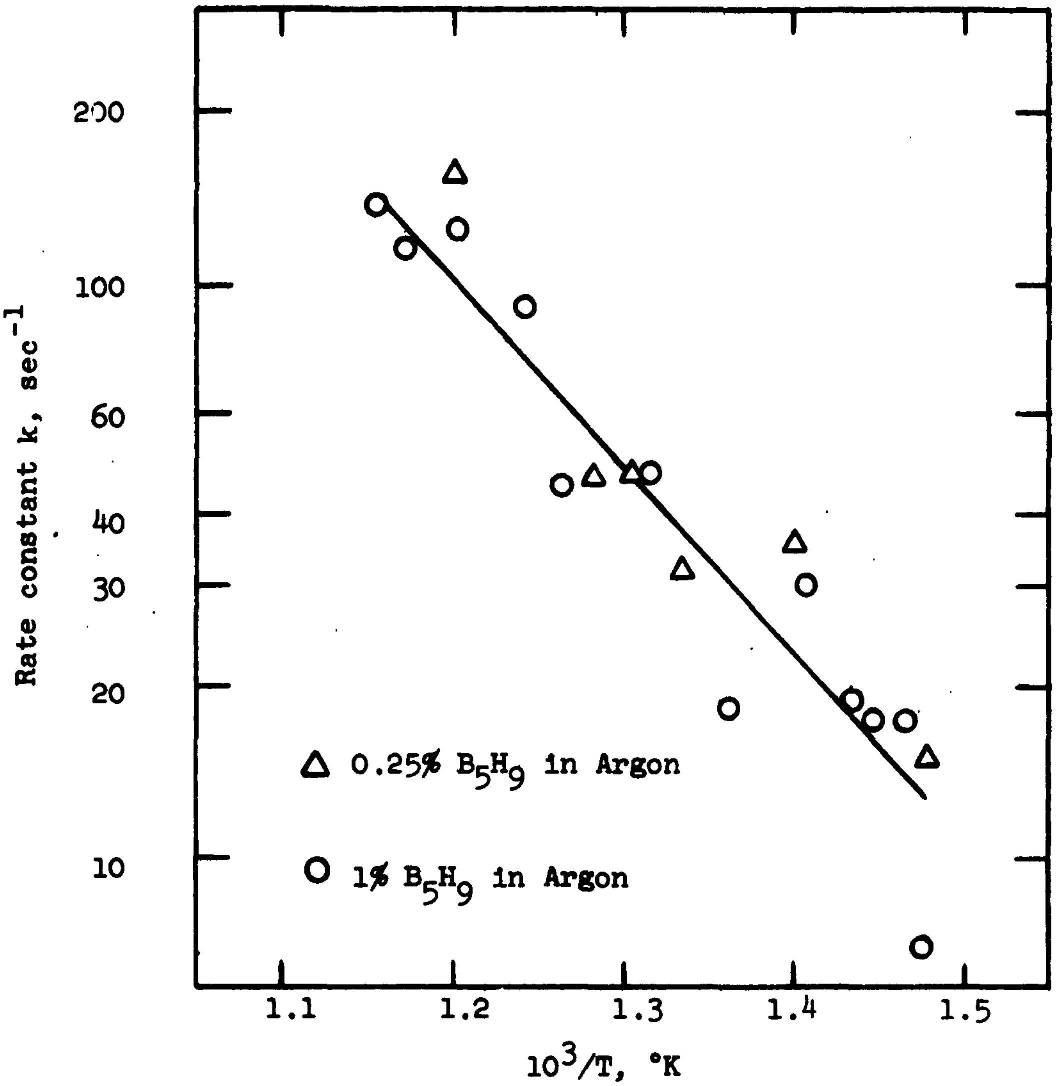


Figure 16. Rate constants for pyrolysis of pentaborane

Table 13

Results for Pyrolysis of Gas Mixture Containing 1% Pentaborane in Argon

Temp., °K	Time, Millisec.	B_5H_9 Unreacted, %	First Order Rate Const., sec^{-1}
677	17	89	7
682	20	70	18
691	20	58	28
697	17	60	29
710	20	56	30
734	22	66	19
760	15	49	47
791	20	41	45
805	14	26	92
831	14	17	125
853	14	21	115
866	14	14	139

4.2.1.3 Pyrolysis Mechanism Owing to the complex structure of the B_5H_9 molecule, there are many possible decomposition mechanisms that could, qualitatively, give the observed first-order reaction rates. Therefore, we feel it would be premature to propose a mechanism based on our experimental data.

4.2.2 Ignition of B_5H_9 - O_2 - Argon Mixtures

4.2.2.1 Experimental Procedure Three uninhibited B_5H_9 - O_2 - argon mixtures were studied. All contained 0.25% B_5H_9 by volume, while the oxygen contents were 0.75%, 1.5% and 3% O_2, corresponding to equivalence ratios of 2, 1 and 0.5 based on the overall reaction.

$$2\ B_5H_9 + 12\ O_2 \longrightarrow 5\ B_2O_3 + 9\ H_2O$$

In order to avoid spontaneous ignition of the B_5H_9 with O_2 on mixing, which can occur under some conditions (Ref. 18), mixtures of B_5H_9 in argon, and of O_2 in argon, were made up separately; then these dilute mixtures combined to produce the final reaction mixture. With this technique, no difficulty was experienced.

As with the diborane-containing mixtures, ignition induction times were measured from oscilloscope records of the light outputs as functions of time, the onset of combustion being signalled by a rapid increase in light output.

4.2.2.2 Experimental Results The experimental induction times are given in Tables 14 to 16. Least-squares equations were calculated for each equivalence ratio, in the form

$$\log t_i = A + B/T$$

as for diborane. The calculated values for each equivalence ratio are given below, along with the temperature at which the induction time was 5 milliseconds.

Equivalence Ratio	A	B	ΔH Kcal.	T,°K for t_i=5 msec.
2.0	-5.834	3,763	17.2	576
1.0	-4.810	3,202	14.7	581
0.5	-6.350	4,134	18.9	586

As with the ignition of diborane-oxygen-argon mixtures, the results are nearly the same for the three mixtures, as is seen when the data are plotted together (Figure 17).

4.2.2.3 Ignition Mechanism The independence of the induction times on oxygen concentration, similar to that found in diborane oxidation, suggests that pyrolysis of pentaborane is the controlling step in the ignition process. The observed activation energy for pentaborane pyrolysis, 13.6 Kcal/mole, is fairly close to those for oxidation (14.7 to 18.9 Kcal/mole) although the agreement is not quite as close as in the case of diborane.

In the time-temperature range studied, pentaborane is more stable toward both pyrolysis and oxidation than is diborane even though the activation energies for the pentaborane reactions are lower. Undoubtedly these reactions of pentaborane are complex, and the observed activation energies are not those of any individual steps in the reactions.

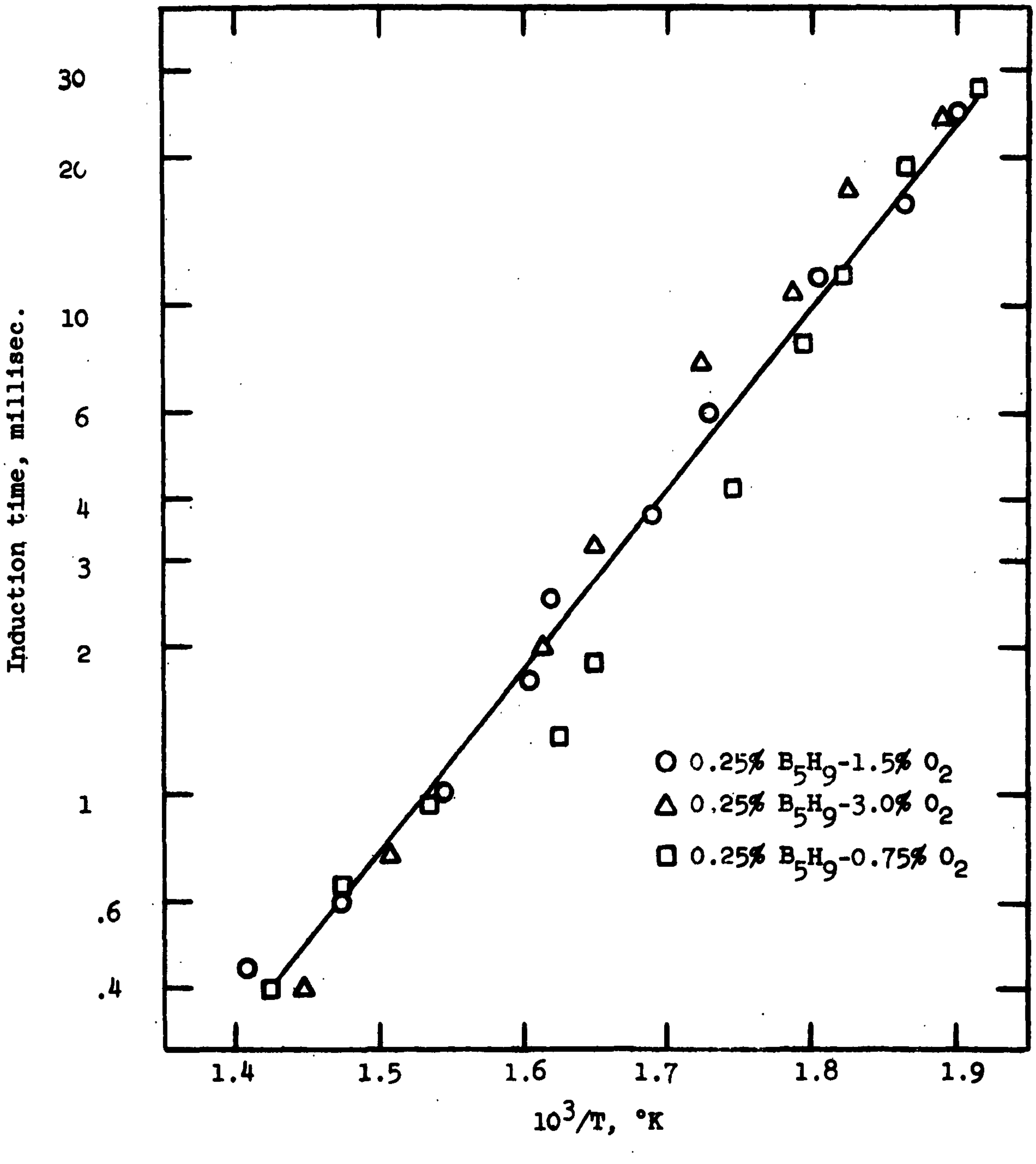


Figure 17. Ignition induction times for pentaborane-oxygen-argon mixtures

Table 14

Ignition Induction Times for Gas Mixtures Containing 0.25% B_5H_9, 0.75% O_2 and 99% Argon (Equivalence Ratio 2.0)

T, °K	Induction Time, milliseconds
522	28
536	19
549	11.5
557	8.4
572	4.2
606	1.8
615	1.3
652	0.95
678	0.65
701	0.40

Table 15

Ignition Induction Times for Gas Mixture Containing 0.25% B_5H_9, 1.5% O_2 and 98.25% Argon (Equivalence Ratio 1.0)

T, °K	Induction Time, milliseconds
526	24
536	16
554	11.4
578	6.0
592	3.7
617	2.5
623	1.7
647	1.0
678	0.6
710	0.44

Table 16

Ignition Induction Times for Gas Mixture Containing 0.25% B_5H_9, 3.0% O_2 and 96.75% Argon (Equivalence Ratio 0.5)

T, °K	Induction Time, milliseconds
529	24
548	17
559	10.5
580	7.6
606	3.2
620	2.0
663	0.75
690	0.40

4.2.3 Shock Tube Inhibition Studies The effects of adding small amounts of toluene, 1,2-dibromotetrafluoroethane and 1,3-butadiene to the stoichiometric pentaborane-oxygen-argon mixture studied above were measured. In each case 0.135% of additive (by volume) was added to the basic 0.25% B_5H_9, 1.5% O_2 mixture. This is approximately twice the amount added to the diborane-oxygen-argon mixture described earlier, since there was twice as much oxygen (and an equivalent amount of pentaborane) in the pentaborane-containing mixture.

Infrared analysis of the gas mixtures showed that the additives did not react with the pentaborane on mixing.

The experimental results are shown in Tables 17 to 19, and in Figure 18. Butadiene and toluene increased the ignition induction times, whereas dibromotetrafluoroethane did not. The least-squares constants for these data, corresponding to those given above for the uninhibited mixtures, are:

Inhibitor	A	B	ΔH Kcal	T, °K for t_i = 5 msec
$C_2F_4Br_2$	-5.602	3,653	16.7	580
C_7H_8	-8.405	6,489	29.7	713
C_4H_6	-8.240	7,290	33.4	816

The curve for $C_2F_4Br_2$ is essentially that of the uninhibited mixture, whereas from Figure 18 it can be seen that at 750°K ($10^3/T = 1.33$) the induction time of the butadiene-inhibited mixture is over 100 times as long as that of the uninhibited mixture.

Table 17

Ignition Induction Times for Gas Mixture Containing 0.25% B_5H_9, 1.5% O_2, 98.115% Argon and 0.135% Toluene

T, °K	Induction Time, milliseconds
656	27
674	18
690	10.4
701	6.2
725	4.2
766	1.6
782	0.75
805	0.40

Table 18

Ignition Induction Times for Gas Mixture Containing 0.25% B_5H_9, 1.5% O_2, 98.115% Argon, and 0.135% $C_2F_4Br_2$

T, °K	Induction Time, milliseconds
528	30
547	20
554	10.6
559	7.4
574	5.0
589	3.0
613	2.0
628	1.4
650	1.0
677	0.55
715	0.35
758	0.24

Table 19

Ignition Induction Times for Gas Mixture Containing
0.25% B_5H_9, 1.5% O_2, 98.115% Argon and 0.135% Butadiene

T, °K	Induction Time, milliseconds
763	21
765	18
777	16
783	10
790	16
797	7.4
819	4.4
825	3.4
870	1.0
909	0.6
956	0.3

4.2.4 Low Pressure Burner Studies-Uninhibited Flames

4.2.4.1 Stability Regions The regions of stable burning of pentaborane-air mixtures were determined at low pressure for equivalence ratios of 0.75, 1.0 and 2.0. An equivalence ratio of 1 corresponds to a 1:6 pentaborane-oxygen ratio, which could react completely according to the equation

$$B_5H_9 + 6O_2 \longrightarrow 5/2\ B_2O_3 + 9/2\ H_2O$$

The regions are presented in Figure 19 where the average linear velocity of the unburned gas mixture is plotted versus the absolute pressure in mm at which blow-off and flash-back occurred.

4.2.4.2 Effect of Equivalence Ratio on Flame Speeds The flame speeds of uninhibited pentaborane-air mixtures were studied as a function of equivalence ratio at a pressure of 7.0 mm. This value was chosen, since the higher flame speed mixtures would be stable at this pressure on the 2.6 cm burner. The equivalence ratio was varied from

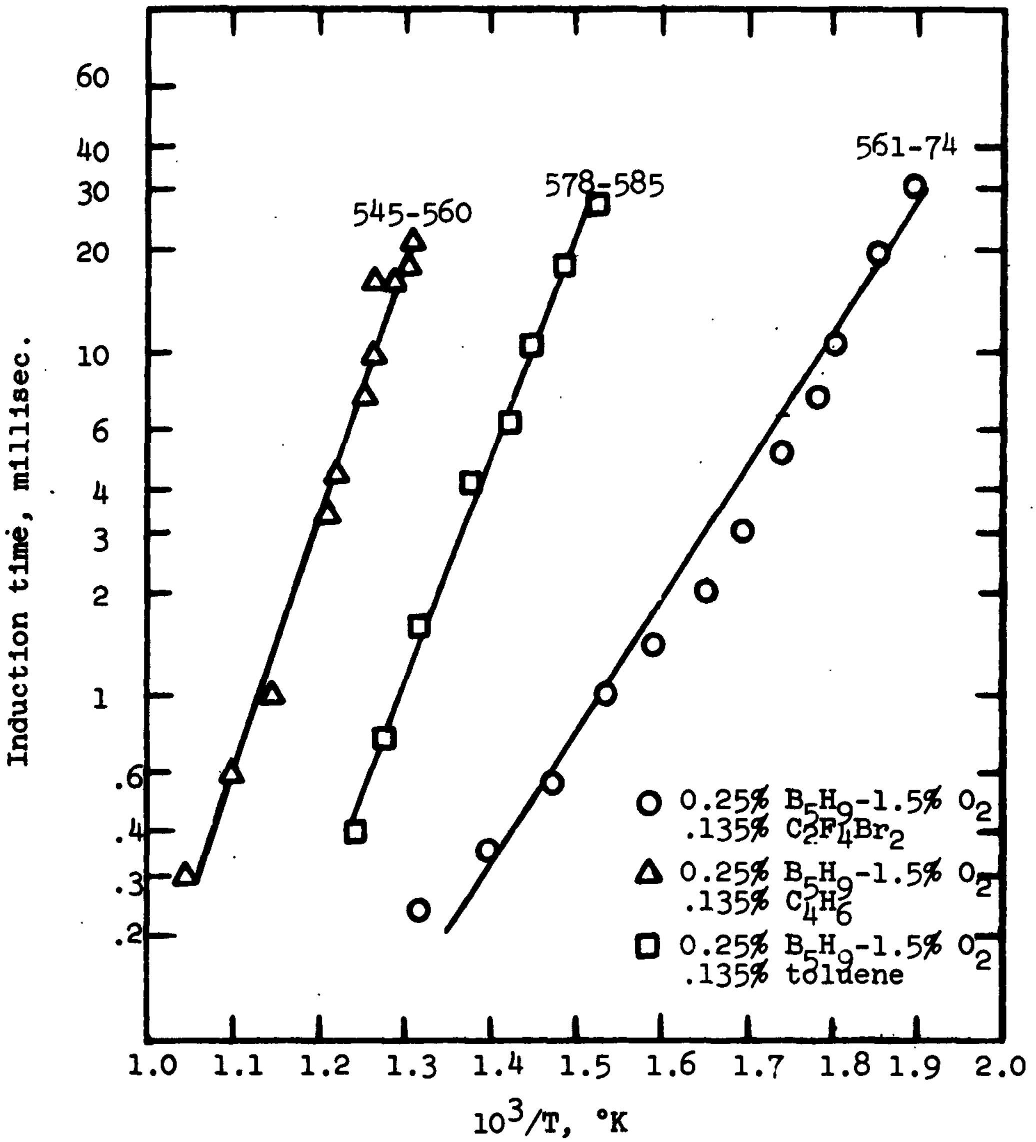


Figure 18. Ignition induction times for inhibited pentaborane-oxygen-argon mixtures

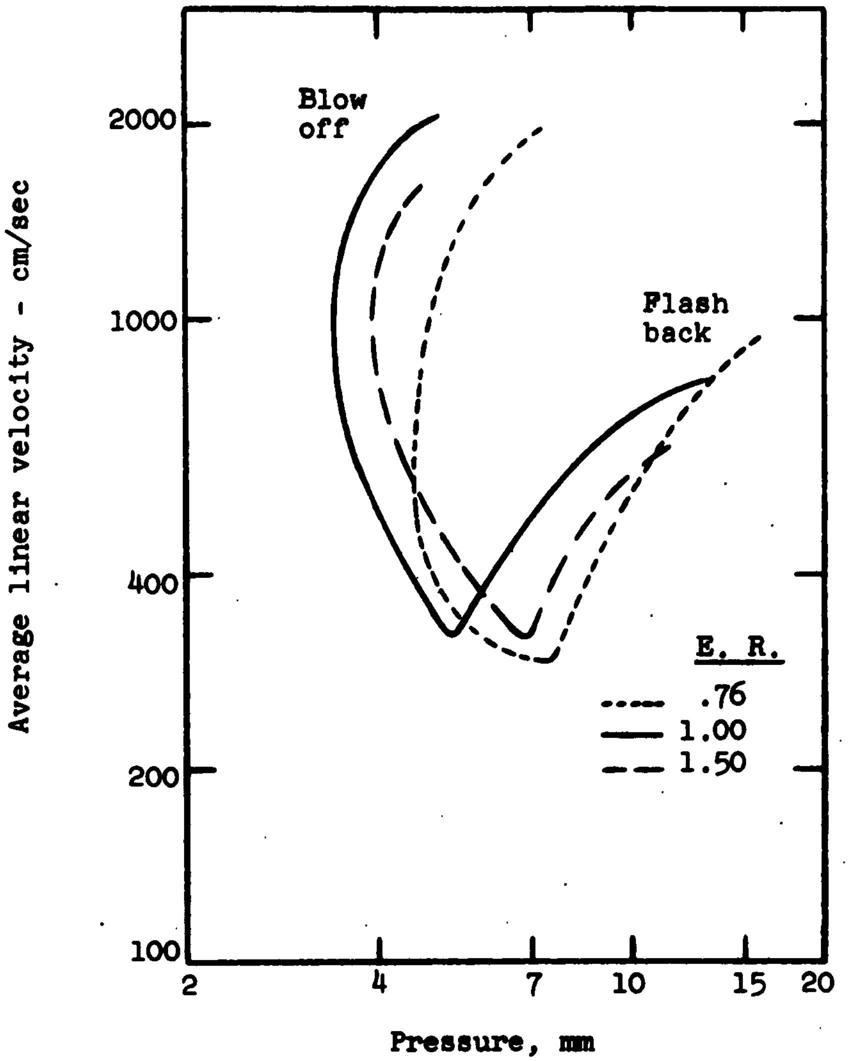


Figure 19. Stable regions of B_5H_9-air flames for several equivalence ratios

0.69 to 1.53. The resulting flame speed data are represented in Table 20 and average values are plotted in Figure 20. The maximum flame speed of 720 cm/sec is found to occur at an equivalence ratio of 1.1. In this respect the pentaborane-air system is similar to the diborane-air system where the maximum occurs at an equivalence ratio of 1.16, although diborane does have a higher flame speed. At atmospheric pressure the flame speeds of the two boranes have been found to be essentially equal (Ref. 2 and 19).

Table 20

Flame Speeds of Uninhibited Pentaborane-Air Mixtures at 7 mm on 2.6 cm Burner

Equivalence Ratio	Flame Speed cm/sec	Average Flame Speed cm/sec
0.69	480 640	560
0.79	580 640	610
0.91	620 700	660
1.00	690 680	680
1.11	720 720	720
1.31	680 680	680
1.42	620 580	600
1.53	560 560	560

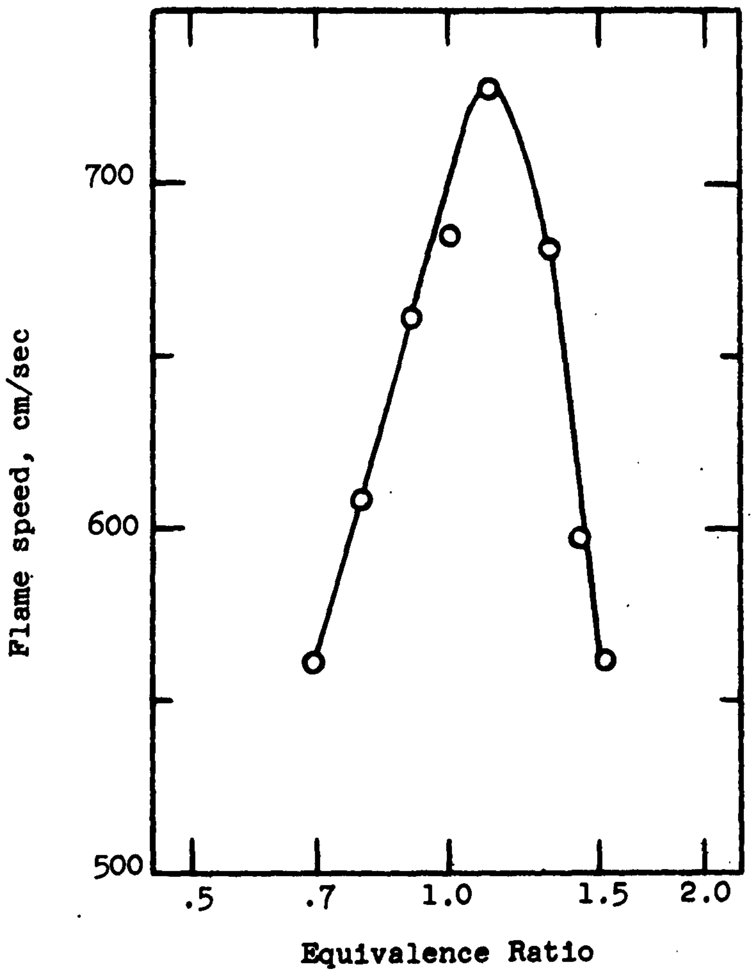


Figure 20. Flame speeds of uninhibited pentaborane-air mixtures at 7 mm on 2.6 cm burner

4.2.4.3 Effect of Pressure on Flame Speeds

The pressure dependence of the flame speed of the fastest burning pentaborane-air mixture (1.1 equivalence ratio) was studied. Flame speeds at different pressures were obtained by varying the burner tube diameter inversely with the desired pressure. The experimental results are given in Table 21, and plotted in Figure 21. The value of 540 cm/sec determined by Berl et al (Ref. 19) at 760 mm is also shown.

As was the case with diborane-air mixtures, the flame speed is shown to fall off at high pressures. The values of flame speed of uninhibited pentaborane-air mixtures at a given pressure were employed in calculating the effectiveness of candidate inhibitors in later screening experiments. This was necessary since in the presence of inhibitors, a stable flame could not always be obtained at 7.0 mm.

Table 21

Pressure Dependence of Pentaborane-Air Flame Speed
(Equivalence Ratio 1.10)

Pressure, mm	Tube Diameter, cm	Flame Speed, cm/sec	Average Flame Speed cm/sec
7.0	2.61	720 720	720
10.4	1.76	660 680	670
24.2	0.76	610 620	620
760 (Ref. 19)			540

4.2.5 Inhibition of Pentaborane-Air Flames

4.2.5.1 Inhibitor Screening

The effects on the flame speed produced by adding 2 per cent by volume of 33 gases and vaporized liquids were studied employing the 1.1 equivalence ratio flame as a standard. The results

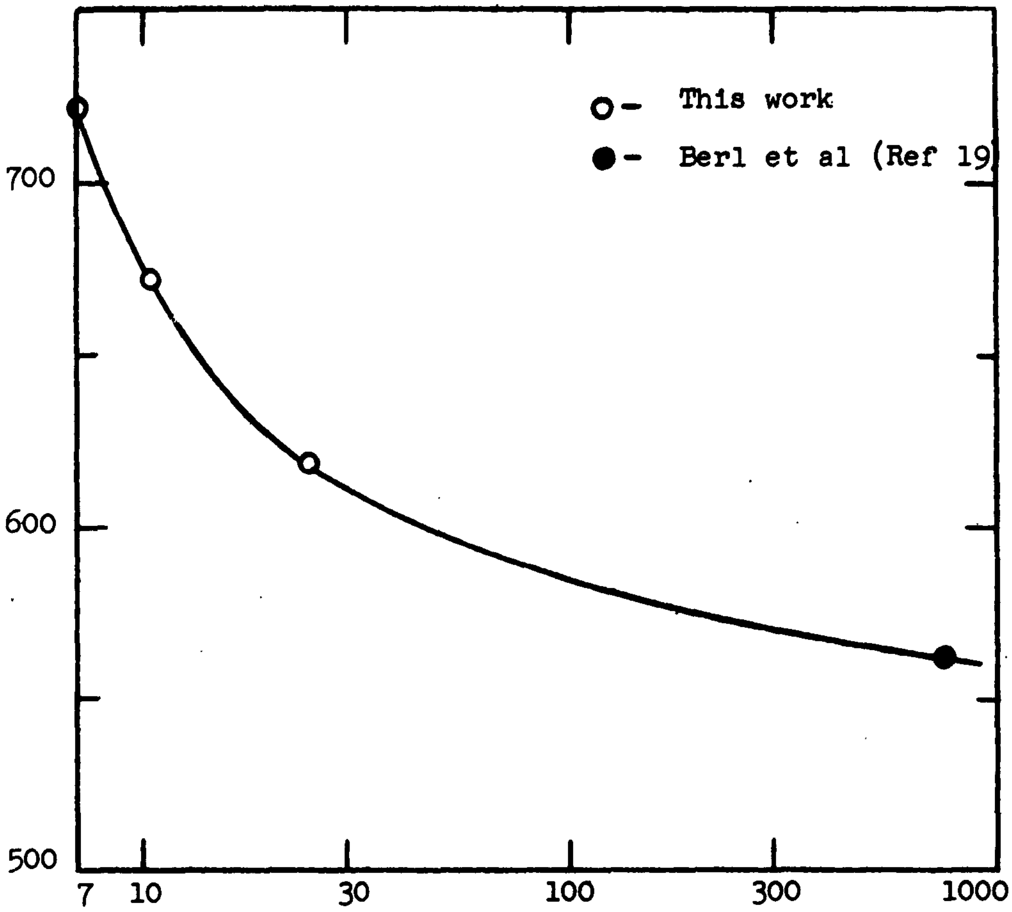


Figure 21. Pressure dependence of pentaborane-air flame speed (equivalence ratio 1.10)

are given in Table 22. The additives are listed in order of decreasing effectiveness. The results entered are the average of from 2 to 4 separate experiments.

The general similarity between the effectiveness of inhibitors in the case of the flames systems hydrogen-air and diborane-air was pointed out earlier (Ref. 20). When pentaborane-air mixtures are considered in addition the following similarities among the three systems can be observed:

1. In general, the presence of bromine and iodine in alkyl hydrocarbons are more effective than chlorine or fluorine substitutions. In the case of the boranes the presence of bromine and chlorine both appear to add inhibitory power over that of the unsubstituted hydrocarbon. This was not the case for hydrogen flames.

2. In general the effect of degree of unsaturation is that the inhibition decreases as double, and then triple bonds are substituted for single bonds.

$$C-C > C=C > C \equiv C$$

3. However, conjugated double bonds and aromatic rings appear to be particularly effective.

$-C=C-C=C-$ and  $>>$ $C-C-C-C$

4. Sulfur and oxygen in sulfides and ethers appear equally effective while sulfur in CS_2 and H_2S is more effective than oxygen in CO_2 and water.

5. Saturated alkylhalides are more effective than unsaturated alkylhalides.

The most striking difference between the action of inhibitors on the two borane flames is that methyl amine and ammonia appear to be relatively more effective in the case of pentaborane while SO_2 apparently sensitizes the flame reaction.

The similarities between the order of effectiveness of inhibitors in hydrogen-air and borane-air flames suggest that the mechanisms of flame propagation in these systems resemble one another. The additives appear to be operable through a hydrogen atom abstraction mechanism. This is highly likely since the presence of OH has not been observed by emission spectroscopy in uninhibited borane flames.

Table 22

Flame Speeds of Pentaborane-Air-Inhibitor Mixtures

Pentaborane: 3.7 parts by volume
Air: 96.3 parts by volume
Inhibitor: 2.0 parts by volume
Equivalence Ratio: 1.10

Inhibitor	Flame Speed cm/sec	Uninhibited Flame Speed	% of Uninhibited Flame Speed
A. Gaseous Inhibitors			
Butadiene	225	652	36
Methylamine	328	672	49
Ethyl chloride	474	722	66
Ethylene oxide	482	722	67
Ethylene	500	722	69
Hydrogen sulfide	533	722	74
Bromotrifluoromethane	552	722	76
Ammonia	561	722	78
Methyl bromide	593	722	82
Acetylene	606	722	84
Phosgene	609	722	84
Methane	938	722	84
Vinyl chloride	641	722	89
Carbon monoxide	650	722	90
Nitric oxide	670	722	93
Sulfur dioxide	844	722	117
B. Vaporized Liquids			
Toluene	233	621	38
Benzene	246	630	39
Dimethyl sulfide	342	672	51
Dibromotetrafluoroethane	342	656	52
Ethyl iodide	345	656	53
Bromochloromethane	393	720	55
Stannic chloride	394	716	55
Phosphorus trichloride	430	722	60
Diethyl ether	405	661	61
Acetone	466	664	70
Acetonitrile	521	718	73
Carbon tetrachloride	526	722	73
Methanol	527	722	73
Chloroform	574	722	80
Carbon disulfide	615	722	85
Nitromethane	620	722	86
Water	709	722	98

Recently Wolfhard et al (Ref. 16) have shown that the flame speed versus flame temperature plot for diborane-oxygen-nitrogen mixtures lies on a high temperature extension of a similar plot for hydrogen-oxygen-nitrogen mixtures. The similar plots for hydrocarbons such as acetylene and methane are displaced toward much lower values of flame speed. This result further confirms the similarity between the borane and hydrogen flame mechanisms.

4.3 Detonation of B_2H_6-O_2-Argon Mixtures

When an attempt was being made to measure induction times of a diborane-oxygen-argon mixture at higher temperatures than those reported above in Section 4.1.2, detonation of the gas mixture occurred behind the incident shock wave. A brief study of the conditions leading to detonation was made.

The gas mixture used contained 0.25% B_2H_6, 0.75% O_2 and 99% argon (one of those used earlier in the work described in Section 4.1.2). This gas mixture, containing only 1% reaction mixture and 99% argon, behaves aerodynamically like pure argon, except for the available chemical energy. Complete reaction according to the equation

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3(l) + H_2O$$

would generate enough heat to raise the gas temperature by 240°K.

The shock speed is calculated from the time required for the shock wave to travel between two piezoelectric transducers located respectively 55 and 7 inches from the closed end of the shock tube. For a given driver and sample gas, the shock speed is normally a monotonic function of the driver/sample pressure ratio. In Figure 22 the circular points are a set of data obtained with a constant helium driver pressure of 85 psia, and various argon sample pressures as shown on the horizontal axis. When the gas mixture containing diborane and oxygen was shocked in the same way, the shock speeds indicated by the triangles in Figure 22 were obtained.

At the lowest shock speeds, (pressures of 500 and 550 mm) the two curves match almost exactly, indicating that reaction was not occurring immediately behind the incident shock wave. This conclusion is borne out by the pressure and light emission records, which indicate that in the 500-mm run there was an

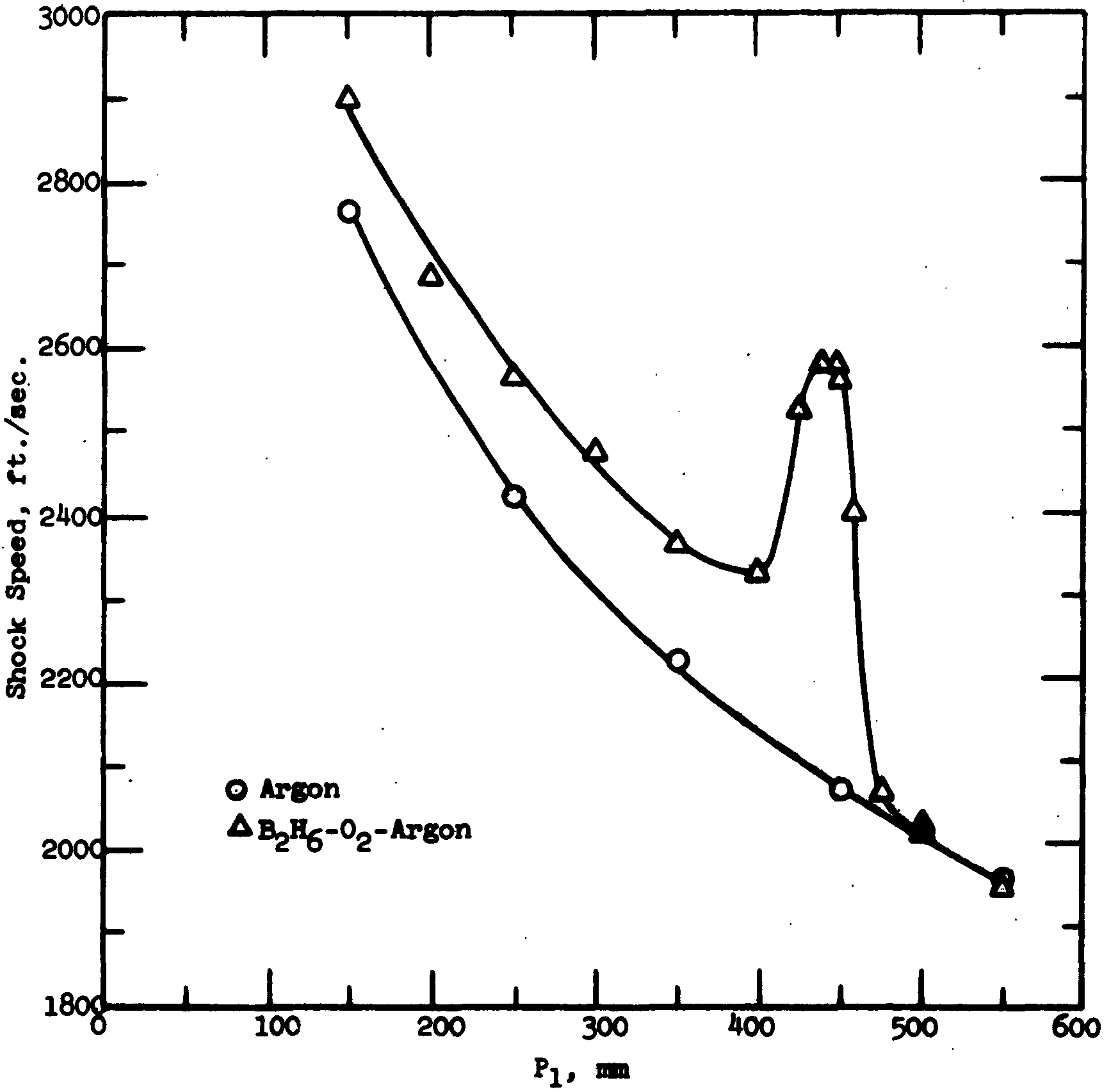


Figure 22. Shock speeds for gas mixtures containing 0.25% B_2H_6, 0.75% O_2, 99% argon, and for pure argon, at various initial gas pressures

induction time of 0.36 msec, while in the 500-mm run no reaction occurred until the reflected shock wave passed the observation port. This agreement between shock speeds for pure argon and reactive mixture would continue to still higher initial pressures and correspondingly lower shock speeds.

With initial sample pressures of 400 mm and below, the curve for the reaction mixture runs approximately parallel to that for pure argon. This would be expected if heat is released immediately behind the shock wave. By calculation, however, the actual separation between the two curves is less than it would be if all of the heat of reaction were released immediately behind the shock wave.

Figure 23 shows the results of the calculation. The lowest curve shows the dependence of shock speed on sample pressure for 85 psia helium driver pressure for pure argon, where no heat would be released by chemical reaction. The three upper curves show the shock speeds that would be obtained when various fractions of the total energy available in the 0.25% B_2H_6, 0.75% O_2, 99% argon reaction mixture are released immediately behind the shock wave.

Comparison of Figures 22 and 23 indicates that at 150-400 mm pressure about 30% of the total energy was released behind the shock wave. At the peak near 450 mm pressure, release of almost 100% of the available energy would be needed to produce the observed shock speeds.

Theoretical analysis of the results indicates that at initial pressures below 400 mm a steady detonation wave had formed, whereby chemical reaction was occurring close behind the incident shock wave. The chemical energy released by reaction caused the shock wave to be more rapid than without energy release. Since the energy is released a finite distance behind the shock wave, the shock speed is less than it would be if the energy was released in the wave.

The high shock speed observed at 450 mm pressure is a transient one that is reached only while the detonation wave is forming. If the pressure gauges used for shock speed determination had been closer to the diaphragm, the peak would have occurred at a lower sample gas pressure.

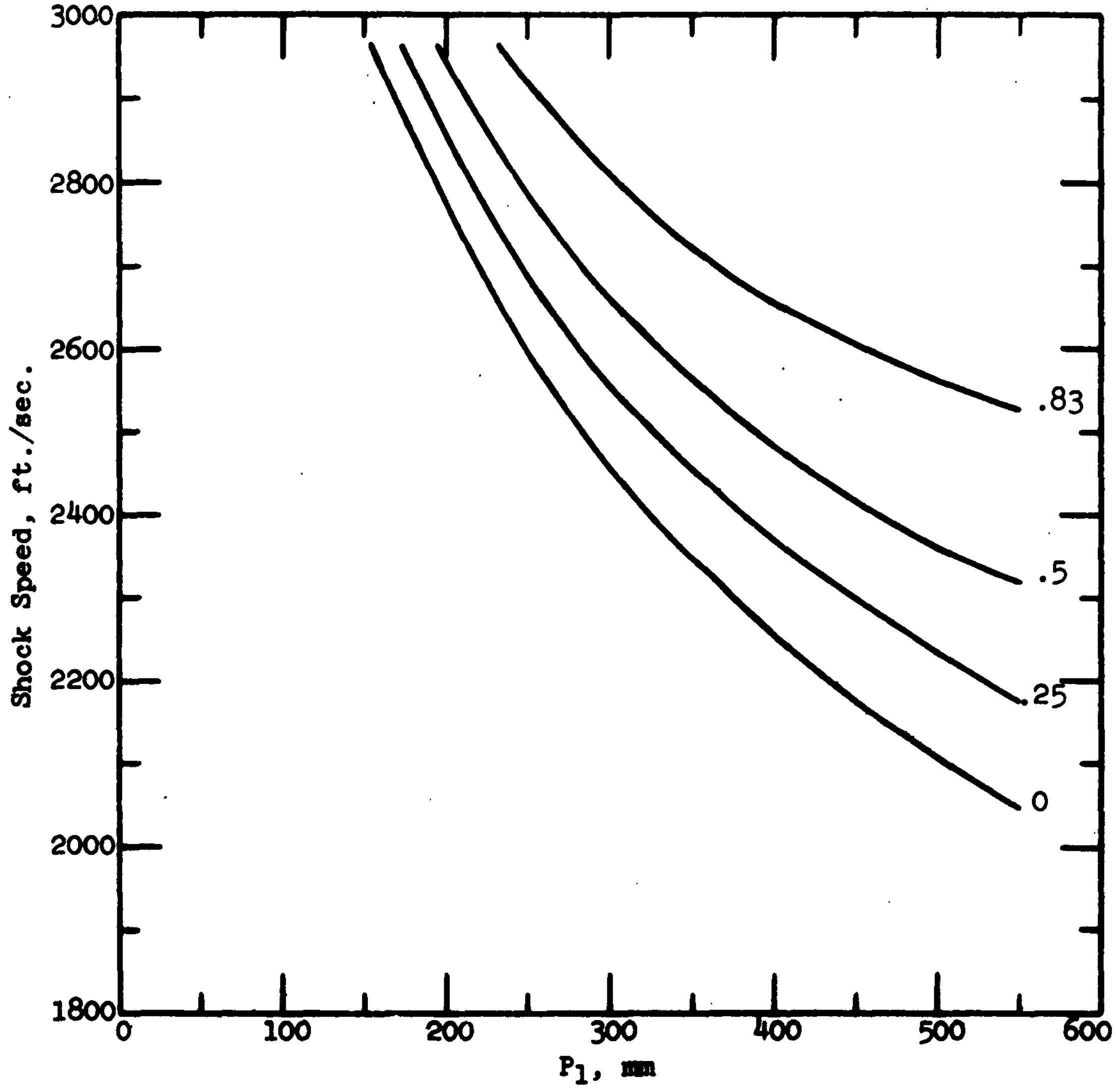


Figure 23. Calculated shock speeds for various fractions of heat release for gas mixture containing 0.25% B_2H_6, 0.75% O_2 and 99% argon

This type of detonation process is not limited to the diborane-oxygen system, but is typical of branching chain reactions where there is an induction period followed by a period of rapid reaction. In other studies, we have observed it with the hydrogen-oxygen reaction, although in this case lower sample gas pressures (higher shock temperatures) were needed to produce detonation waves.

4.4 Calculations on the Inhibition of Hydrogen Oxidation

In an earlier report (Ref. 20) we described experiments in which ignition induction times of hydrogen-oxygen-argon mixtures, with and without inhibitors, were measured by means of a shock tube. Also, several calculations of induction times were made, based on the known or estimated kinetics of a group of elementary reactions.

During the past year additional calculations have been made. These have given results that agreed more closely with the experimental results than the earlier ones did. This good agreement is evidence that the reaction mechanisms postulated for the inhibition process are correct.

4.4.1 Summary of Experimental Data

Ignition induction times were measured from oscilloscope records of the intensity of light emission from the gas. Usually the light intensity remained at a low, undetectable value for a while, then rose sharply to a peak value. In the earlier report the induction time was defined as the time required for the emission intensity to reach 10% of its peak value. This was a somewhat arbitrary definition. After discussing the matter with other investigators working in the same general area, we decided that the most satisfactory value to use for the end of the induction period would be the time of peak intensity, rather than that of 10% of the peak. In many cases, because of the steep rise of light intensity with time, the redefined induction time is very little longer than that used previously. (For example, an induction time of 15.0 milliseconds by the old definition became 16.6 milliseconds by the new one.)

In the following table are summarized the experimental data, based on this new definition. The data of Tables 23, 24, 25, 26 and 27 are equivalent to Tables 14, 22, 23, 20 and 21, respectively, of Ref. 20.

Table 23

Induction Times for Gas Mixture Containing 8% H_2 and 2% O_2 in Argon

Temp., °K	Induction Time, millisec.
964	16.6
965	11.8
981	7.2
1004	2.0
1005	2.8
1024	1.0
1075	0.28

Table 24

Induction Times for Gas Mixture Containing 8% H_2, 2% O_2 and 0.8% CH_4 in Argon

Temp., °K	Induction Time, millisec.
973	19
985	17
992	14
1027	4.0
1037	2.7
1048	2.6
1058	2.6
1096	1.1
1125	0.7

Table 25

Induction Times for Gas Mixtures Containing 8% H_2, 2% O_2 and 0.4% C_2H_4 in Argon

Temp., °K	Induction Time, millisec.
1018	16
1022	17
1029	16
1051	7.4
1108	2.3
1143	1.6
1172	1.1
1183	1.1

Table 26

Induction Times for Gas Mixture Containing 8% H_2, 2% O_2 and 0.8% CF_3Br in Argon

Temp., °K	Induction Time, millisec.
1105	15.0
1141	9.0
1181	2.4
1191	2.5
1215	1.6
1223	1.4
1271	1.0
1284	0.8

Table 27

Induction Times for Gas Mixtures Containing 8% H_2, 2% O_2 and 0.4% $C_2F_4Br_2$ in Argon

Temp., °K	Induction Time, millisec.
1128	14.6
1144	12.6
1167	6.4
1224	2.4
1269	1.1
1286	1.1

4.4.2 Reactions Used in Kinetic Calculations

In the calculations reported in Ref. 20, ten elementary reactions were considered for uninhibited combustion. These were:

1. $H_2 + O_2 \longrightarrow 2\ OH$
2. $H + O_2 \longrightarrow OH + O$
3. $O + H_2 \longrightarrow OH + H$
4. $OH + H_2 \longrightarrow H_2O + H$
5. $H + O_2 + Ar \longrightarrow HO_2 + Ar$
6. $H + H + Ar \longrightarrow H_2 + Ar$
7. $H + OH + Ar \longrightarrow H_2O + Ar$
8. $H + H + H_2O \longrightarrow H_2 + H_2O$
9. $H + OH + H_2O \longrightarrow H_2O + H_2O$
10. $OH + OH \longrightarrow H_2O + O$

In this reaction scheme HO_2, once it formed, tended to remain as a stable product since at the concentrations usually existing during the calculations Reaction 5 proceeded chiefly from left to right. Since Lewis and Van Elbe (Ref. 21) have shown that HO_2 can react with hydrogen, the reaction scheme has been made more realistic by addition of one more elementary reaction, as follows:

11. $HO_2 + H_2 \longrightarrow H_2O_2 + H$

Since the gas mixture being inhibited is a rich one, it is most likely that inhibitors act primarily by removing hydrogen atoms, the most numerous reactive species present. Therefore, the initial step for inhibition by each of the inhibitors was reaction with a hydrogen atom. It was shown in Ref. 20 that the inhibitors disappear much more rapidly by reaction with combustion intermediates than by thermal decomposition. Therefore, thermal decomposition reactions were not considered to be important.

For CH_4 the additional reactions producing inhibition were considered to be:

12. $CH_4 + H \longrightarrow CH_3 + H_2$

13. $CH_3 + H + Ar \longrightarrow CH_4 + Ar$

14. $CH_3 + H + H_2 \longrightarrow CH_4 + H_2$

15. $2\ CH_3 \longrightarrow C_2H_6$

16. $C_2H_5 + H \longrightarrow C_2H_6$

17. $2C_2H_5 \longrightarrow C_2H_4 + C_2H_6$

18. $C_2H_6 + H \longrightarrow C_2H_5 + H_2$

For C_2H_4 as inhibitor, reactions considered were:

19. $C_2H_4 + H \longrightarrow C_2H_5$

16. $C_2H_5 + H \longrightarrow C_2H_6$

17. $2C_2H_5 \longrightarrow C_2H_4 + C_2H_6$

18. $C_2H_6 + H \longrightarrow C_2H_5 + H_2$

For CF_3 as inhibitor, reactions considered were:

20. $CF_3Br + H \longrightarrow CF_3 + H\ Br$

21. $CF_3 + H + Ar \longrightarrow CF_3H + Ar$

22. $CF_3 + H + H_2 \longrightarrow CF_3H + H_2$

23. $CF_3 + H_2 \longrightarrow CF_3 + H$

24. $H\ Br + H \longrightarrow Br + H_2$

while for $C_2F_4Br_2$ the reactions were:

25. $C_2F_4Br_2 + H \longrightarrow C_2F_4Br + HBr$

26. $C_2F_4Br \longrightarrow C_2F_4 + Br$

27. $C_2F_4Br + H \longrightarrow C_2F_4 + HBr$

24. $HBr + H \longrightarrow Br + H_2$

Although these are by no means all of the reactions that could possibly occur they are the most important ones, and their use in calculations has resulted in agreement with experimental values.

The rate constants used in the calculations were expressed in the form

$$k = A\, T^B\, e^{-E/RT}$$

where k is the rate constant in units of sec^{-1} for unimolecular, mole^{-1} cc sec^{-1} for bimolecular, and mole^{-2} cc^2 sec^{-1} for termolecular reactions. Equilibrium constants were used to relate forward and reverse rate constants.

Considerable, but inconsistent, data have been published on the rates of these reactions, a fairly complete survey for the uninhibited reaction being given in Ref. 20. These calculations were considered to be a means of checking the literature data, and arriving at better values for the rate constants. After a number of trials, a set of rate constants was arrived at which was thermodynamically consistent, in reasonable agreement with literature data, and gave induction times in agreement with experiment. The constants used in the final calculations are given in Table 28.

Table 28

Constants for Rate Expressions in Induction Time Calculations

Reaction	A	B	E
(a) Forward Reactions			
1	2.50 E 14	0	6.700 E 4
2	1.00 E 15	0	1.775 E 4
3	1.20 E 13	0	9.200 E 3
4	1.48 E 14	0	6.430 E 3
5	8.25 E 15	0	0
6	1.50 E 18	-1	0
7	3.60 E 19	-1	0
8	3.00 E 19	-1	0
9	7.20 E 20	-1	
10	7.40 E 14	0	3.820 E 3
11	3.20 E 16	0	3.460 E 4
12	7.94 E 13	0	8.000 E 3
13	1.20 E 22	-1	0
14	2.40 E 22	-1	0
15	3.16 E 12	0	-1.500 E 3
16	4.40 E 15	0	0
17	4.40 E 15	0	0
18	4.00 E 13	0	6.200 E 3
19	4.00 E 13	0	1.580 E 3
20	4.36 E 15	0	1.745 E 4
21	2.00 E 20	-1	0
22	4.00 E 20	-1	0
23	7.75 E 11	0	2.514 E 4
24	6.14 E 13	0	2.190 E 3
25	1.00 E 16	0	1.450 E 4
26	9.95 E 12	0	5.000 E 4
27	2.00 E 16	0	1.150 E 4

Table 28 (Cont'd)

Reaction	A	B	E
(b) Reverse Reactions			
1	7.05 E 12	0	4.860 E 4
2	6.16 E 13	0	1.190 E 3
3	5.50 E 12	0	7.370 E 3
4	6.92 E 14	0	2.162 E 4
5	1.01 E 20	-1	5.000 E 4
6	3.48 E 22	-2	1.080 E 5
7	3.95 E 24	-2	1.232 E 5
8	6.96 E 23	-2	1.080 E 5
9	7.90 E 25	-2	1.232 E 5
10	7.60 E 15	0	2.084 E 4
11	2.46 E 16	0	1.822 E 4
12	3.16 E 12	0	1.020 E 4
13	5.56 E 27	-2	1.053 E 5
14	1.10 E 28	-2	1.053 E 5
15	1.72 E 19	-1	8.616 E 4
16	2.09 E 21	-1	1.054 E 5
17	4.04 E 17	0	6.896 E 4
18	1.56 E 12	0	4.050 E 3
19	2.08 E 17	-1	3.800 E 4
20	5.14 E 10	0	8.421 E 4
21	2.38 E 25	-2	8.713 E 4
22	4.76 E 25	-2	8.713 E 4
23	5.00 E 12	0	5.000 E 3
24	1.73 E 14	0	1.917 E 4
25	1.18 E 13	0	5.120 E 4
26	6.95 E 09	1	2.500 E 3
27	9.12 E 16	0	5.456 E 4

4.4.3 Results of the Calculations Calculations were made for seven sets of experimental gas concentrations, as follows:

1. 4% H_2, 2% O_2, 94% Ar, 1 atmosphere
2. 1% H_2, 2% O_2, 97% Ar, 1 atmosphere
3. 8% H_2, 2% O_2, 90% Ar, 5 atmospheres
4. 8% H_2, 2% O_2, 0.8% CH_4, 89.2% Ar, 5 atmospheres
5. 8% H_2, 2% O_2, 0.4% C_2H_4, 89.6% Ar, 5 atmospheres
6. 8% H_2, 2% O_2, 0.8% CF_3Br, 89.2% Ar, 5 atmospheres
7. 8% H_2, 2% O_2, 0.4% $C_2F_4Br_2$, 89.6% Ar, 5 atmospheres

The first two concentrations were studied by Schott and Kinsey (Ref. 9) and the others by us. Induction times were calculated at temperatures between 800 and 2500°K,

The FORTRAN computer program for the calculations is described in Supplement I of this report, under separate cover. Briefly, a numerical integration over a large number of small time increments is carried out. Concentrations of all species are known at the beginning of a given time increment. The amount of conversion by a certain reaction in an increment is determined by multiplying the rate constant by the species concentrations and the time increment. For example, for the forward Reaction 1, the "amount of reaction" would be

$$k_1\ (H_2)\ (O_2)\,\Delta t$$

This type of calculation is made for all reactions, both forward and reverse, that are included in the overall calculation. and from these "amounts of reaction" the net change in concentration of each chemical species during the increment is calculated. From these net changes, the concentrations of all the species at the end of the increment are calculated, and calculations on the next increment can begin. These calculations were performed on an ASD IBM 7094 digital computer at Wright-Patterson Air Force Base. Calculations for the CF_3Br inhibited reactions involving 14 species and 16 reactions required about 7.5 minutes of computer time per millisecond of reaction.

The results of the calculations are summarized in the following tables. A more detailed listing of the results is given in Appendix II of this report.

Table 29

Calculated Ignition Induction Times for Uninhibited H_2-O_2-Argon Mixtures

	Calculated Induction Times, Millisec.		
Temp., °K	#1	#2	#3
900	~31	~160	
970			9.8
1000	1.1	2.3	3.4
1050			0.54
1100	0.44	0.84	
1150			0.070
1250	0.18	0.34	0.030
1600	0.052	0.10	0.0068
2000	0.022	0.051	0.0027
2500	0.010	0.027	0.0013

Table 30

Calculated Ignition Induction Times for Inhibited H_2-O_2-Argon Mixtures

Temp., °K	Calculated Induction Times, Millisec., for Inhibition by			
	CH_4	C_2H_4	CF_3Br	$C_2F_4Br_2$
1000	8.4			
1030		13.		
1100	1.2	3.6		
1150	0.34	1.3	~7.	11.
1225				2.8
1250		0.18		
1300			0.62	0.87
1600		0.0072		
2000		0.0026		
2500		0.0013		

In Figure 24 we have plotted our data on the uninhibited mixture along with data obtained by Schott and Kinsey (Ref. 9). Instead of giving experimental induction times directly, they presented the data by plotting the product of induction time, t_i, in seconds, and initial oxygen concentration $[O_2]$, in mole l^{-1}, as a function of temperature. They could draw a single curve through all of the data when they were plotted in this way, although the experimental scatter was rather large. We have used the same method of plotting in Figure 24.

Their points for composition 1 are shown as open circles in Figure 24, while the triangular points correspond to composition 2. It can be seen from the figure that they tend to lie above the points for composition 1, as does the calculated curve. Curve 3 passes through the diamonds which are our data points for composition 3.

Schott also recorded the maximum OH concentrations produced in his experiments (Ref. 22). In general, our calculated values agree well with his experimental values, although

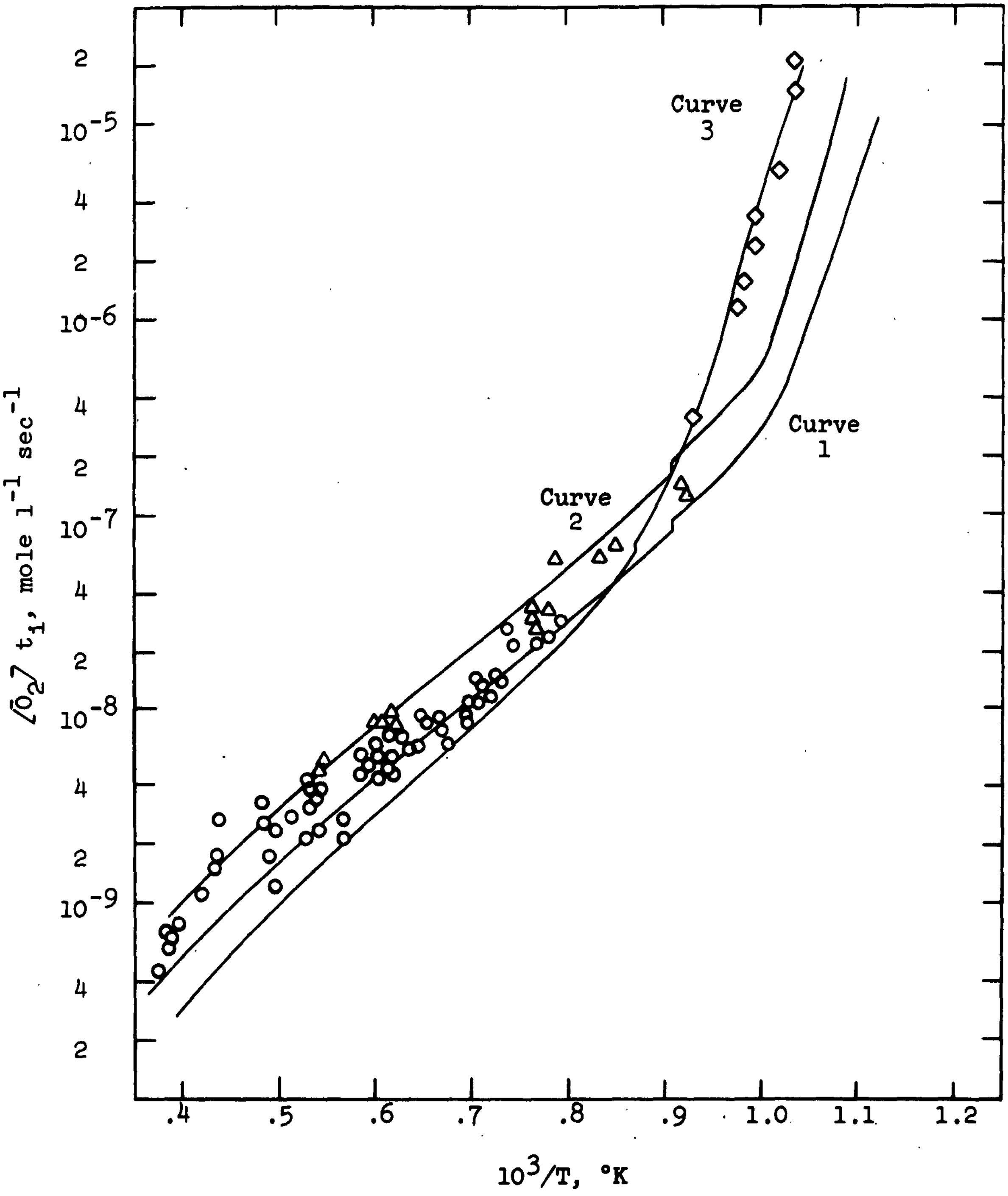


Figure 24. Induction times for H_2-O_2-Ar mixtures

at the lower temperatures the calculated values tend to be lower than the experimental ones. The error is probably greater in the experimental results since, as Schott points out, he did not have a good calibration point for OH concentration at the lower temperature.

The agreement between observed and calculated induction times for the inhibited gas mixtures, shown in Figure 25, is very good. The rate constants used gave the correct temperature dependence of the induction times, as well as the right absolute values. As the data for ethylene show, the inhibitors are less effective at high temperatures where the chain-branching reactions are very fast and control the reaction rate.

For CF_3Br, the calculated induction times were very sensitive to changes in the rate constant of Reaction 20, a 2% change in rate constant causing a change in induction time of a factor of two. For this reason, it was easy to arrive at the correct value of the rate constant (Table 28) within a few per cent, but difficult to obtain calculated rate constants to match the experimental values. Therefore, the calculated curve for CF_3Br in Figure 23 is shown as a dotted line. As shown in Appendix II, induction times calculated at 1150°K, with rate constants for Reaction 20 differing by only 2%, gave times of 4.7 and over 10 milliseconds. The constants given in Table 28 are between those used in these two calculations.

It should be emphasized that the main result of the calculations is the group of rate data contained in Table 28. These indicate how rapidly the several inhibitors react with H atoms to slow the ignition process. Since the data were obtained over a limited temperature range (950 - 1300°K), caution should be used in extrapolating these data to higher or lower temperatures.

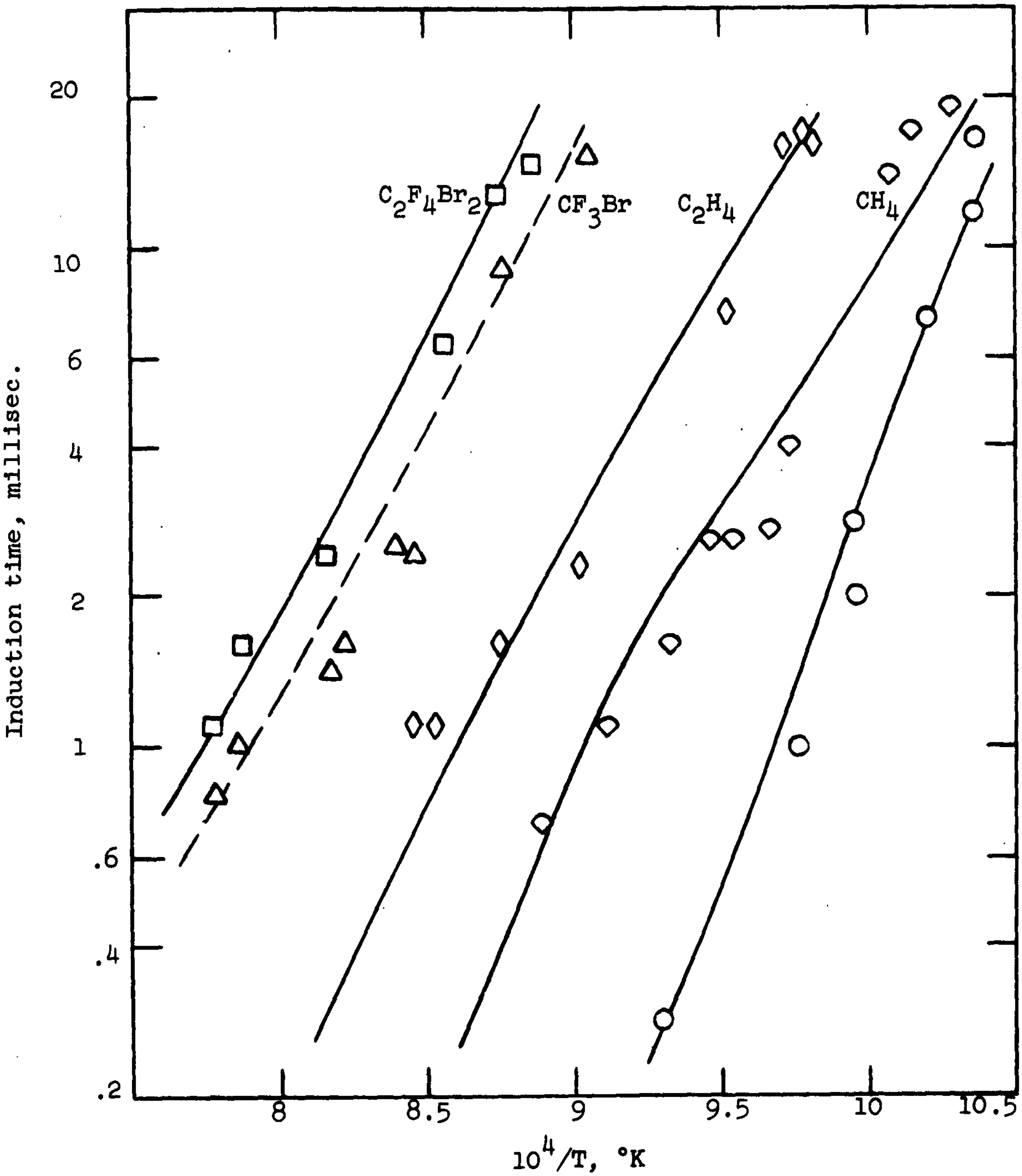


Figure 25. Induction times for mixture of 8% H_2, 2% O_2 in argon, uninhibited and inhibited by 0.8% CH_4, 0.4% C_2H_4, 0.8%, CF_3Br and 0.4% $C_2F_4Br_2$

4.5 Flame Speed Calculations The calculation of the flame speed of a premixed gas from chemical kinetics and transport properties was undertaken in an attempt to relate postulated reaction mechanisms for chemical flame inhibition to experimentally observed flame behavior. A detailed description of the calculation method may be formed in Supplement I to this report.

In a previous report (Ref. 20) the results of satisfactory calculations for a simple, two-species reaction $X \longrightarrow Y$ were described. It was apparent at that time, however, that the transition from this two species, one reaction system, to the hydrogen-air flame with 8 species and 17 reactions would not be simple. During the present contract period, we have come much closer to achieving a satisfactory calculation but because of the limited time available a complete calculation was not realized.

The work this year centered upon the proper selection of the starting conditions of the individual species at the hot (equilibrium) end of the flame. A detailed description of the starting conditions calculations is contained in Supplement I. Suffice to say here, that starting values of mole fraction and flux fraction are necessary for each species, as well as a temperature for the gas mixture.

For the simple $X \longrightarrow Y$ case, the choice of a perturbed mole fraction of X, uniquely defines the associated mole fraction of Y, and readily permits the calculation of flux fractions and temperature. For the hydrogen-air systems, however, the selection of one perturbed mole fraction does not uniquely define the remaining mole fractions and herein lies our present difficulty.

One possible solution to this problem has resulted in partial success. For the hydrogen-air system it is thought that as the burned gases approach equilibrium, all of the radicals are in slight excess, but are in chemical equilibrium with one another. This approximation was programmed into the calculations with the result that satisfactory values of the flux fractions were obtained, but the calculated temperature corresponding to these initial conditions was not correct. The next logical step to achieve a self-consistent set of set of starting conditions would be to relate the perturbed mole fraction calculation to the perturbed temperature calculation. If agreement is reached here, it is expected that a satisfactory integration would result.

5. RECOMMENDATIONS

The research carried out under this contract and its predecessors, reported here and in References 20, 23 and 24, has added considerably to the understanding of combustion mechanisms in the hydrogen-oxygen, hydrazine-nitrogen tetroxide, diborane-oxygen and pentaborane-oxygen systems, and of the way in which various additives inhibit combustion of these systems. These studies were necessarily carried out under laboratory conditions far removed from those encountered in practical fire-fighting, so that the results are not directly applicable to field use.

A logical extension of the program would be a study of some of the same additives on diffusion flames, since most uncontrolled fires are of this type, using the knowledge gained in the past work in the interpretation of the experimental results. The relatively small amount of research carried out to date in this area, exemplified by the work of Simmons and Wolfhard (Ref. 25) and Creitz (Ref. 26) indicate that the method of addition of inhibitor to a diffusion flame may have a strong influence on the effectiveness in extinguishing the flame. With the fundamental knowledge now available on the chemistry of combustion reactions and the interactions of additives with the combustion process, further studies on inhibition of diffusion flames could lead to a scientific determination of the most effective methods of using chemical fire extinguishing agents.

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APPENDIX I

LITERATURE SURVEY ON COMBUSTION OF BORANES

LITERATURE SURVEY ON COMBUSTION OF BORANES

A literature survey has been completed covering the oxidation of boron hydrides. The survey includes investigations of slow oxidation processes, as well as flame and explosive reactions, that have been reported in the open literature. An excellent review of the work on combustion of boron hydrides covering the period up to July 1958 has been published by Berl and Renich (Ref. 1, 2). The following discussion is based primarily on publications since this date.

1. FLAMES OF BORON HYDRIDES

The burning velocity of the following systems has been measured: diborane-air (Ref. 3, 6), diborane-hydrogen-air (Ref. 3), diborane-ethane-air (Ref. 3), diborane-ethylene-air (Ref. 3), diborane-acetylene-air (Ref. 3), diborane-propane-air (Ref. 4, 5, 6), pentaborane-oxygen-nitrogen (Ref. 7), diborane-oxygen (Ref. 8), and diborane-hydrazine (Ref. 8, 9).

The majority of these investigations employed the conventional Bunsen burner total area technique at atmospheric pressure. Due to the high burning velocities of diborane-air mixtures (approximately 5 meters/second) it was necessary to use very small burner tubes (0.4 mm dia.) to avoid flash-back. In view of the small flame size, and burner plugging from solid deposits, the accuracies of these measurements were not better than ± 30%.

The work of Wolfhard et al (Ref. 8) on diborane-oxygen mixtures was conducted at low pressures where the increased mean free path allowed the use of burners with diameters up to 40 mm. The burning velocity for stoichiometric diborane-oxygen was found to be 42-1/2 meters/second, while that of premixed hydrazine-diborane was about 5 meters/second. In the latter case the effect of the hydrazine-diborane ratio was obscured by the scatter of experimental points. It is not clear whether this scatter can be attributed to vagaries in combustion of diborane-hydrazine system, or to the experimental method. It is true that at these low pressures, the density gradients across the flame boundaries are not sufficiently great for schlieren photographic techniques. The velocities are therefore calculated by surface area measurements of the direct photograph. Even at atmospheric pressure, the apparent reaction zone thickness of the visible flame is much thicker than that of the schlieren or shadowgraph image. These difficulties would be further accentuated at low pressures where the reaction zone becomes much thicker.

Another technique found useful for measurement of these high propagating velocities is the flame kernel method of Olsen (Ref. 10). This method arrives at the burning velocity through the measurement of the expansion rate of a spherical combustion wave in an unconfined volume of gas. The results for pentaborane-oxygen-nitrogen mixtures indicate that the maximum velocity of B_5H_9-air mixtures of about 5.5 meters/second occurs at an equivalence ratio of 1.2. However, when the oxygen/oxygen + nitrogen ratio was increased at constant equivalence ratio, the burning velocity increased markedly to a value of 11.5 meters/second at an oxygen/oxygen + nitrogen ratio of 0.25. This observation is partially corroborated by Wolfhard's observation that the B_2H_6 velocity increased from 5 meters/second in air to 42.5 meters/second in pure oxygen. Breisacher, Dembrow and Berl (Ref. 6) studied the low pressure lean diborane-air flame and the diborane-hydrocarbon-air flame. They employed a 1-inch dia. flat flame burner at about 100 mm Hg pressure. This study included sampling of the flame at various distances beyond the luminous reaction zone and indicated that molecular hydrogen was formed in the flame zone and its subsequent reaction to form water occurred slowly downstream from the reaction zone. The measured flame temperature between equivalence ratios of 0.1 to 0.3 increased from 750 to 850°K compared to the calculated flame temperatures of from 900 to about 1300°K. About 90% of the unreacted hydrogen disappeared 10 mm beyond the reaction zone. Therefore, the oxidation of hydrogen to water is slow and only loosely comparable to the main reactions involved in the diborane oxidation. The coolest flame, approximately 0.935% diborane in air, had 80% of the original hydrogen unreacted at the luminous zone. Any water that may have formed in the flame zone continues to react with diborane to form additional hydrogen through the hydrolysis reaction studied by Weiss and Shapiro (Ref. 11). As the original diborane concentration increases to 1.49% diborane in air, the fraction of unreacted hydrogen decreases to 12.5%.

From this work it appears that as the percentage diborane is increased, with the associated increase in temperature, the percentage of unreacted hydrogen found after the flame front decreases markedly by a factor of 6.4, indicating, possibly, an increase in efficiency of the flame process. However, over this same diborane concentration range the discrepancy between the measured and calculated flame temperature increases from about 15% to 33% lower than the theoretical, showing a decrease in efficiency with increased per cent diborane. The authors made no effort to account for this discrepancy. Since only the gas composition was analyzed, it might be assumed that solid, partially oxidized species, were formed. This could occur at the higher temperatures by pyrolysis of diborane with the formation of solid polymers of the type $(B_xH_y)_n$ or $(B_xO_yH_z)_n$, both of which could contain significant quantities of hydrogen and unreacted boron. These difficulties can be surmounted to some extent by burning diborane in air at more nearly the stoichiometric ratio. At higher temperatures the pyrolysis reaction (Ref. 12) should more nearly approach the products elemental boron and hydrogen. It is highly probable that the apparent absence of OH in the luminous zone of the boron hydride flames is due to the extremely rapid rate of the hydrolysis of these fuels. The total flame process will then be one with competing rates between oxidation, pyrolysis and hydrolysis.

The burning velocity of hydrogen- or hydrocarbon-boron hydride mixtures has been studied by several investigators. In every case the hydrocarbon content studied was well in excess of 25% of the total fuel mixture, the studies being more concerned with the effects of small quantitities of the hydride on the burning velocity of the more conventional fuels. There is little or no information concerning the effects of small additive quantities of potential inhibitors on the propagating velocity of the boron hydride flames. None of the mixtures studied appear to follow the Spaulding rule (Ref. 18) for mixed fuel laminar flame speeds. Kurz reported that small additives of diborane to propane-air flames appeared to exhibit an inhibitory effect.

2. IGNITION AND EXPLOSION LIMITS

Lean and rich ignition limits for diborane-air and diborane-ethane-air have been determined by Parker and Wolfhard (Ref. 3) and the lean limits for pentaborane-air were measured by Berl (Ref. 14). Successful ignition for diborane-air mixtures can be obtained between 0.8 and 87.5 volume per cent fuel, while the lean ignition limit for pentaborane occurs at 0.4 volume per cent. The calculated flame temperatures for these mixtures falls between about 750 and 850°K.

A great deal of information has been garnered in studies of the spontaneous explosion limits of boron hydride-oxygen mixtures, including the early work of Price (Ref. 15) and Schalla (Ref. 16) on pentaborane and of Whatley and Pease (Ref. 17) on diborane. By far the greatest insight into the mechanism of borane explosions and slow oxidations results from the work of W. H. Bauer and students (Ref. 18-28). These workers report investigations concerning the explosive and controlled oxidation of diborane, tetraborane, pentaborane, and decaborane with both oxygen and air. An excellent review of this work has been published by Bauer and Wiberly (Ref. 25).

In general it has been concluded that the borane-oxygen explosions occur through a branched free radical chain mechanism similar to that previously established for the hydrogen-oxygen system. The first, second, and third explosion limits of the diborane-oxygen system have been defined by Roth, et al (Ref. 18, 20, 21). This work included the effects of mixture ratio, inert gas, and hydrogen addition on the second limit. In addition, Snyder (Ref. 23) has studied the effects of NO_2, NO, and $Fe(CO)_5$ on the second explosion limit. It was observed that NO and NO_2 sensitized the explosive reaction, but iron carbonyl inhibited.

When the oxidation of decaborane was studied (Ref. 23), explosive mixtures were prepared by slow vaporization of a weighed quantity of decaborane into an oxygen atmosphere of known pressure. The mixture was then equilibrated at a temperature at which decaborane was completely vaporized, and at which no slow oxidation occurred. The first and second explosion limits were then defined by suddenly increasing the temperature.

Price's early work on pentaborane-oxygen explosions identified a first pressure limit at room temperature, when compressed oxygen was rapidly expanded into pentaborane. Baden (Ref. 19, 22) was able to define an explosion peninsula between 25 and 85°C when 0.1% of iron carbonyl was added to the pentaborane-oxygen mixture. Baden and Hammond (Ref. 27) found that stable mixtures of pentaborane-oxygen could be prepared in the pressure-temperature region previously thought to be explosive by slow addition of one reactant to the other. The temperature-pressure explosion regions defined by Hammond were complicated in that double explosion peninsulas were obtained ... one in the pressure region 20 - 40 mm Hg, and one at 60 - 80 mm Hg.

Goldstein (Ref. 24, 26) determined the temperature-composition explosion limits of diborane-air at 1 atm. pressure. The limit extends from about 190°C at 5 mole per cent diborane to 155°C at 20 mole per cent. Ludlum (Ref. 28) found rather broad and poorly defined explosion limits for tetraborane. The limit appeared to be sensitive to vessel diameter, indicating that he was investigating the first explosion limit, where the explosion is dependent on the wall, and is not a homogeneous gas phase reaction.

Except for explosions of pentaborane-oxygen mixtures, which appear to involve competing mechanisms, the borane-oxygen explosion investigations strongly suggest a branch-chain explosion mechanism very similar to that of hydrogen-oxygen. At the second limit, a homogeneous gas phase reaction occurs which involves bimolecular chain-branching and trimolecular chain-breaking. It is interesting that reaction products of explosions always contained water and B_2O_3, but no boric acid.

This observation is contrary to that from flame spectra work (Ref. 29) where the absence of OH emission lines suggests that water is not formed. The absence of OH bands in pentaborane-air explosions has been reported. Roth (Ref. 30) reports the absence of OH following explosion of 3:1 mixtures of NO and B_2H_6, but the appearance of OH following explosion of 6:1 mixtures.

Wolfhard, et al (Ref. 8) report that the main spectral features of borane-air flames are the well-known fluctuation bands usually ascribed to B_2O_3 in the burnt gas. Studies of the reaction zone indicated the presence of BO bands from 3370 to 6200 A, the α head of the BH band at 4431.6 A and the boron line near 2500 A. The fact that these last species did not emit from the hot burned gases suggests that they are intermediates in the combustion. Berl, et al (Ref. 29), however, did not observe the BH band in either diffusion flames of pentaborane-air or explosions. They also report the absence of BN and OH in the diffusion flame and the absence of BO bands in the explosions.

3. SLOW OXIDATION OF BORON HYDRIDES

Even though the mechanism of the oxidation of boron hydrides is far from being understood, much valuable information has been obtained through studies of the slow oxidation of boron hydrides by W. H. Bauer, et al. These investigations include work on diborane, tetraborane, and pentaborane. Since the boranes, the intermediates found, and the final products all have distinctive infrared absorption spectra, studies of the progress of the slow oxidation reactions in cells equipped with rock salt windows have been very informative. In addition, the work of Fehlner and Strong (Ref. 31) on the reaction of oxygen atom with diborane is of interest. Hammond (Ref. 27) studied the slow oxidation of pentaborane by addition of oxygen at a known leak rate of from 40 to 100 x 10^{-5} moles per hour, to an excess of pentaborane in an infrared cell. The reaction products were diborane, hydrogen, B_2O_3, possibly tetraborane, and an oxidation intermediate subsequently identified by Ditter and Shapiro (Ref. 32) as $B_2H_2O_3$, a highly symmetrical compound, intermediate in volatility between pentaborane and diborane. This same intermediate was found by Goldstein (Ref. 26) in diborane-oxygen mixtures heated at temperatures between the second explosion limit and the third or thermal limit of explosion. The kinetics of the reaction were studied from 120 to 170°C and between 60 and 100 mm Hg total pressure. The slow oxidation reaction was shown to proceed according to the requirements of the degenerate chain-branching process. The initial rate of reaction before acceleration was found to be 3/2 order with respect to diborane concentration and independent of oxygen concentration. The apparent activation energy was 35 kilocalories per mole. The equation estimating the over-all stoichiometry is:

$$B_2H_6 + 2O_2 \longrightarrow B_2H_2O_4 + 2H_2$$

In some cases, explosions occurred. Analysis of the resultant mixtures indicated that in the explosive reaction diborane was stripped of its hydrogen and then the species reacted successively with oxygen. The relative rates at which these species reacted decreased in the order boron suboxide<boron<hydrogen.

Fehlner and Strong (Ref. 31) studied the reaction of diborane with oxygen atoms generated by the mercury-photosensitized decomposition of N_2O. At 25 and 100°C, the products identified were nitrogen, hydrogen, tetraborane, pentaborane, and a white solid with an empirical formula BHO. Ludlum (Ref. 28) followed the partial oxidation of tetraborane by slow addition of oxygen to an infrared cell containing the borane. The reaction produced diborane, hydrogen, boric oxide, and the partial oxidation product found in the slow oxidation of both pentaborane and diborane. The main reaction can be represented as:

$$B_4H_{10} + 3/2\ O_2 \longrightarrow B_2H_6 + B_2H_2O_3 + H_2$$

Evidence was also found that the partial oxidation product slowly reacts as follows:

$$B_2H_2O_3 \longrightarrow B_2O_3 + H_2$$

When a few millimeters pressure of water vapor or diethyl ether were present in the tetraborane, no reaction occurred on the slow addition of oxygen.

4. MECHANISM OF BORANE OXIDATION REACTION

Many highly hypothetical mechanisms have been proposed for the oxidation of boron hydrides, as a result of the investigations reviewed above. Unfortunately, the proof of a firm oxidation path awaits isolation and identification of many proposed intermediates and chain carriers. Roth and Bauer's (Ref. 20, 21) original mechanism for diborane explosions was constructed on an analogy with the well-known mechanism for hydrogen-oxygen at the second explosion limit, and is presented as follows:

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$BH_3 + O_2 \longrightarrow BH_3O + O$$

$$O + B_2H_6 \longrightarrow BH_3 + BH_3O$$

$$BH_3O + B_2H_6 \longrightarrow BH_3 + B_2H_6O$$

$$BH_3 + O_2 + M \longrightarrow HBO_2 + H_2 + M$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2$$

$$B_3H_7 \longrightarrow \text{higher hydrides}$$

$$B_2H_6O \longrightarrow \text{further oxidation}$$

If H is substituted for BH_3 in this scheme, hydrogen-oxygen mechanism is immediately evident. The equilibrium constant between diborane and borine (BH_3) species has been calculated by McCoy and Bauer (Ref. 33) to be:

$$\log K_p \text{ (atm.)} = 7.478 - \frac{6205}{T}$$

This was arrived at through the entropy for BH_3 and the change in entropy for the equilibrium reaction calculated by Shepp and Bauer (Ref. 34). The only partially oxidized species as yet identified is $B_2H_2O_3$. The transient existence of BH_3O and B_2H_6O are therefore as yet to be proved. Triborane, B_3H_7, has never been established, though there exists mass spectrometric evidence for the charged fragment. Triborane, however, most probably exists since it has the stable hydride ratio of $B_nH_n + 4$. Triborane has been proposed in the majority of papers on the mechanisms of borane reactions. The species BH_3O (or BH_2OH) has been proposed by Weiss and Shapiro (Ref. 11) as the intermediate in the stepwise hydrolysis of diborane. Goldstein's (Ref. 26) mechanism for diborane slow oxidation is as follows:

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$BH_3 + O_2 \rightleftharpoons BH_3OO$$

$$BH_3OO + M \longrightarrow BH_3 + O_2 + M$$

$$BH_3OO + B_2H_6 \longrightarrow B_3H_7OO + H_2$$

$$B_3H_7OO \longrightarrow 1/2\ H_2B_2O_4 + B_2H_6$$

$$B_3H_7OO \longrightarrow H_4B_2O_2 + H_2 + BH_3$$

$$H_4B_2O_2 + O_2 \longrightarrow H_2B_2O_4 + H_2$$

This mechanism accounts for the observations made during the slow oxidation studies. In addition, the following reactions are proposed to account for the explosive reactions:

$$BH_3OO + BH_3 \longrightarrow 2BH_3O$$

$$BH_3O + O_2 \longrightarrow BH_3OO + O$$

$$O + B_2H_6 \longrightarrow BH_3O + BH_3$$

$$BH_3O + B_2H_6 \longrightarrow B_2H_6O + BH_3$$

$$BH_3 + O_2 + M \longrightarrow 1/2\ H_2B_2O_4 + H_2 + M$$

$$BH_3 + O_2 \longrightarrow BH_3O + O$$

Fehlner and Strong (Ref. 31) proposed the following mechanism for oxygen atom-diborane reaction:

$$O + B_2H_6 \longrightarrow BH_3O + BH_3$$

$$BH_3O \longrightarrow H_2 + \text{solids } [BHO]_x$$

$$2BH_3 \rightleftharpoons B_2H_6$$

$$BH_3 + B_2H_6 \longrightarrow B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \longrightarrow B_4H_{10} + BH_3$$

$$B_3H_7 + B_2H_6 \longrightarrow B_5H_9 + 2H_2$$

$$B_4H_{10} + O \longrightarrow BH_3O + B_3H_7$$

Ludlum (Ref. 28) proposes the following mechanism for oxidation of tetraborane:

$$B_4H_{10} \rightleftharpoons BH_3 + B_3H_7$$

$$BH_3 + O_2 \longrightarrow BH_3O + O$$

$$O + B_4H_{10} \longrightarrow BH_3O + B_3H_7$$

$$BH_3O + B_4H_{10} \longrightarrow B_2H_6 + B_3H_7O$$

$$B_3H_7O + O_2 \longrightarrow B_2H_2O_3 + BH_3 + H_2$$

$$B_2H_2O_3 \longrightarrow B_2O_3 + H_2$$

$$2BH_2 \rightleftharpoons B_2H_6$$

$$B_3H_7,\ BH_3O,\ O \longrightarrow \text{destruction at surface}$$

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APPENDIX II

RESULTS OF KINETIC CALCULATIONS OF SHOCK TUBE INDUCTION TIMES

(The calculations are arranged in the same order as they are listed in Tables 29 and 30 on pages 70 and 71.)

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                  MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                   INITIAL
                                      SPECIES   CONCENTRATIONS
                                                  (MOLES/CC)

                                      H2           4.000E-02
                                      O2           2.000E-02
                                      ARGON        9.400E-01

               REACTION TEMPERATURE      900.0 (DEG. K.)         PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)          1.0000        2.0000        3.0000        4.0000        5.0000        6.0000

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                 5.42E-07      5.42E-07      5.41E-07      5.41E-07      5.41E-07      5.41E-07
        O2                 2.71E-07      2.71E-07      2.71E-07      2.71E-07      2.71E-07      2.71E-07
        H2O                2.73E-17      9.57E-17      2.23E-16      4.56E-16      8.79E-16      1.65E-15
        H                  1.66E-18      3.40E-18      6.32E-18      1.16E-17      2.12E-17      3.88E-17
        O                  5.66E-19      1.16E-18      2.17E-18      4.00E-18      7.31E-18      1.33E-17
        OH                 2.15E-20      2.86E-20      7.73E-20      1.41E-19      2.56E-19      4.65E-19
        HO2                2.50E-17      9.12E-17      2.15E-16      4.40E-16      8.50E-16      1.60E-15
        H2O2               6.09E-19      4.34E-18      1.44E-17      3.61E-17      7.89E-17      1.60E-16


ELAPSED TIME (MSEC)          7.0000        8.0000        9.0000       10.0000

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                 5.41E-07      5.41E-07      5.41E-07      5.41E-07
        O2                 2.71E-07      2.71E-07      2.71E-07      2.71E-07
        H2O                3.05E-15      5.59E-15      1.02E-14      1.86E-14
        H                  7.06E-17      1.28E-16      2.34E-16      4.25E-16
        O                  2.43E-17      4.42E-17      8.04E-17      1.46E-16
        OH                 8.45E-19      1.54E-18      2.79E-18      5.08E-18
        HO2                2.95E-15      5.42E-15      9.90E-15      1.80E-14
        H2O2               3.11E-16      5.90E-16      1.10E-15      2.03E-15
            *   INDUCTION TIME (MAX OH CONC)
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              MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                       INITIAL
                           SPECIES  CONCENTRATIONS
                                      (MOLES/CC)

                            H2       4.000E-02
                            O2       2.000E-02
                            ARGON    9.400E-01

            REACTION TEMPERATURE    1000.0 (DEG. K.)       PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)          0.2000      0.4000      0.6000      0.8000      1.0000      1.1200*

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2               4.87E-07    4.87E-07    4.87E-07    4.86E-07    4.19E-07    2.48E-07
          O2               2.44E-07    2.44E-07    2.44E-07    2.43E-07    1.96E-07    7.46E-08
          H2O              8.04E-16    7.80E-14    7.38E-12    6.94E-10    4.74E-08    1.67E-07
          H                3.42E-16    3.26E-14    3.09E-12    2.90E-10    1.98E-08    6.35E-08
          O                1.37E-16    1.31E-14    1.24E-12    1.16E-10    6.31E-09    8.22E-09
          OH               6.64E-18    6.29E-16    5.95E-14    5.59E-12    3.48E-10    8.17E-10
          HO2              3.24E-16    3.22E-14    3.05E-12    2.87E-10    2.08E-08    8.10E-08
          H2O2             5.40E-18    5.99E-16    5.69E-14    5.28E-12    1.41E-10    1.07E-10


ELAPSED TIME (MSEC)          1.2000      1.4000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2               1.84E-07    1.58E-07
          O2               2.81E-08    2.81E-09
          H2O              2.19E-07    2.44E-07
          H                6.98E-08    4.95E-08
          O                3.97E-09    3.74E-10
          OH               6.50E-10    2.21E-10
          HO2              1.06E-07    1.10E-07
          H2O2             9.25E-11    1.21E-10

        *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                  INITIAL
                                    SPECIES    CONCENTRATIONS
                                                 (MOLES/CC)

                                     H2          4.000E-02
                                     O2          2.000E-02
                                     ARGON       9.400E-01

                 REACTION TEMPERATURE     1100.0 (DEG. K.)         PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)             0.0500      0.1000      0.1500      0.2000      0.2500      0.3000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                   4.43E-07    4.43E-07    4.43E-07    4.43E-07    4.43E-07    4.42E-07
          O2                   2.22E-07    2.22E-07    2.22E-07    2.22E-07    2.22E-07    2.21E-07
          H2O                  7.21E-16    1.29E-14    2.13E-13    3.51E-12    5.77E-11    9.48E-10
          H                    4.14E-16    7.15E-15    1.18E-13    1.24E-12    3.19E-11    5.24E-10
          O                    1.94E-16    3.46E-15    5.71E-14    9.43E-13    1.55E-11    2.53E-10
          OH                   1.28E-17    2.12E-16    3.49E-15    5.75E-14    9.44E-13    1.55E-11
          HO2                  1.14E-16    2.28E-15    3.81E-14    6.30E-13    1.03E-11    1.70E-10
          H2O2                 2.70E-18    7.23E-17    1.26E-15    2.10E-14    3.45E-13    5.53E-12

                                                       *
ELAPSED TIME (MSEC)             0.3500      0.4000      0.4406      0.5000      0.5500      0.6000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                   4.23E-07    2.80E-07    1.42E-07    9.08E-08    8.63E-08    8.78E-08
          O2                   2.10E-07    1.30E-07    5.32E-08    1.56E-08    6.97E-09    3.69E-09
          H2O                  1.45E-08    1.15E-07    2.13E-07    2.62E-07    2.74E-07    2.79E-07
          H                    8.13E-09    6.97E-08    1.19E-07    1.07E-07    8.85E-08    7.37E-08
          O                    3.65E-09    1.70E-08    1.27E-08    4.90E-09    2.40E-09    1.33E-09
          OH                   2.38E-10    1.80E-09    2.62E-09    2.02E-09    1.49E-09    1.14E-09
          HO2                  2.67E-09    2.50E-08    5.40E-08    7.15E-08    7.56E-08    7.69E-08
          H2O2                 5.94E-11    7.42E-11    4.70E-11    4.31E-11    5.22E-11    6.46E-11

             *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                     INITIAL
                                        SPECIES   CONCENTRATIONS
                                                    (MOLES/CC)

                                        H2          4.000E-02
                                        O2          2.000E-02
                                        ARGON       9.400E-01

                 REACTION TEMPERATURE    1250.0 (DEG. K.)        PRESSURE    1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)          0.0200      0.0400      0.0600      0.0800      0.1000      0.1200

                                        CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  3.90E-07    3.90E-07    3.90E-07    3.90E-07    3.90E-07    3.87E-07
        O2                  1.95E-07    1.95E-07    1.95E-07    1.95E-07    1.95E-07    1.93E-07
        H2O                 6.70E-15    8.91E-14    1.09E-12    1.33E-11    1.62E-10    1.96E-09
        H                   3.99E-15    5.13E-14    6.28E-13    7.64E-12    9.31E-11    1.13E-09
        O                   2.36E-15    3.24E-14    3.99E-13    4.86E-12    5.90E-11    7.08E-10
        OH                  8.81E-02    2.62E-15    3.19E-14    3.89E-13    4.74E-12    5.77E-11
        HO2                 3.52E-16    5.33E-15    6.64E-14    8.11E-13    9.87E-12    1.20E-10
        H2O2                2.07E-17    4.36E-16    5.77E-15    7.11E-14    8.62E-13    9.81E-12

                                                    *
ELAPSED TIME (MSEC)          0.1400      0.1600      0.1810      0.2000

                                        CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  3.60E-07    2.04E-07    8.26E-08    6.45E-08
        O2                  1.78E-07    1.05E-07    4.83E-08    3.36E-08
        H2O                 2.22E-08    1.31E-07    2.18E-07    2.38E-07
        H                   1.35E-08    9.38E-08    1.47E-07    1.37E-07
        O                   7.20E-09    2.36E-08    1.98E-08    1.50E-08
        OH                  7.02E-10    4.51E-09    6.45E-09    6.05E-09
        HO2                 1.45E-09    1.07E-08    2.44E-08    3.20E-08
        H2O2                5.80E-11    4.24E-11    2.43E-11    2.65E-11

           *   INDUCTION TIME (MAX OH CONC)
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            MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                         INITIAL
                              SPECIES   CONCENTRATIONS
                                         (MOLES/CC)

                               H2         4.000E-02
                               O2         2.000E-02
                               ARGON      9.400E-01

          REACTION TEMPERATURE    1600.0 (DEG. K.)        PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)         0.0050      0.0100      0.0150      0.0200      0.025C      0.03CC

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                 3.05E-07    3.05E-07    3.06E-07    3.05E-07    3.04E-C7    3.02E-07
        O2                 1.52E-07    1.52E-07    1.52E-07    1.52E-07    1.52E-07    1.51E-07
        H2O                2.38E-13    1.73E-12    1.02E-11    6.03E-11    3.57E-10    2.15E-09
        H                  1.30E-13    8.39E-13    5.02E-12    2.97E-11    1.77E-10    1.07E-09
        O                  1.07E-13    8.26E-13    5.08E-12    3.02E-11    1.78E-10    1.04E-09
        OH                 1.77E-14    1.05E-13    6.20E-13    3.66E-12    2.18E-11    1.35E-10
        HO2                1.59E-15    1.20E-14    7.37E-14    4.38E-13    2.61E-12    1.61E-11
        H2O2               4.50E-16    5.24E-15    3.59E-14    2.19E-13    1.29E-12    7.04E-12


ELAPSED TIME (MSEC)         0.0350      0.0400      0.0450      0.0500      0.0520*     0.0600

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                 2.87E-07    2.07E-07    9.03E-08    6.11E-08    5.87E-08    5.67E-08
        O2                 1.42E-07    1.02E-07    5.35E-08    4.18E-08    4.06E-08    3.89E-08
        H2O                1.31E-08    7.02E-08    1.49E-07    1.70E-07    1.72E-07    2.63E-06
        H                  7.19E-09    4.79E-08    1.14E-07    1.29E-07    1.28E-07    1.24E-07
        O                  5.75E-09    2.13E-08    3.01E-08    2.97E-08    2.92E-08    2.76E-08
        OH                 9.87E-10    6.78E-09    1.42E-08    1.55E-08    1.56E-08    1.54E-08
        HO2                1.15E-10    7.72E-10    2.08E-09    2.92E-09    3.14E-09    3.67E-09
        H2O2               2.65E-11    2.60E-11    1.28E-11    1.04E-11    1.08E-11    1.26E-11

     *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                       INITIAL
                                         SPECIES   CONCENTRATIONS
                                                     (MOLES/CC)

                                          H2          4.000E-02
                                          O2          2.000E-02
                                          ARGON       9.400E-01

                 REACTION TEMPERATURE    2000.0 (DEG. K.)       PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)          0.0020        0.0040        0.0060        0.0080        0.0100        0.0120

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                2.44E-07      2.44E-07      2.44E-07      2.43E-07      2.42E-07      2.38E-07
          O2                1.22E-07      1.22E-07      1.22E-07      1.22E-07      1.21E-07      1.18E-07
          H2O               3.10E-12      1.64E-11      6.70E-11      2.60E-10      1.01E-09      4.08E-09
          H                 1.61E-12      7.13E-12      2.79E-11      1.08E-10      4.25E-10      1.85E-09
          O                 1.56E-12      9.43E-12      3.93E-11      1.53E-10      5.85E-10      2.17E-09
          OH                4.35E-13      1.71E-12      6.54E-12      2.53E-11      1.02E-10      4.76E-10
          HO2               2.89E-15      1.37E-14      5.42E-14      2.11E-13      8.59E-13      4.06E-12
          H2O2              2.65E-15      2.10E-14      9.56E-14      3.81E-13      1.44E-12      4.92E-12


ELAPSED TIME (MSEC)          0.0140        0.0160        0.0180        0.0200        0.0220*       0.024C

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                2.19E-07      1.46E-07      7.37E-08      5.67E-08      5.43E-08      5.40E-08
          O2                1.07E-07      6.98E-08      3.78E-08      3.09E-08      2.99E-08      2.97E-08
          H2O               1.82E-08      6.85E-08      1.16E-07      1.28E-07      1.30E-07      1.30E-07
          H                 9.91E-09      4.60E-08      8.54E-08      9.48E-08      9.54E-08      9.48E-08
          O                 8.26E-09      2.23E-08      2.98E-08      3.05E-08      3.03E-08      3.00E-08
          OH                2.88E-09      1.31E-08      2.17E-08      2.34E-08      2.36E-08      2.36E-08
          HO2               2.51E-11      1.07E-10      1.55E-10      1.45E-10      1.38E-10      1.35E-10
          H2O2              1.09E-11      7.49E-12      2.87E-12      1.84E-12      1.66E-12      1.63E-12

       *   INDUCTION TIME (MAX OH CONC)
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         MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                               INITIAL
                                 SPECIES   CONCENTRATIONS
                                             (MOLES/CC)

                                 H2          4.000E-02
                                 O2          2.000E-02
                                 ARGON       9.400E-01

        REACTION TEMPERATURE     2500.0 (DEG. K.)        PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)         0.0010      0.0020      0.0030      0.0040      0.0050      0.0060

                                 CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                  1.95E-07    1.95E-07    1.95E-07    1.94E-07    1.90E-07    1.77E-07
      O2                  9.75E-08    9.74E-08    9.71E-08    9.64E-08    9.42E-08    8.61E-08
      H2O                 2.53E-11    1.16E-10    3.81E-10    1.17E-09    3.69E-09    1.30E-08
      H                   1.40E-11    4.73E-11    1.42E-10    4.35E-10    1.52E-09    6.60E-09
      O                   1.49E-11    7.58E-11    2.51E-10    7.46E-10    2.19E-09    6.44E-09
      OH                  6.25E-12    1.91E-11    5.67E-11    1.80E-10    6.87E-10    3.34E-09
      HO2                 3.39E-15    1.18E-14    3.60E-14    1.15E-13    4.41E-13    2.19E-12
      H2O2                8.15E-15    4.79E-14    1.68E-13    5.05E-13    1.36E-12    2.64E-12

                                                             *
ELAPSED TIME (MSEC)         0.0070      0.0080      0.0090      0.0100

                                 CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                  1.31E-07    7.36E-08    5.34E-08    4.97E-08
      O2                  6.06E-08    3.16E-08    2.24E-08    2.08E-08
      H2O                 4.36E-08    8.09E-08    9.39E-08    9.64E-08
      H                   2.70E-08    5.54E-08    6.62E-08    6.81E-08
      O                   1.66E-08    2.53E-08    2.72E-08    2.73E-08
      OH                  1.36E-08    2.55E-08    2.90E-08    2.96E-08
      HO2                 7.41E-12    8.71E-12    7.27E-12    6.85E-12
      H2O2                1.85E-12    5.77E-13    2.85E-13    2.41E-13

           *   INDUCTION TIME (MAX OH CONC)
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                        MONSANTO RESEARCH CORPCRATION - SHCCK TUBE INDUCTION TIME CALCULATICNS

                                                          INITIAL
                                              SPECIES  CONCENTRATIONS
                                                         (MOLES/CC)

                                               H2        10.000E-03
                                               C2         2.000E-02
                                               ARGON      9.700E-01

                    REACTION TEMPERATURE      900.0 (DEG. K.)        PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)             1.0000       2.0000       3.0000       4.0000       5.0000       6.0CC0

                                             CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                     1.35E-07     1.35E-07     1.35E-07     1.35E-07     1.35E-07     1.35E-07
        02                     2.71E-07     2.71E-07     2.71E-07     2.71E-07     2.57E-07     2.71E-07
        H20                    3.70E-18     1.10E-17     2.07E-17     3.24E-17     4.60E-17     6.19E-17
        H                      1.89E-19     2.92E-19     3.71E-19     4.45E-19     5.23E-19     6.09E-19
        0                      2.45E-19     3.96E-19     5.08E-19     6.11E-19     7.19E-19     8.38E-19
        OH                     1.06E-20     1.56E-20     1.95E-20     2.30E-20     2.68E-20     3.09E-20
        HO2                    3.27E-18     1.03E-17     9.25E-18     3.13E-17     4.48E-17     6.04E-17
        H2O2                   2.09E-20     1.33E-19     3.68E-19     8.23E-19     1.47E-18     2.37E-18

ELAPSED TIME (MSEC)             7.0000       8.C000       9.0C00      10.0000

                                             CONCENTRATICN IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                     1.35E-07     1.35E-07     4.42E-04     1.35E-07
        02                     2.71E-07     2.71E-07     2.71E-07     2.71E-07
        H20                    8.01E-17     1.01E-16     1.25E-16     1.53E-16
        H                      7.06E-19     8.18E-19     9.47E-19     1.09E-18
        0                      9.72E-19     1.13E-18     1.30E-18     1.51E-18
        OH                     3.56E-20     4.09E-20     4.69E-20     5.41E-20
        HO2                    7.84E-17     9.91E-17     1.23E-16     1.50E-16
        H2O2                   3.56E-18     5.07E-18     6.97E-18     9.31E-18

            *   INDUCTION TIME (MAX OH CONC)
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              MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                           INITIAL
                               SPECIES  CONCENTRATIONS
                                          (MOLES/CC)

                                H2        10.000E-03
                                O2         2.000E-02
                                ARGON      9.700E-01

            REACTION TEMPERATURE     1000.0 (DEG. K.)          PRESSURE     1.00 (ATMOSPHERE)


ELAPSED TIME (MSEC)            0.2000       0.4000       0.6000       0.8000       1.0000       1.200C

                                       CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                   1.22E-07     1.22E-07     1.22E-07     1.22E-07     1.22E-07     1.22E-07
        O2                   2.44E-07     2.44E-07     2.44E-07     2.44E-07     2.44E-07     2.44E-07
        H2O                  4.07E-17     4.69E-16     4.65E-15     4.51E-14     4.37E-13     4.23E-12
        H                    1.07E-17     1.11E-16     1.08E-15     1.05E-14     1.01E-13     9.81E-13
        O                    1.26E-17     1.38E-16     1.35E-15     1.31E-14     1.27E-13     1.23E-12
        OH                   7.75E-19     7.73E-18     7.50E-17     7.27E-16     7.03E-15     6.81E-14
        HO2                  1.74E-17     2.20E-16     2.21E-15     2.16E-14     2.09E-13     2.02E-12
        H2O2                 1.03E-19     1.86E-18     2.03E-17     2.01E-16     1.95E-15     1.89E-14

                                                                                                    *
ELAPSED TIME (MSEC)            1.4000       1.6000       1.8000       2.0000       2.2000       2.3160

                                       CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                   1.22E-07     1.21E-07     1.17E-07     9.26E-08     4.92E-08     3.14E-08
        O2                   2.44E-07     2.43E-07     2.40E-07     2.19E-07     1.79E-07     1.60E-07
        H2O                  4.09E-11     3.93E-10     3.52E-09     2.09E-08     5.05E-08     6.23E-08
        H                    9.48E-12     9.09E-11     8.07E-10     4.39E-09     7.33E-09     6.30E-09
        O                    1.19E-11     1.14E-10     9.81E-10     4.60E-09     6.05E-09     4.95E-09
        OH                   6.58E-13     6.30E-12     5.49E-11     2.86E-10     5.55E-10     5.95E-10
        HO2                  1.95E-11     1.88E-10     1.73E-09     1.18E-08     3.62E-08     4.93E-08
        H2O2                 1.83E-13     1.74E-12     1.48E-11     6.17E-11     7.25E-11     7.36E-11

             *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                     INITIAL
                                      SPECIES    CONCENTRATIONS
                                                   (MOLES/CC)

                                       H2          10.000E-03
                                       O2           2.000E-02
                                       ARGON        9.700E-01

                REACTION TEMPERATURE     1100.0 (DEG. K.)          PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)             0.1000        0.2000        0.3000        0.4000        0.5000        0.6000

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                   1.11E-07      1.11E-07      1.11E-07      1.11E-07      1.11E-07      7.09E-08
         O2                   2.22E-07      2.22E-07      2.22E-07      2.22E-07      2.22E-07      1.50E-07
         H2O                  4.88E-16      1.01E-14      1.94E-13      3.72E-12      7.12E-11      1.33E-09
         H                    1.73E-16      3.40E-15      6.53E-14      1.25E-12      2.40E-11      4.50E-10
         O                    2.18E-16      4.50E-15      8.65E-14      1.66E-12      3.17E-11      5.87E-10
         OH                   1.82E-17      3.50E-16      6.72E-15      1.29E-13      2.46E-12      4.57E-11
         HO2                  9.76E-17      2.17E-15      4.20E-14      8.05E-13      1.54E-11      2.92E-10
         H2O2                 1.16E-18      3.29E-17      6.59E-16      1.27E-14      2.43E-13      4.40E-12

                                                          *
ELAPSED TIME (MSEC)             0.7000        0.8000        0.8400        0.9000        1.0000        1.1000

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                   8.76E-08      3.17E-08      1.89E-08      9.61E-09      4.31E-09      2.51E-09
         O2                   2.05E-07      1.61E-07      1.48E-07      1.35E-07      1.25E-07      1.21E-07
         H2O                  1.75E-08      5.70E-08      6.56E-08      7.15E-08      7.45E-08      7.54E-08
         H                    6.17E-09      1.76E-08      1.67E-08      1.27E-08      7.00E-09      3.99E-09
         O                    6.68E-09      1.27E-08      1.15E-08      8.97E-09      5.73E-09      3.84E-09
         OH                   5.61E-10      1.56E-09      1.65E-09      1.57E-09      1.30E-09      1.08E-09
         HO2                  4.56E-09      2.49E-08      3.43E-08      4.51E-08      5.56E-08      6.07E-08
         H2O2                 3.68E-11      3.30E-11      2.81E-11      2.39E-11      2.19E-11      2.19E-11
              *   INDUCTION TIME (MAX OH CONC)
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                  MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTICN TIME CALCULATIONS

                                                    INITIAL
                                        SPECIES   CCNCENTRATIONS
                                                    (MOLES/CC)

                                        H2          1C.000E-03
                                        O2           2.000E-02
                                        ARGON        9.70CE-01

             REACTION TEMPERATURE     1250.0 (DEG. K.)           PRESSURE     1.00 (ATMOSPHERE)

ELAPSEC TIME (MSEC)            0.0300      0.06C0      0.0900      0.1200      0.1500      0.1800

                                          CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                  9.75E-08    9.75E-C8    9.75E-08    9.75E-08    9.75E-08    9.74E-08
          O2                  1.95E-07    1.95E-07    1.95E-07    1.95E-07    1.95E-07    1.95E-07
          H2O                 2.09E-15    1.79E-14    1.32E-13    9.55E-13    6.86E-12    4.96E-11
          H                   8.32E-16    6.45E-15    4.67E-14    3.38E-13    2.43E-12    1.76E-11
          O                   1.12E-15    1.C1E-14    7.49E-14    5.44E-13    3.91E-12    2.82E-11
          OH                  1.56E-16    1.13E-15    8.13E-15    5.88E-14    4.22E-13    3.05E-12
          HO2                 1.35E-16    1.32E-15    9.94E-15    7.25E-14    5.21E-13    3.77E-12
          H2O2                3.21E-18    4.77E-17    4.01E-16    3.00E-15    2.17E-14    1.57E-13

                                                                                      *
ELAPSED TIME (MSEC)            0.2100      0.2400      0.2700      C.3000      0.3450      0.3800

                                          CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                  9.70E-08    9.44E-08    7.92E-08    4.06E-08    9.84E-09    5.68E-09
          O2                  1.95E-07    1.93E-C7    1.82E-07    1.58E-07    1.34E-07    1.27E-07
          H2O                 3.54F-10    2.48E-C9    1.44E-08    4.30E-08    6.47E-08    6.74E-08
          H                   1.26E-10    8.98E-10    5.67E-09    1.91E-08    2.50E-08    2.09E-08
          O                   2.01E-10    1.39E-09    7.36E-09    1.75E-08    1.90E-08    1.63E-08
          OH                  2.18E-11    1.54E-10    9.05E-10    2.65E-09    3.58E-09    3.41E-09
          HO2                 2.71E-11    1.94E-10    1.30E-09    5.87E-09    1.73E-C8    2.45E-C8
          H2O2                1.11E-12    7.18E-12    2.61E-11    2.33E-11    1.22E-11    1.16E-11

      *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                             INITIAL
                                  SPECIES  CONCENTRATIONS
                                             (MOLES/CC)

                                  H2         10.000E-03
                                  O2          2.000E-02
                                  ARGON       9.700E-01

                  REACTION TEMPERATURE    1600.0 (DEG. K.)        PRESSURE    1.00 (ATMOSPHERE)


ELAPSED TIME (MSEC)          0.0100      0.0200      0.0300      0.0400      0.0500      0.0600

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2               7.62E-08    7.62E-08    7.62E-08    7.61E-08    7.59E-08    7.49E-08
           O2               1.52E-07    1.52E-07    1.52E-07    1.52E-07    1.52E-07    1.51E-07
           H2O              1.34E-13    9.61E-13    5.63E-12    3.20E-11    1.81E-10    1.03E-09
           H                4.59E-14    2.79E-13    1.59E-12    9.01E-12    5.13E-11    3.00E-10
           O                8.77E-14    6.73E-13    3.99E-12    2.27E-11    1.28E-10    7.22E-10
           OH               2.08E-14    1.19E-13    6.70E-13    3.79E-12    2.16E-11    1.28E-10
           HO2              1.21E-15    8.70E-15    5.07E-14    2.88E-13    1.64E-12    9.53E-12
           H2O2             1.71E-16    1.94E-15    1.27E-14    7.39E-14    4.17E-13    2.25E-12


ELAPSED TIME (MSEC)          0.0700      0.0800      0.0900      0.1000

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2               6.88E-08    4.32E-08    1.48E-08    7.24E-09
           O2               1.47E-07    1.30E-07    1.12E-07    1.07E-07
           H2O              5.91E-09    2.56E-08    4.69E-08    5.24E-08
           H                1.92E-09    1.01E-08    2.06E-08    2.31E-08
           O                3.92E-09    1.51E-08    2.47E-08    2.65E-08
           OH               8.42E-10    4.08E-09    7.42E-09    8.20E-09
           HO2              6.11E-11    3.67E-10    1.05E-09    1.60E-09
           H2O2             9.50E-12    1.26E-11    5.88E-12    3.81E-12

       *   INDUCTION TIME (MAX OH CONC)
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                     MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                     INITIAL
                                          SPECIES  CONCENTRATIONS
                                                    (MOLES/CC)

                                          H2         10.000E-03
                                          02          2.000E-02
                                          ARGON       9.700E-01

                REACTION TEMPERATURE    2000.0 (DEG. K.)         PRESSURE    1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)          0.0050      0.0100      0.0150      0.0200      0.0250      0.0300

                                          CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                 6.09E-08    6.09E-08    6.08E-08    6.05E-08    5.90E-08    5.06E-08
         02                 1.22E-07    1.22E-07    1.22E-07    1.22E-07    1.20E-07    1.14E-07
         H2O                2.48E-12    1.53E-11    7.25E-11    3.30E-10    1.56E-09    8.05E-09
         H                  7.13E-13    3.46E-12    1.56E-11    7.20E-11    3.76E-10    2.40E-09
         O                  1.81E-12    1.19E-11    5.70E-11    2.57E-10    1.18E-09    5.64E-09
         OH                 6.19E-13    2.82E-12    1.26E-11    5.88E-11    3.22E-10    2.16E-09
         HO2                2.47E-15    1.24E-14    5.63E-14    2.60E-13    1.36E-12    9.18E-12
         H2O2               1.45E-15    1.14E-14    5.72E-14    2.59E-13    1.12E-12    3.41E-12

                                                                 *
ELAPSED TIME (MSEC)          0.0350      0.0400      0.0450      0.0510      0.0550      0.0600

                                          CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                 2.45E-08    8.36E-09    5.68E-09    5.35E-09    5.32E-09    5.30E-09
         02                 9.50E-08    8.39E-08    8.21E-08    8.20E-08    8.20E-08    8.20E-08
         H2O                2.76E-08    3.94E-08    4.14E-08    4.17E-08    4.18E-08    4.19E-08
         H                  9.63E-09    1.45E-08    1.53E-08    1.53E-08    1.53E-08    1.52E-08
         O                  1.79E-08    2.46E-08    2.56E-08    2.56E-08    2.56E-08    2.55E-08
         OH                 8.14E-09    1.17E-08    1.23E-08    1.23E-08    1.23E-08    1.23E-08
         HO2                3.80E-11    5.68E-11    5.99E-11    5.99E-11    5.97E-11    5.94E-11
         H2O2               2.26E-12    7.22E-13    4.72E-13    4.42E-13    4.39E-13    4.38E-13

            *   INDUCTION TIME (MAX OH CONC)
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                 MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                    INITIAL
                                       SPECIES  CONCENTRATIONS
                                                  (MOLES/CC)

                                       H2          10.000E-03
                                       O2           2.000E-02
                                       ARGON        9.700E-01

              REACTION TEMPERATURE   2500.0 (DEG. K.)        PRESSURE     1.00 (ATMOSPHERE)

ELAPSED TIME (MSEC)         0.0030       0.0060       0.0090       0.0120       0.0150       0.0180

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  4.87E-08     4.86E-08     4.80E-08     4.52E-08     3.19E-08     1.14E-08
       O2                  9.75E-08     9.73E-08     9.68E-08     9.46E-08     8.41E-08     6.81E-08
       H2O                 2.59E-11     1.47E-10     6.13E-10     2.71E-09     1.23E-08     2.69E-08
       H                   6.79E-12     2.75E-11     1.15E-10     6.24E-10     3.46E-09     7.97E-09
       O                   2.19E-11     1.25E-10     5.06E-10     2.10E-09     8.82E-09     1.89E-08
       OH                  9.69E-12     3.82E-11     1.65E-10     9.72E-10     5.61E-09     1.29E-08
       HO2                 2.56E-15     1.05E-14     4.39E-14     2.45E-13     1.35E-12     2.60E-12
       H2O2                4.68E-15     2.90E-14     1.20E-13     4.33E-13     6.58E-13     1.97E-13

                                                   *
ELAPSED TIME (MSEC)         0.0210       0.0240       0.0270       0.0300

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  5.21E-09     4.42E-09     4.33E-09     4.32E-09
       O2                  6.33E-08     6.27E-08     6.27E-08     6.27E-08
       H2O                 3.13E-08     3.19E-08     3.20E-08     3.20E-08
       H                   9.32E-09     9.47E-09     9.47E-09     9.46E-09
       O                   2.19E-08     2.23E-08     2.23E-08     2.23E-08
       OH                  1.51E-08     1.54E-08     1.54E-08     1.54E-08
       HO2                 2.84E-12     2.86E-12     2.86E-12     2.85E-12
       H2O2                7.84E-14     6.44E-14     6.29E-14     6.27E-14

           *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                    INITIAL
                                        SPECIES  CONCENTRATIONS
                                                  (MOLES/CC)

                                         H2        8.000E-02
                                         O2        2.000E-02
                                         ARGON     9.000E-01

              REACTION TEMPERATURE      970.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          1.0000      2.0000      3.0000      4.0000      5.0000      6.0000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                   5.02E-06    5.02E-06    5.01E-06    5.01E-06    5.00E-06    5.00E-06
        O2                   1.26E-06    1.25E-06    1.25E-06    1.25E-06    1.25E-06    1.25E-06
        H2O                  1.32E-14    1.02E-13    7.08E-13    4.81E-12    3.27E-11    2.23E-10
        H                    1.08E-16    7.88E-16    5.42E-15    3.68E-14    2.50E-13    1.70E-12
        O                    2.65E-17    1.94E-16    1.33E-15    9.05E-15    6.15E-14    1.02E-13
        OH                   1.12E-18    7.57E-18    5.15E-17    3.50E-16    2.38E-15    1.68E-14
        HO2                  1.30E-14    1.01E-13    7.01E-13    4.77E-12    3.24E-11    2.20E-10
        H2O2                 1.16E-14    1.24E-13    9.21E-13    6.36E-12    4.33E-11    2.93E-10


ELAPSED TIME (MSEC)          7.0000      8.0000      9.0000      9.7800*    10.0000     11.0000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                   4.99E-06    4.96E-06    4.68E-06    3.65E-06    3.37E-06    3.03E-06
        O2                   1.25E-06    1.22E-06    9.94E-07    2.30E-07    5.44E-08    9.21E-09
        H2O                  1.59E-09    1.45E-08    2.21E-07    1.09E-06    1.34E-06    1.76E-06
        H                    1.20E-11    9.95E-11    1.27E-09    1.17E-08    2.41E-08    2.60E-08
        O                    2.93E-12    2.39E-11    2.48E-10    5.00E-10    2.42E-10    4.20E-11
        OH                   1.18E-13    1.15E-12    1.75E-11    5.93E-11    5.06E-11    3.80E-11
        HO2                  1.51E-09    1.13E-08    1.09E-07    4.54E-07    5.14E-07    3.49E-07
        H2O2                 1.96E-09    1.22E-08    3.65E-08    2.12E-08    1.34E-08    8.34E-09

            *   INDUCTION TIME (MAX OH CONC)
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               MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                 INITIAL
                                       SPECIES   CONCENTRATIONS
                                                  (MOLES/CC)

                                        H2         8.000E-02
                                        O2         2.000E-02
                                        ARGON      9.000E-01

              REACTION TEMPERATURE     1000.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)            0.3000       0.6000       0.9000       1.2000       1.5000       1.8CC0

                                       CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                 4.87E-06     4.87E-06     4.87E-06     4.87E-06     4.87E-C6     4.87E-C6
          O2                 1.22E-06     1.22E-06     1.22E-06     1.22E-06     1.22E-C6     1.22E-C6
          H2O                1.18E-14     7.72E-14     4.36E-13     2.41E-12     1.33E-11     7.29E-11
          H                  2.37E-16     1.40E-15     7.78E-15     4.28E-14     4.57E-12     1.29E-12
          O                  6.61E-17     3.90E-16     2.17E-15     1.20E-14     6.57E-14     3.61E-13
          OH                 2.91E-18     1.60E-17     8.80E-17     4.84E-16     2.66E-15     1.46E-14
          HO2                1.15E-14     7.54E-14     4.26E-13     2.36E-12     1.30E-11     7.12E-11
          H2O2               5.31E-15     2.03E-14     3.10E-13     1.76E-12     9.71E-12     5.34E-11


ELAPSED TIME (MSEC)            2.1000       2.4000       2.7000       3.0000       3.3000       3.4500*

                                       CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                 4.86E-06     4.86E-06     4.84E-06     4.72E-06     4.20E-06     3.74E-06
          O2                 1.22E-06     1.21E-06     1.19E-06     1.08E-06     6.55E-07     2.90E-07
          H2O                4.01E-10     2.23E-09     1.30E-08     8.60E-08     4.83E-07     8.54E-07
          H                  7.11E-12     3.93E-11     2.20E-10     1.28E-09     7.24E-09     1.73E-08
          O                  1.98E-12     1.09E-11     6.02E-11     3.17E-10     1.05E-09     1.07E-09
          OH                 8.05E-14     4.49E-13     2.63E-12     1.69E-11     7.72E-11     1.05E-10
          HO2                3.91E-10     2.15E-09     1.10E-08     6.41E-08     2.87E-07     4.75E-07
          H2O2               2.93E-10     1.58E-09     8.00E-09     2.82E-05     3.29E-08     2.35E-08

        *   INDUCTION TIME (MAX OH CONC)
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                 MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                  INITIAL
                                      SPECIES  CONCENTRATIONS
                                                 (MOLES/CC)

                                      H2         8.000E-02
                                      O2         2.000E-02
                                      ARGON      9.000E-01

            REACTION TEMPERATURE     1050.0 (DEG. K.)         PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)         0.0500       0.1000       0.1500       0.2000       0.2500       0.3000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    4.64E-06     4.64E-06     4.64E-06     4.64E-06     4.64E-06     4.64E-06
      O2                    1.16E-06     1.16E-06     1.16E-06     1.16E-06     1.16E-06     1.16E-06
      H2O                   1.43E-14     1.24E-13     9.10E-13     6.55E-12     4.70E-11     3.37E-10
      H                     1.47E-15     1.10E-14     7.91E-14     5.68E-13     4.07E-12     2.92E-11
      O                     4.78E-16     3.58E-15     2.59E-14     1.86E-13     1.33E-12     9.53E-12
      OH                    2.21E-17     1.59E-16     1.14E-15     8.20E-15     5.88E-14     4.21E-13
      HO2                   1.23E-14     1.09E-13     8.05E-13     5.79E-12     4.16E-11     2.98E-10
      H2O2                  1.77E-15     2.31E-14     1.86E-13     1.36E-12     9.82E-12     7.03E-11

ELAPSED TIME (MSEC)         0.3500       0.4000       0.4500       0.5000       0.5370*      0.6000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    4.64E-06     4.61E-06     4.49E-06     4.14E-06     3.78E-06     3.37E-06
      O2                    1.16E-06     1.13E-06     1.02E-06     6.98E-07     3.75E-07     5.93E-08
      H2O                   2.40E-09     1.64E-08     9.20E-08     3.27E-07     5.90E-07     9.09E-07
      H                     2.07E-10     1.37E-09     6.64E-09     2.01E-08     3.84E-08     6.88E-08
      O                     6.74E-11     4.38E-10     1.92E-09     3.87E-09     3.85E-09     1.05E-09
      OH                    2.98E-12     1.97E-11     9.28E-11     2.35E-10     3.00E-10     1.73E-10
      HO2                   2.12E-09     1.45E-08     8.13E-08     2.74E-07     4.68E-07     6.32E-07
      H2O2                  4.97E-10     3.23E-09     1.38E-08     2.28E-08     1.97E-08     1.36E-08

          *   INDUCTION TIME (MAX OH CONC)
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                MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                 INITIAL
                                    SPECIES   CONCENTRATIONS
                                               (MOLES/CC)

                                    H2          8.000E-02
                                    O2          2.000E-02
                                    ARGON       9.000E-01

             REACTION TEMPERATURE    1150.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)         0.0100      0.0200      0.0300      0.0400      0.050C      0.060C

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  4.24E-06    4.24E-06    4.24E-06    4.24E-06    4.23E-06    4.C9E-C6
        O2                  1.06E-06    1.06E-06    1.06E-06    1.06E-06    1.05E-C6    9.40E-C7
        H2O                 3.74E-14    7.96E-13    1.56E-11    3.05E-10    5.87E-09    1.02E-07
        H                   1.52E-14    3.06E-13    5.90E-12    1.17E-10    2.24E-09    3,84E-08
        O                   3.64E-14    1.14E-13    2.23E-12    4.33E-11    8.29E-10    1.27E-08
        OH                  3.24E-16    6.35E-15    1.24E-13    2.41E-12    6.64E-11    7.75E-10
        HO2                 1.67E-14    3.77E-13    7.43E-12    1.45E-10    2.80E-C9    5.83E-08
        H2O2                6.84E-15    4.38E-14    8.94E-13    1.74E-11    3.28E-10    3.65E-C9

                                  *
ELAPSED TIME (MSEC)         0.0700      0.0800      0.0900      0.1000      0.110C      0.12CC

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  3.21E-06    2.79E-06    2.79E-06    2.79E-06    2,79E-C6    2.78E-C6
        O2                  3.29E-07    8.10E-02    8.93E-09    7.87E-09    8.96E-09    1.01E-08
        H2O                 7.06E-07    1.01E-06    1.09E-06    1.11E-06    1.13E-C6    1.15E-06
        H                   2.68E-07    2.21E-07    2.10E-07    1.67E-07    1.44E-C7    4.23E-C6
        O                   3.02E-08    3.27E-09    6.07E-10    3.97E-10    3.76E-10    3.77E-10
        OH                  3.34E-09    1.09E-09    5.91E-10    4.74E-10    4.28E-10    4.06E-10
        HO2                 3.56E-07    4.99E-07    5.00E-07    4.88E-07    4.76E-C7    4.63E-C7
        H2O2                4.26E-09    4.60E-09    6.31E-09    7.75E-09    8.74E-09    5.32E-C9

            *   INDUCTION TIME (MAX OH CONC)
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               MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                            INITIAL
                                SPECIES  CONCENTRATIONS
                                           (MOLES/CC)

                                 H2        8.000E-02
                                 O2        2.000E-02
                                 ARGON     9.000E-01

          REACTION TEMPERATURE    1250.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)

                                                   *
ELAPSED TIME (MSEC)        0.0100      0.0200      0.0300      0.0400      0.0500      0.0600

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                 3.90E-06    3.89E-06    2.72E-06    2.24E-06    2.28E-06    2.29E-06
       O2                 9.75E-07    9.72E-07    3.09E-07    5.89E-09    7.03E-09    8.66E-09
       H2O                4.42E-12    3.07E-09    8.19E-07    1.30E-06    1.34E-06    1.37E-06
       H                  2.36E-12    1.64E-09    4.76E-07    3.82E-07    2.49E-07    1.98E-07
       O                  9.98E-13    6.92E-10    5.60E-08    1.03E-09    6.34E-10    5.60E-10
       OH                 6.73E-14    4.68E-11    9.94E-09    2.42E-09    1.63E-09    1.37E-09
       HO2                1.07E-12    7.46E-10    2.22E-07    3.12E-07    6.16E-07    2.74E-07
       H2O2               1.76E-13    1.23E-10    2.27E-09    3.20E-09    4.68E-09    5.50E-09

        *   INDUCTION TIME (MAX OH CONC)
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            MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                          INITIAL
                               SPECIES  CONCENTRATIONS
                                          (MOLES/CC)

                               H2         8.000E-02
                               O2         2.000E-02
                               ARGON      9.000E-01

          REACTION TEMPERATURE    1600.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)


ELAPSED TIME (MSEC)           0.0010      0.0020      0.0030      0.0040      0.0050      0.0060

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                  3.05E-06    3.05E-06    3.05E-06    3.04E-06    2.99E-06    2.47E-06
         O2                  7.62E-07    7.62E-07    7.61E-07    7.59E-07    7.30E-07    4.84E-07
         H2O                 3.22E-12    3.69E-11    3.86E-10    4.02E-09    4.21E-08    4.08E-07
         H                   1.97E-12    2.18E-11    2.27E-10    2.37E-09    2.56E-08    3.01E-07
         O                   1.17E-12    1.41E-11    1.48E-10    1.53E-09    1.50E-08    8.52E-08
         OH                  1.42E-13    1.48E-12    1.54E-11    1.61E-10    1.83E-09    2.36E-08
         HO2                 8.61E-14    1.03E-12    1.09E-11    1.15E-10    1.39E-09    1.77E-08
         H2O2                4.56E-14    7.48E-13    8.27E-12    8.44E-11    6.69E-10    1.12E-09

                                     •
ELAPSED TIME (MSEC)           0.0068      0.0080      0.0090      0.0100

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                  1.50E-06    1.22E-06    1.24E-06    1.26E-06
         O2                  1.21E-07    2.07E-08    9.06E-07    1.08E-08
         H2O                 1.07E-06    1.33E-06    1.37E-06    1.40E-06
         H                   8.70E-07    9.16E-07    8.02E-07    7.08E-07
         O                   7.20E-08    2.84E-08    1.99E-08    1.51E-08
         OH                  5.05E-08    4.10E-08    3.54E-08    3.11E-08
         HO2                 4.44E-08    4.27E-08    3.44E-08    2.72E-08
         H2O2                5.80E-10    4.28E-10    4.00E-10    3.66E-10

           •   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                       INITIAL
                                         SPECIES   CONCENTRATIONS
                                                     (MOLES/CC)

                                          H2          8.000E-02
                                          O2          2.000E-02
                                          ARGON       9.000E-01

              REACTION TEMPERATURE     2000.0 (DEG. K.)         PRESSURE     5.00 (ATMOSPHERES)

                                                                                   *
ELAPSED TIME (MSEC)            0.0005       0.0010       0.0015       0.0020       0.0027       0.0030

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2                2.44E-06     2.44E-06     2.43E-06     2.30E-06     1.07E-06     9.70E-07
           O2                6.09E-07     6.09E-07     6.03E-07     5.37E-07     6.09E-08     3.05E-08
           H2O               7.50E-11     8.37E-10     8.57E-09     9.79E-08     9.20E-07    10.00E-07
           H                 4.14E-11     4.38E-10     4.56E-09     6.15E-08     7.98E-07     8.40E-07
           O                 3.43E-11     3.98E-10     3.99E-09     3.58E-08     7.55E-08     6.14E-08
           OH                5.57E-12     5.60E-11     5.99E-10     9.66E-09     9.41E-08     9.21E-08
           HO2               2.51E-13     2.72E-12     3.08E-11     5.90E-10     3.64E-09     2.04E-09
           H2O2              5.16E-13     7.03E-12     6.97E-11     4.09E-10     1.05E-10     5.01E-11


ELAPSED TIME (MSEC)            0.0035       0.0040       0.0045       0.0050

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2                9.66E-07     9.76E-07     9.86E-07     9.95E-07
           O2                2.35E-08     2.05E-08     1.79E-08     1.58E-08
           H2O               1.03E-06     1.05E-06     1.07E-06     1.08E-06
           H                 7.94E-07     7.42E-07     6.95E-07     6.53E-07
           O                 5.21E-08     4.52E-08     3.94E-08     3.45E-08
           OH                8.68E-08     8.16E-08     7.68E-08     7.24E-08
           HO2               1.07E-09     8.02E-10     6.51E-10     5.35E-10
           H2O2              2.78E-11     2.24E-11     1.95E-11     1.72E-11

        *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                             INITIAL
                                 SPECIES   CONCENTRATIONS
                                             (MOLES/CC)

                                  H2          8.000E-02
                                  O2          2.000E-02
                                  ARGON       9.000E-01

               REACTION TEMPERATURE    2500.0 (DEG. K.)       PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.0002      0.0004      0.0006      0.0008      0.0010      0.0012

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                1.95E-06    1.95E-06    1.94E-06    1.88E-06    1.51E-06    9.33E-07
          O2                4.87E-07    4.86E-07    4.79E-07    4.45E-07    2.70E-07    5.43E-08
          H2O               3.46E-10    2.10E-09    1.02E-08    5.32E-08    2.99E-07    6.65E-07
          H                 2.01E-10    1.02E-09    4.94E-09    3.02E-08    2.27E-07    5.78E-07
          O                 1.79E-10    1.15E-09    5.34E-09    2.30E-08    7.12E-08    7.62E-08
          OH                4.69E-11    2.23E-10    1.13E-09    8.08E-09    6.36E-08    1.25E-07
          HO2               1.69E-13    8.93E-13    4.88E-12    4.02E-11    2.69E-10    1.84E-10
          H2O2              7.62E-13    5.70E-12    2.70E-11    9.47E-11    9.16E-11    1.49E-11


ELAPSED TIME (MSEC)          0.0013*     0.0014      0.0016      0.0018      0.0020

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                8.54E-07    8.33E-07    8.28E-07    8.29E-07    8.31E-07
          O2                3.03E-08    2.41E-08    2.17E-08    2.09E-08    2.03E-08
          H2O               7.18E-07    7.34E-07    7.44E-07    7.50E-07    7.55E-07
          H                 6.29E-07    6.38E-07    6.31E-07    6.19E-07    6.07E-07
          O                 6.90E-08    6.57E-08    6.27E-08    6.05E-08    5.83E-08
          OH                1.27E-07    1.26E-07    1.25E-07    1.23E-07    1.21E-07
          HO2               1.05E-10    7.79E-11    6.65E-11    6.30E-11    6.12E-11
          H2O2              6.95E-12    4.91E-12    4.20E-12    3.92E-12    2.58E-12

       *   INDUCTION TIME (MAX OH CONC)
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                       MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                      INITIAL
                                          SPECIES   CONCENTRATIONS
                                                      (MOLES/CC)

                                           H2          8.000E-02
                                           O2          2.000E-02
                                           ARGON       8.920E-01
                                           CH4         8.000E-03

                 REACTION TEMPERATURE      1000.0 (DEG. K.)          PRESSURE     5.00 (ATMOSPHERES)


ELAPSED TIME (MSEC)             1.0000         2.0000         3.0000         4.0000         5.0000         6.0000

                                             CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  4.87E-06       4.86E-06       4.85E-06       4.83E-06       4.80E-06       4.77E-06
        O2                  1.22E-06       1.22E-06       1.21E-06       1.20E-06       1.18E-06       1.16E-06
        H2O                 3.75E-13       3.77E-11       1.60E-09       9.52E-09       2.44E-08       4.34E-08
        H                   5.46E-15       5.29E-13       1.25E-11       2.76E-11       3.26E-11       3.29E-11
        O                   1.53E-15       1.48E-13       3.51E-12       7.69E-12       8.93E-12       8.89E-12
        OH                  6.19E-17       5.98E-15       1.45E-13       3.64E-13       4.96E-13       5.49E-13
        HO2                 3.32E-13       3.28E-11       1.07E-09       2.97E-09       3.53E-09       3.44E-09
        CH4                 4.87E-07       4.87E-07       4.86E-07       4.86E-07       4.85E-07       4.84E-07
        CH3                 3.95E-14       3.82E-12       8.40E-11       1.67E-10       1.91E-10       1.94E-10
        C2H4                3.96E-25       3.90E-19       1.82E-14       1.14E-12       6.38E-12       1.61E-11
        C2H5                5.37E-27       5.07E-21       1.24E-16       3.27E-15       1.11E-14       2.05E-14
        C2H6                1.13E-18       1.10E-14       1.14E-11       1.32E-10       3.50E-10       5.92E-10
        H2O2                2.92E-13       3.09E-11       1.55E-09       9.58E-09       1.99E-08       2.81E-08


ELAPSED TIME (MSEC)             7.0000         8.0000         8.4C00*

                                             CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  4.74E-06       4.70E-06       4.69E-06
        O2                  1.14E-06       1.13E-06       1.12E-06
        H2O                 6.41E-08       8.55E-08       9.42E-08
        H                   3.22E-11       3.14E-11       3.11E-11
        O                   8.56E-12       8.22E-12       8.09E-12
        OH                  5.67E-13       5.72E-13       5.73E-13
        HO2                 3.24E-09       3.08E-09       3.02E-09
        CH4                 4.84E-07       4.83E-07       4.83E-07
        CH3                 1.91E-10       1.88E-10       1.87E-10
        C2H4                2.90E-11       4.38E-11       5.02E-11
        C2H5                3.00E-14       3.93E-14       4.29E-14
        C2H6                8.28E-10       1.06E-09       1.14E-09
        H2O2                3.40E-08       3.81E-08       3.94E-08

             *   INDUCTION TIME (MAX OH CONC)
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                MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                          SPECIES    INITIAL
                                                  CONCENTRATIONS
                                                    (MOLES/CC)

                                           H2        8.000E-02
                                           O2        2.000E-02
                                           ARGON     8.920E-01
                                           CH4       8.000E-03

            REACTION TEMPERATURE      1100.0 (DEG. K.)         PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)            0.2000       0.4CC0       0.6C00       0.8000       1.0000       1.2000*

                                            CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                       4.43E-06     4.42E-06     4.39E-06     4.37E-06     4.35E-06     4.32E-06
      O2                       1.11E-06     1.10E-06     1.08E-06     1.07E-06     1.05E-06     1.04E-06
      H2O                      2.10E-10     8.93E-09     2.32E-08     3.86E-08     5.46E-08     7.07E-08
      H                        1.40E-11     9.64E-11     1.08E-10     1.08E-10     1.06E-10     1.04E-10
      O                        5.55E-12     3.96E-11     4.36E-11     4.27E-11     4.11E-11     3.55E-11
      OH                       2.59E-13     1.85E-12     2.13E-12     2.19E-12     2.20E-12     2.21E-12
      HO2                      1.03E-10     1.99E-09     2.66E-09     2.78E-09     2.83E-09     2.84E-09
      CH4                      4.43E-07     4.42E-07     4.42E-07     4.41E-07     4.41E-07     4.40E-07
      CH3                      7.07E-11     4.38E-10     4.75E-10     4.76E-10     4.72E-10     4.66E-10
      C2H4                     8.31E-17     1.50E-12     1.12E-11     3.02E-11     5.70E-11     9.02E-11
      C2H5                     1.96E-18     5.01E-15     1.81E-14     3.37E-14     5.04E-14     6.79E-14
      C2H6                     3.87E-13     1.39E-10     3.99E-10     6.65E-10     9.20E-10     1.16E-09
      H2O2                     4.32E-11     3.91E-09     1.15E-08     1.89E-08     2.53E-08     3.08E-08

          *   INDUCTION TIME (MAX OH CONC)
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MONSANTO RESEARCH CORPORATION - SHCCK TUBE INDUCTION TIME CALCULATIONS

                                   INITIAL
                        SPECIES   CONCENTRATIONS
                                   (MOLES/CC)

                         H2          8.000E-02
                         O2          2.000E-02
                         ARGON       8.920E-01
                         CH4         8.000E-03

            REACTION TEMPERATURE     1150.0 (DEG. K.)         PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)         0.0500      C.1000      0.1500      0.2000      0.2500      0.3000

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                4.24E-C6    4.24E-C6    4.23E-06    4.22E-06    4.21E-06    4.20E-06
         O2                1.06E-06    1.06E-06    1.05E-06    1.05E-06    1.04E-06    1.03E-06
         H2O               4.81E-12    5.75E-10    5.62E-09    1.33E-08    2.17E-08    3.04E-08
         H                 5.84E-13    5.18E-11    1.54E-10    1.83E-10    1.91E-10    1.92E-10
         O                 2.60E-13    2.40E-11    7.52E-11    8.83E-11    9.13E-11    9.09E-11
         OH                1.32E-14    1.19E-12    3.67E-12    4.37E-12    4.60E-12    4.66E-12
         HO2               1.73E-12    1.93E-10    1.25E-09    1.91E-09    2.23E-09    2.40E-09
         CH4               4.24E-07    4.24E-07    4.23E-07    4.23E-07    4.22E-07    4.22E-07
         CH3               2.32E-12    2.13E-10    6.12E-10    6.87E-10    7.08E-10    7.12E-10
         C2H4              7.54E-22    1.03E-15    4.31E-13    3.02E-12    8.61E-12    1.72E-11
         C2H5              2.13E-23    2.14E-17    2.43E-15    8.49E-15    1.37E-14    2.47E-14
         C2H6              1.63E-16    1.91E-12    7.19E-11    2.01E-10    3.97E-10    4.90E-10
         H2O2              5.82E-13    8.05E-11    1.32E-09    4.01E-09    7.22E-09    1.05E-08

                                *
ELAPSEC TIME (MSEC)         C.3400      0.3500      0.4C00      0.45C0      0.5C00

                                      CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

         H2                4.19E-06    4.18E-06    4.17E-06    4.16E-06    4.15E-06
         O2                1.03E-06    1.C2E-06    1.C2E-06    1.01E-06    1.00E-06
         H2C               3.74E-08    3.91E-08    4.78E-08    5.65E-08    6.52E-08
         H                 1.92E-10    1.91E-10    1.89E-10    1.87E-10    1.85E-10
         O                 8.96E-11    8.93E-11    8.73E-11    8.53E-11    8.32E-11
         OH                4.67E-12    4.67E-12    4.66E-12    4.64E-12    4.61E-12
         HO2               2.49E-09    2.50E-09    2.58E-09    2.64E-09    2.69E-09
         CH4               4.22E-07    4.22E-C7    4.22E-07    4.21E-07    4.21E-07
         CH3               7.11E-10    7.11E-10    7.08E-10    7.04E-10    7.00E-10
         C2H4              2.62E-11    2.87E-11    4.27E-11    5.90E-11    7.75E-11
         C2H5              3.18E-14    3.37E-14    4.30E-14    5.26E-14    6.25E-14
         C2H6              6.C4E-10    6.33E-10    7.72E-1C    9.07E-10    1.04E-09
         H2C2              1.31E-08    1.37E-C8    1.67E-08    1.96E-08    2.23E-08

      *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                          INITIAL
                              SPECIES  CONCENTRATIONS
                                         (MOLES/CC)

                              H2         8.000E-02
                              O2         2.000E-02
                              ARGON      8.960E-01
                              C2H4       4.000E-03

           REACTION TEMPERATURE    1030.0 (DEG. K.)       PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)       2.0000      4.0C00      6.0000      8.0000      10.0000     12.0000

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

     H2                 4.69E-06    4.61E-06    4.52E-06    4.42E-06    4.29E-06    4.14E-06
     O2                 1.17E-06    1.15E-06    1.12E-06    1.09E-06    1.04E-06    9.73E-07
     H2O                5.59E-09    2.19E-08    4.89E-08    9.42E-08    1.71E-07    2.89E-07
     H                  1.38E-11    1.88E-11    2.69E-11    4.14E-11    6.58E-11    9.02E-11
     O                  4.38E-12    5.94E-12    8.34E-12    1.24E-11    1.87E-11    2.35E-11
     OH                 1.96E-13    3.03E-13    4.81E-13    8.07E-13    1.36E-12    1.92E-12
     HO2                9.69E-10    1.30E-09    1.40E-09    2.69E-09    4.17E-09    5.64E-09
     C2H4               2.16E-07    1.72E-07    1.28E-07    8.66E-08    5.30E-08    3.48E-08
     C2H5               1.86E-11    1.74E-11    2.28E-11    2.52E-11    2.74E-11    2.84E-11
     C2H6               2.10E-08    6.42E-08    1.08E-07    1.50E-07    1.83E-07    2.01E-07
     H2O2               5.41E-09    1.78E-08    2.97E-08    4.04E-08    4.79E-08    5.08E-08

ELAPSED TIME (MSEC)       13.3000*    14.0000

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

     H2                 4.04E-06    4.00E-06
     O2                 9.26E-07    9.05E-07
     H2O                3.79E-07    4.25E-07
     H                  9.52E-11    9.45E-11
     O                  3.16E-10    2.22E-11
     OH                 7.41E-11    2.01E-12
     HO2                1.33E-02    5.80E-09
     C2H4               4.04E-06    2.98E-08
     C2H5               9.26E-07    2.75E-11
     C2H6               3.80E-07    2.06E-07
     H2O2               1.67E-10    5.01E-08

         *    INDUCTION TIME (MAX OH CONC)
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                 MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                   INITIAL
                                         SPECIES  CONCENTRATIONS
                                                   (MOLES/CC)

                                          H2        8.000E-02
                                          O2        2.000E-02
                                          ARGON     8.960E-01
                                          C2H4      4.000E-03

             REACTION TEMPERATURE     1100.0 (DEG. K.)          PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)            0.5000        1.0000       1.5000       2.0000       2.5000       3.0000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                 4.38E-06      4.29E-06     4.20E-06     4.10E-06     1.20E-03     3.88E-06
          O2                 1.09E-06      1.05E-06     1.02E-06     9.74E-07     9.29E-07     8.80E-07
          H2O                1.84E-08      5.28E-08     9.89E-08     1.60E-07     2.37E-07     3.28E-07
          H                  8.52E-11      1.05E-10     1.30E-10     1.62E-10     1.96E-10     4.77E-10
          O                  3.48E-11      4.14E-11     4.91E-11     5.73E-11     6.44E-11     6.75E-11
          OH                 1.68E-12      2.21E-12     2.92E-12     3.81E-12     4.79E-12     5.60E-12
          HO2                2.04E-09      2.77E-09     3.66E-09     4.73E-09     5.87E-09     6.78E-09
          C2H4               1.97E-07      1.62E-07     1.30E-07     5.12E-02     8.09E-08     6.63E-08
          C2H5               4.62E-11      4.77E-11     4.87E-11     4.92E-11     4.91E-11     4.83E-11
          C2H6               2.42E-08      5.91E-08     9.12E-08     1.19E-07     1.41E-07     1.55E-07
          H2O2               9.47E-09      2.47E-08     3.77E-08     4.73E-08     5.30E-08     5.52E-08

                                            *
ELAPSED TIME (MSEC)            3.5000        3.6200       4.0000       4.5000

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

          H2                 3.77E-06      3.75E-06     3.67E-06     3.58E-06
          O2                 8.30E-07      8.19E-07     7.83E-07     7.41E-07
          H2O                4.26E-07      4.49E-07     5.21E-07     6.09E-07
          H                  2.38E-10      2.39E-10     2.35E-10     2.23E-10
          O                  6.49E-11      6.36E-11     5.82E-11     5.04E-11
          OH                 5.96E-12      5.97E-12     5.86E-12     5.49E-12
          HO2                7.16E-09      7.17E-09     7.01E-09     6.54E-09
          C2H4               5.82E-08      5.71E-08     5.48E-08     5.42E-08
          C2H5               4.68E-11      4.63E-11     4.48E-11     4.25E-11
          C2H6               1.63E-07      1.64E-07     1.66E-07     1.67E-07
          H2O2               5.52E-08      5.50E-08     5.41E-08     5.26E-08

      *   INDUCTION TIME (MAX OH CONC)
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                         MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                                  INITIAL
                                      SPECIES  CONCENTRATIONS
                                                (MOLES/CC)

                                       H2        8.000E-02
                                       O2        2.000E-02
                                       ARGON     8.960E-01
                                       C2H4      4.000E-03

                 REACTION TEMPERATURE     1150.0 (DEG. K.)       PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.2000      0.4000      0.6000      0.8000      1.0000      1.2000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    4.17E-06    4.07E-06    3.95E-06    3.84E-06    3.72E-06    3.61E-06
      O2                    1.03E-06    9.86E-07    9.37E-07    8.86E-07    8.33E-07    7.81E-07
      H2O                   3.04E-08    8.45E-08    1.51E-07    2.33E-07    3.25E-07    4.26E-07
      H                     2.68E-10    3.21E-10    3.82E-10    4.48E-10    5.06E-10    5.41E-10
      O                     1.27E-10    1.42E-10    1.56E-10    1.65E-10    1.67E-10    1.58E-10
      OH                    6.51E-12    8.19E-12    1.02E-11    1.25E-11    1.45E-11    1.56E-11
      HO2                   3.20E-09    4.78E-09    6.48E-09    8.22E-09    9.67E-09    1.05E-08
      C2H4                  1.88E-07    1.54E-07    1.25E-07    1.01E-07    8.31E-08    7.21E-08
      C2H5                  7.45E-11    7.45E-11    7.33E-11    7.15E-11    6.92E-11    6.64E-11
      C2H6                  2.34E-08    5.75E-08    8.72E-08    1.11E-07    1.29E-07    1.40E-07
      H2O2                  9.87E-09    2.65E-08    3.98E-08    4.85E-08    5.28E-08    5.40E-08

ELAPSED TIME (MSEC)          1.3100*     1.4000      1.6000      1.8000      2.0000      2.2000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    3.55E-06    3.50E-06    3.41E-06    3.33E-06    3.26E-06    3.20E-06
      O2                    7.54E-07    7.32E-07    6.87E-07    6.48E-07    6.14E-07    5.84E-07
      H2O                   4.82E-07    5.26E-07    6.18E-07    7.01E-07    7.74E-07    8.37E-07
      H                     5.46E-10    5.43E-10    5.20E-10    4.84E-10    4.46E-10    4.09E-10
      O                     1.50E-10    1.42E-10    1.22E-10    1.03E-10    8.64E-11    7.33E-11
      OH                    1.58E-11    1.57E-11    1.49E-11    1.37E-11    1.24E-11    1.12E-11
      HO2                   1.06E-08    1.06E-08    1.01E-08    9.26E-09    8.35E-09    7.57E-09
      C2H4                  6.84E-08    6.63E-08    6.43E-08    6.44E-08    6.57E-08    6.76E-08
      C2H5                  6.47E-11    6.33E-11    6.00E-11    5.68E-11    5.37E-11    5.10E-11
      C2H6                  1.43E-07    1.45E-07    1.48E-07    1.47E-07    1.46E-07    1.44E-07
      H2O2                  5.38E-08    5.35E-08    5.22E-08    5.07E-08    4.91E-08    4.77E-08

        *   INDUCTION TIME (MAX OH CONC)
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            MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                              INITIAL
                                    SPECIES   CONCENTRATIONS
                                              (MOLES/CC)

                                    H2        8.000E-02
                                    O2        2.000E-02
                                    ARGON     8.960E-01
                                    C2H4      4.000E-03

               REACTION TEMPERATURE     1200.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.0500      0.1000      0.1500      0.2000      0.2500      0.3000

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  4.04E-06    3.96E-06    3.88E-06    3.80E-06    3.72E-06    3.63E-06
       O2                  1.01E-06    9.72E-07    9.37E-07    8.99E-07    8.61E-07    8.22E-07
       H2O                 1.22E-08    5.36E-08    1.01E-07    1.53E-07    2.11E-07    2.74E-07
       H                   6.20E-10    7.72E-10    8.63E-10    9.58E-10    1.06E-09    1.16E-09
       O                   3.48E-10    4.10E-10    4.27E-10    4.38E-10    4.46E-10    4.46E-10
       OH                  1.81E-11    2.32E-11    2.65E-11    3.02E-11    3.42E-11    3.82E-11
       HO2                 2.32E-09    5.03E-09    6.99E-09    9.05E-09    1.12E-08    1.33E-08
       C2H4                1.97E-07    1.73E-07    1.51E-07    1.30E-07    1.12E-07    9.72E-08
       C2H5                9.90E-11    1.08E-10    1.06E-10    1.03E-10    1.00E-10    9.70E-11
       C2H6                6.35E-09    2.95E-08    5.22E-08    7.28E-08    9.07E-08    1.06E-07
       H2O2                1.62E-09    1.11E-08    2.12E-08    3.01E-08    3.73E-08    4.26E-08

                                                                     •
ELAPSED TIME (MSEC)          0.3500      0.4000      0.4500      0.4720      0.5000      0.5500

                                    CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  1.93E-03    3.46E-06    3.39E-06    3.35E-06    3.31E-06    3.24E-06
       O2                  7.83E-07    7.45E-07    7.07E-07    6.92E-07    6.72E-07    6.40E-07
       H2O                 3.41E-07    4.11E-07    4.82E-07    5.13E-07    5.53E-07    6.18E-07
       H                   1.25E-09    1.32E-09    1.36E-09    1.36E-09    1.36E-09    1.33E-09
       O                   4.37E-10    4.18E-10    3.45E-10    3.75E-10    3.54E-10    3.16E-10
       OH                  4.18E-11    4.45E-11    4.59E-11    4.60E-11    4.58E-11    4.45E-11
       HO2                 1.51E-08    1.65E-08    1.74E-08    1.76E-08    1.77E-08    1.74E-08
       C2H4                8.51E-08    7.59E-08    6.96E-08    6.76E-08    6.55E-08    6.35E-08
       C2H5                9.38E-11    9.06E-11    8.74E-11    8.60E-11    8.41E-11    8.10E-11
       C2H6                1.18E-07    1.27E-07    1.33E-07    1.35E-07    1.37E-07    1.40E-07
       H2O2                4.62E-08    4.82E-08    4.90E-08    4.92E-08    4.92E-08    4.88E-08

          •   INDUCTION TIME (MAX OH CONC)
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MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                        INITIAL
                             SPECIES  CONCENTRATIONS
                                       (MOLES/CC)

                              H2        8.000E-02
                              O2        2.000E-02
                              ARGON     8.960E-01
                              C2H4      4.000E-03

          REACTION TEMPERATURE    1250.0 (DEG. K.)         PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)        0.0200      0.0400      0.0600      0.0800      0.1000      0.1200

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                3.90E-06    3.83E-06    3.73E-06    3.64E-06    3.54E-06    3.44E-06
       O2                9.74E-07    9.43E-07    9.02E-07    8.59E-07    8.14E-07    7.67E-07
       H2O               1.19E-09    4.35E-08    7.34E-08    1.65E-07    2.34E-07    3.09E-07
       H                 4.30E-10    1.84E-09    2.12E-09    2.38E-09    2.67E-09    2.96E-09
       O                 2.15E-10    1.12E-09    1.17E-09    1.18E-09    1.18E-09    1.15E-09
       OH                1.34E-11    6.61E-11    7.83E-11    9.02E-11    1.03E-10    1.16E-10
       HO2               2.66E-10    4.95E-09    8.37E-09    1.19E-08    1.57E-08    1.96E-08
       C2H4              1.95E-07    1.75E-07    1.49E-07    1.26E-07    1.05E-07    8.78E-08
       C2H5              4.33E-11    1.44E-10    1.42E-10    1.36E-10    1.30E-10    1.24E-10
       C2H6              2.26E-10    1.97E-08    4.56E-08    6.93E-08    8.99E-08    1.07E-07
       H2O2              5.54E-11    4.87E-09    1.32E-08    2.12E-08    2.79E-08    3.30E-08


                                                  *
ELAPSED TIME (MSEC)        0.1400      0.1600      0.1790      0.2000      0.2200      0.2400

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                3.34E-06    3.25E-06    3.16E-06    3.08E-06    3.00E-06    2.94E-06
       O2                7.20E-07    6.74E-07    6.33E-07    5.91E-07    5.55E-07    5.24E-07
       H2O               3.87E-07    4.69E-07    5.45E-07    6.26E-07    6.97E-07    7.62E-07
       H                 3.23E-09    3.42E-09    3.49E-09    3.45E-09    3.31E-09    3.12E-09
       O                 1.11E-09    1.03E-09    9.31E-10    8.10E-10    6.95E-10    5.91E-10
       OH                1.27E-10    1.35E-10    1.37E-10    1.34E-10    1.27E-10    1.18E-10
       HO2               2.34E-08    2.65E-08    2.84E-08    2.92E-08    2.88E-08    2.77E-08
       C2H4              7.44E-08    6.48E-08    5.88E-08    5.52E-08    5.38E-08    5.40E-08
       C2H5              1.18E-10    1.12E-10    1.08E-10    1.03E-10    9.83E-11    9.42E-11
       C2H6              1.20E-07    1.30E-07    1.36E-07    1.40E-07    1.41E-07    1.41E-07
       H2O2              3.67E-08    3.90E-08    4.04E-08    4.12E-08    4.15E-08    4.16E-08

          *   INDUCTION TIME (MAX OH CONC)
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                 MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                             INITIAL
                                   SPECIES   CONCENTRATIONS
                                              (MOLES/CC)

                                   H2          8.000E-02
                                   O2          2.000E-02
                                   ARGON       8.960E-01
                                   C2H4        4.000E-03

              REACTION TEMPERATURE    1600.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)         0.0010      0.0020      0.0030      0.0040      0.0050      0.0060

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                  3.05E-06    3.05E-06    3.05E-06    3.04E-06    2.99E-06    2.67E-06
      O2                  7.62E-07    7.62E-07    7.61E-07    7.58E-07    7.32E-07    5.89E-07
      H2O                 3.22E-12    3.76E-11    4.00E-10    4.19E-09    4.06E-08    2.64E-07
      H                   1.96E-12    2.21E-11    2.35E-10    2.43E-09    2.15E-08    1.08E-07
      O                   1.17E-12    1.43E-11    1.53E-10    1.58E-09    1.37E-08    4.74E-08
      OH                  1.42E-13    1.50E-12    1.59E-11    1.66E-10    1.60E-09    1.02E-08
      HO2                 8.57E-14    1.04E-12    1.17E-11    1.19E-10    1.26E-09    9.38E-09
      C2H4                1.52E-07    1.52E-07    1.52E-07    1.52E-07    1.50E-07    1.09E-07
      C2H5                8.64E-15    9.74E-14    1.03E-12    1.23E-11    8.44E-11    2.38E-10
      C2H6                3.81E-15    5.48E-14    8.04E-13    3.04E-11    2.01E-09    4.29E-08
      H2O2                4.55E-14    7.61E-13    8.55E-12    8.79E-11    6.75E-10    1.70E-09

                                       *
ELAPSED TIME (MSEC)         0.0070      0.0072      0.0080      0.0090      0.0100

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                  1.99E-06    1.87E-06    1.60E-06    1.52E-06    1.51E-06
      O2                  3.10E-07    2.59E-07    1.26E-07    6.90E-08    5.17E-08
      H2O                 7.82E-07    8.84E-07    1.17E-06    1.32E-06    1.37E-06
      H                   2.55E-07    2.71E-07    2.40E-07    1.38E-07    8.00E-08
      O                   4.17E-08    3.60E-08    1.43E-08    3.66E-09    1.33E-09
      OH                  2.34E-08    2.40E-08    1.79E-08    8.53E-09    4.49E-09
      HO2                 2.62E-08    2.87E-08    3.18E-08    2.67E-08    2.03E-08
      C2H4                3.10E-08    2.57E-08    2.26E-08    3.13E-08    4.26E-08
      C2H5                1.88E-10    1.80E-10    1.63E-10    1.39E-10    1.12E-10
      C2H6                1.21E-07    1.26E-07    1.30E-07    1.21E-07    1.10E-07
      H2O2                1.55E-09    1.50E-09    1.57E-09    2.14E-09    2.80E-09

           *   INDUCTION TIME (MAX OH CONC)
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MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                          INITIAL
                              SPECIES  CONCENTRATIONS
                                         (MOLES/CC)

                              H2         8.000E-02
                              O2         2.000E-02
                              ARGON      8.960E-01
                              C2H4       4.000E-03

             REACTION TEMPERATURE    2000.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.0005      0.0010      0.0015      0.0020      0.0025      0.0026*

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  2.44E-06    2.44E-06    2.42E-06    2.28E-06    1.31E-06    1.17E-06
       O2                  6.09E-07    6.09E-07    6.02E-07    5.24E-07    1.39E-07    9.13E-08
       H2O                 7.36E-11    8.66E-10    9.35E-09    1.16E-07    7.72E-07    8.77E-07
       H                   4.06E-11    4.53E-10    4.97E-09    7.30E-08    5.55E-07    6.04E-07
       O                   3.36E-11    4.12E-10    4.34E-09    4.08E-08    7.93E-08    6.81E-08
       OH                  5.47E-12    5.80E-11    6.55E-10    1.17E-08    8.08E-08    8.32E-08
       HO2                 2.45E-13    2.81E-12    3.36E-11    7.16E-10    4.02E-09    3.71E-09
       C2H4                1.22E-07    1.22E-07    1.22E-07    1.21E-07    8.51E-08    7.68E-08
       C2H5                1.82E-14    2.03E-13    2.22E-12    3.14E-11    1.59E-10    1.62E-10
       C2H6                3.09E-15    6.67E-14    4.14E-12    6.83E-10    3.66E-08    4.48E-08
       H2O2                5.01E-13    7.26E-12    7.55E-11    4.38E-10    2.04E-10    1.54E-10

ELAPSED TIME (MSEC)          0.0030      0.0035      0.0040      0.0045      0.0050

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  1.01E-06    1.02E-06    1.05E-06    1.08E-06    1.09E-06
       O2                  2.69E-08    1.20E-08    6.72E-09    4.21E-09    2.87E-09
       H2O                 1.06E-06    1.12E-06    1.15E-06    1.17E-06    1.18E-06
       H                   5.66E-07    4.41E-07    3.53E-07    2.93E-07    2.51E-07
       O                   3.54E-08    1.83E-08    1.07E-08    6.90E-09    4.84E-09
       OH                  7.01E-08    5.27E-08    4.11E-08    3.34E-08    2.81E-08
       HO2                 1.59E-09    4.84E-10    1.83E-10    8.48E-11    4.59E-11
       C2H4                7.22E-08    8.12E-08    8.95E-08    9.58E-08    1.01E-07
       C2H5                1.52E-10    1.34E-10    1.18E-10    1.05E-10    9.38E-11
       C2H6                4.95E-08    4.05E-08    3.22E-08    2.59E-08    2.12E-08
       H2O2                6.07E-11    2.41E-11    1.17E-11    6.66E-12    4.28E-12

          *   INDUCTION TIME (MAX OH CONC)
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                         MONSANTO RESEARCH CORPORATION - SHCCK TUBE INDUCTION TIME CALCULATIONS

                                                   INITIAL
                                        SPECIES   CONCENTRATIONS
                                                   (MOLES/CC)

                                         H2          8.COCE-02
                                         O2          2.000E-02
                                         ARGON       8.960E-01
                                         C2H4        4.000E-03

                 REACTION TEMPERATURE    25C0.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.0002       0.0004       0.0006       0.0008       0.0010       0.0012

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  1.95E-06     1.95E-C6     1.93E-06     1.87E-06     1.45E-06     9.12E-07
       O2                  4.87E-07     4.86E-C7     4.79E-07     4.42E-07     2.48E-C7     4.85E-08
       H2O                 3.47E-10     2.12E-09     1.06E-08     5.75E-08     3.32E-07     6.77E-07
       H                   2.01E-10     1.03E-09     5.13E-09     3.29E-08     2.56E-07     5.89E-07
       O                   1.8CE-10     1.16E-C9     5.54E-09     2.46E-08     7.51E-08     7.48E-08
       OH                  4.69E-11     2.24E-10     1.17E-09     8.85E-09     7.11E-C8     1.25E-07
       HO2                 1.69E-13     8.97E-13     5.06E-12     4.41E-11     2.90E-10     1.68E-10
       C2H4                9.75E-08     9.75E-C8     9.75E-08     9.75E-08     9.74E-08     9.72E-08
       C2H5                1.44E-14     7.36E-14     3.67E-13     2.04E-12     1.82E-11     4.20E-11
       C2H6                6.15E-17     8.23E-16     1.67E-14     6.49E-13     3.88E-11     1.97E-10
       H2O2                7.62E-13     5.74E-12     2.79E-11     9.92E-11     8.28E-11     1.29E-11

                                  *
ELAPSED TIME (MSEC)          0.C013       0.0014       0.0016       0.0018       0.0020

                                         CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  8.48E-07     8.30E-C7     8.26E-07     8.27E-07     8.28E-07
       O2                  2.91E-08     2.39E-08     2.16E-08     2.09E-08     2.02E-08
       H2O                 7.20E-07     7.35E-07     7.44E-07     7.49E-07     7.54E-07
       H                   6.29E-07     6.36E-C7     6.27E-07     6.14E-07     6.02E-07
       O                   6.84E-08     6.54E-C8     6.24E-08     6.00E-08     5.78E-08
       OH                  1.27E-07     1.26E-07     1.24E-07     1.22E-07     1.21E-07
       HO2                 9.95E-11     7.65E-11     6.60E-11     6.22E-11     5.90E-11
       C2H4                9.72E-08     9.72E-C8     9.72E-08     9.72E-08     9.72E-C8
       C2H5                4.47E-11     4.54E-11     4.47E-11     4.39E-11     4.30E-11
       C2H6                2.40E-10     2.45E-10     2.38E-10     2.29E-10     1.24E-10
       H2O2                6.53E-12     4.83E-12     4.18E-12     4.03E-12     3.90E-12

           *   INDUCTION TIME (MAX OH CONC)
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              MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                              INITIAL
                                   SPECIES  CONCENTRATIONS
                                              (MOLES/CC)

                                   H2         8.000E-02
                                   O2         2.000E-02
                                   ARGON      8.920E-01
                                   CF3BR      8.000E-03

          REACTION TEMPERATURE     1150.0 (DEG. K.)      PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)        1.0000      2.0000      3.0000      4.0000      4.7500*     5.0000

                                 CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  4.23E-06    4.22E-06    4.21E-06    4.20E-06    4.19E-06    4.18E-06
       O2                  1.06E-06    1.06E-06    1.06E-06    1.05E-06    1.05E-06    1.05E-06
       H2O                 2.41E-11    2.28E-10    1.46E-09    5.33E-09    9.23E-09    1.06E-08
       H                   7.04E-14    5.17E-13    2.69E-12    5.60E-12    5.95E-12    5.94E-12
       O                   3.47E-14    2.55E-13    1.33E-12    2.76E-12    2.92E-12    2.91E-12
       OH                  1.69E-15    1.23E-14    6.42E-14    1.34E-13    1.43E-13    1.42E-13
       HO2                 7.38E-13    5.46E-12    2.91E-11    6.44E-11    7.12E-11    7.18E-11
       BR                  2.28E-16    1.62E-14    5.46E-13    4.19E-12    7.75E-12    8.85E-12
       HBR                 2.35E-11    2.26E-10    1.46E-09    5.29E-09    9.13E-09    1.04E-08
       CF3BR               4.24E-07    4.24E-07    4.22E-07    4.18E-07    4.15E-07    4.13E-07
       CF3                 2.32E-11    2.21E-10    1.41E-09    4.96E-09    8.29E-09    9.35E-09
       CF3H                3.35E-13    5.05E-12    4.80E-11    3.27E-10    8.48E-10    1.08E-09
       H2O2                9.81E-12    9.58E-11    6.22E-10    2.30E-09    4.03E-09    4.61E-09


ELAPSED TIME (MSEC)        6.0000      7.0000

                                 CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

       H2                  4.17E-06    4.15E-06
       O2                  1.04E-06    1.03E-06
       H2O                 1.58E-08    2.09E-08
       H                   5.88E-12    5.86E-12
       O                   2.86E-12    2.83E-12
       OH                  1.41E-13    1.41E-13
       HO2                 7.40E-11    7.67E-11
       BR                  1.31E-11    1.73E-11
       HBR                 1.55E-08    2.05E-08
       CF3BR               4.08E-07    4.03E-07
       CF3                 1.33E-08    1.67E-08
       CF3H                2.27E-09    3.82E-09
       H2O2                6.91E-09    9.17E-09

          *    INDUCTION TIME (MAX OH CONC)
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             MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                               INITIAL
                                   SPECIES  CONCENTRATIONS
                                              (MOLES/CC)

                                    H2        8.000E-02
                                    O2        2.000E-02
                                    ARGON     8.920E-01
                                    CF3BR     8.000E-03

          REACTION TEMPERATURE   1150.0 (DEG. K.)      PRESSURE    5.00 (ATMOSPHERES)

   ELAPSED TIME (MSEC)        1.0000      2.0000      3.0000      4.0000      5.0000      6.0000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2                4.23E-06    4.22E-06    4.21E-06    4.20E-06    4.20E-06    4.19E-06
           O2                1.06E-06    1.06E-06    1.06E-06    1.06E-06    1.05E-06    1.05E-06
           H2O               1.01E-11    4.15E-11    1.23E-10    3.25E-10    7.98E-10    1.79E-09
           H                 2.01E-14    5.42E-14    1.39E-13    3.40E-13    7.67E-13    1.50E-12
           O                 9.95E-15    2.68E-14    6.88E-14    1.69E-13    3.81E-13    7.43E-13
           OH                4.91E-16    1.31E-15    3.33E-15    8.15E-15    1.84E-14    3.60E-14
           HO2               2.17E-13    5.87E-13    1.51E-12    3.70E-12    8.41E-12    1.67E-11
           BR                2.81E-17    3.20E-16    2.46E-15    1.60E-14    8.95E-14    3.93E-13
           HBR               1.00E-11    4.21E-11    1.26E-10    3.35E-10    8.25E-10    1.85E-09
           CF3BR             4.24E-07    4.24E-07    4.24E-07    4.23E-07    4.23E-07    4.22E-07
           CF3               9.86E-12    4.08E-11    1.21E-10    3.20E-10    7.82E-10    1.73E-09
           CF3H              1.73E-13    1.29E-12    4.98E-12    1.54E-11    4.33E-11    1.15E-10
           H2O2              4.11E-12    1.75E-11    5.26E-11    1.40E-10    3.46E-10    7.76E-10


   ELAPSED TIME (MSEC)        7.0000      8.0000      9.0000     10.0000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2                4.18E-06    4.17E-06    4.16E-06    4.14E-06
           O2                1.05E-06    1.05E-06    1.04E-06    1.04E-06
           H2O               3.52E-09    6.03E-09    9.13E-09    1.26E-08
           H                 2.41E-12    3.20E-12    3.77E-12    4.15E-12
           O                 1.19E-12    1.58E-12    1.86E-12    2.04E-12
           OH                5.78E-14    7.70E-14    9.08E-14    1.00E-13
           HO2               2.73E-11    3.72E-11    4.50E-11    5.11E-11
           BR                1.25E-12    2.86E-12    5.10E-12    7.78E-12
           HBR               3.64E-09    6.23E-09    9.42E-09    1.30E-08
           CF3BR             4.20E-07    4.17E-07    4.14E-07    4.10E-07
           CF3               3.36E-09    5.61E-09    8.24E-09    1.10E-08
           CF3H              2.82E-10    6.17E-10    1.18E-09    2.00E-09
           H2O2              1.54E-09    2.64E-09    4.00E-09    5.54E-09

         *   INDUCTION TIME (MAX OH CONC)
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MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                          INITIAL
                              SPECIES   CONCENTRATIONS
                                          (MOLES/CC)

                              H2          8.000E-02
                              O2          2.000E-02
                              ARGON       8.920E-01
                              CF3BR       8.000E-03

     REACTION TEMPERATURE     1300.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)           0.1000      0.2000      0.3000      0.4000      0.5000      0.6000

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                      3.75E-06    3.75E-06    3.75E-06    3.74E-06    3.73E-06    3.71E-06
      O2                      9.37E-07    9.37E-07    9.36E-07    9.34E-07    9.29E-07    9.22E-07
      H2O                     3.63E-11    2.52E-10    1.16E-09    4.35E-09    1.22E-08    2.37E-08
      H                       4.52E-13    2.15E-12    8.55E-12    2.71E-11    5.32E-11    6.36E-11
      O                       3.39E-13    1.61E-12    6.42E-12    2.02E-11    3.94E-11    4.60E-11
      OH                      1.92E-14    9.03E-14    3.60E-13    1.14E-12    2.26E-12    2.73E-12
      HO2                     6.85E-13    3.31E-12    1.34E-11    4.42E-11    9.57E-11    1.28E-10
      BR                      9.66E-16    3.32E-14    6.16E-13    7.41E-12    4.14E-11    9.73E-11
      HBR                     3.50E-11    2.46E-10    1.14E-09    4.26E-09    1.18E-08    2.26E-08
      CF3BR                   3.75E-07    3.75E-07    3.74E-07    3.71E-07    3.63E-07    3.52E-07
      CF3                     3.48E-11    2.44E-10    1.12E-09    4.18E-09    1.14E-08    2.13E-08
      CF3H                    1.66E-13    2.05E-12    1.36E-11    8.36E-11    4.38E-10    1.43E-09
      H2O2                    4.91E-12    3.60E-11    1.68E-10    6.37E-10    1.80E-09    3.54E-09

                                     •
ELAPSED TIME (MSEC)           0.6200      0.7000      0.8000

                              CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                      3.70E-06    3.69E-06    3.67E-06
      O2                      9.20E-07    9.14E-07    9.06E-07
      H2O                     2.61E-08    3.56E-08    4.68E-08
      H                       6.36E-11    6.10E-11    5.73E-11
      O                       4.58E-11    4.31E-11    3.96E-11
      OH                      2.74E-12    2.64E-12    2.50E-12
      HO2                     1.31E-10    1.36E-10    1.38E-10
      BR                      1.07E-10    1.40E-10    1.73E-10
      HBR                     2.49E-08    3.36E-08    4.37E-08
      CF3BR                   3.50E-07    3.41E-07    3.31E-07
      CF3                     2.33E-08    3.07E-08    3.87E-08
      CF3H                    1.71E-09    3.06E-09    5.12E-09
      H2O2                    3.91E-09    5.34E-09    7.02E-09

          •    INDUCTION TIME (MAX OH CONC)
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            MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                              INITIAL
                                 SPECIES   CONCENTRATIONS
                                            (MOLES/CC)

                                 H2         8.000E-02
                                 O2         2.000E-02
                                 ARGON      8.960E-01
                                 C2F4B2     4.000E-03

        REACTION TEMPERATURE   1150.0 (DEG. K.)        PRESSURE    5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)         1.0000      2.0000      3.0000      4.0000      5.0000      6.0000

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2               4.23E-06    4.22E-06    4.22E-06    4.21E-06    4.20E-06    4.19E-06
           O2               1.06E-06    1.06E-06    1.06E-06    1.06E-06    1.05E-06    1.05E-06
           H2O              9.10E-13    3.29E-12    9.51E-12    2.57E-11    6.78E-11    1.76E-10
           H                1.12E-15    3.68E-15    1.04E-14    2.77E-14    7.25E-14    1.86E-13
           O                5.53E-16    1.82E-15    5.12E-15    1.37E-14    3.59E-14    9.22E-14
           OH               3.77E-17    9.88E-17    2.58E-16    6.73E-16    1.75E-15    4.46E-15
           HO2              1.20E-14    3.98E-14    1.12E-13    3.01E-13    7.89E-13    2.03E-12
           BR               1.64E-14    5.96E-14    1.73E-13    4.67E-13    1.23E-12    3.20E-12
           HBR              3.17E-12    1.70E-11    5.87E-11    1.73E-10    4.75E-10    1.26E-09
           C2F4BR           8.80E-13    3.19E-12    9.20E-12    2.49E-11    6.53E-11    1.68E-10
           C2F4B2           2.12E-07    2.12E-07    2.12E-07    2.12E-07    2.12E-07    2.11E-07
           C2F4             1.16E-12    6.94E-12    2.48E-11    7.43E-11    2.05E-10    5.46E-10
           H2O2             2.10E-13    1.06E-12    3.58E-12    1.05E-11    2.86E-11    7.54E-11

ELAPSED TIME (MSEC)         7.0000      8.0000      9.0000     10.0000     11.0000     11.4000*

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

           H2               4.19E-06    4.18E-06    4.17E-06    4.15E-06    4.13E-06    4.12E-06
           O2               1.05E-06    1.05E-06    1.05E-06    1.05E-06    1.04E-06    1.04E-06
           H2O              4.47E-10    1.09E-09    2.44E-09    4.72E-09    7.69E-09    8.96E-09
           H                4.60E-13    1.05E-12    2.04E-12    3.06E-12    3.55E-12    3.59E-12
           O                2.28E-13    5.22E-13    1.01E-12    1.52E-12    1.76E-12    1.78E-12
           OH               1.10E-14    2.52E-14    4.90E-14    7.37E-14    8.59E-14    8.69E-14
           HO2              5.04E-12    1.16E-11    2.29E-11    3.54E-11    4.24E-11    4.34E-11
           BR               8.10E-12    1.94E-11    4.11E-11    6.94E-11    9.09E-11    9.58E-11
           HBR              3.23E-09    7.90E-09    1.77E-08    3.40E-08    5.46E-08    6.32E-08
           C2F4BR           4.19E-10    9.78E-10    2.00E-09    3.34E-09    4.55E-09    4.93E-09
           C2F4B2           2.10E-07    2.07E-07    2.02E-07    1.93E-07    1.82E-07    1.78E-07
           C2F4             1.41E-09    3.47E-09    7.85E-09    1.54E-08    2.51E-08    2.92E-08
           H2O2             1.93E-10    4.74E-10    1.06E-09    2.07E-09    3.38E-09    3.94E-09

      *   INDUCTION TIME (MAX OH CONC)
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                MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                            INITIAL
                                 SPECIES   CONCENTRATIONS
                                             (MOLES/CC)

                                  H2          8.000E-02
                                  O2          2.000E-02
                                  ARGON       8.960E-01
                                  C2F4B2      4.000E-03

          REACTION TEMPERATURE     1225.0 (DEG. K.)       PRESSURE    5.00 (ATMOSPHERES)
                                                                                            *
ELAPSED TIME (MSEC)          0.5000      1.0000      1.5000      2.0000      2.5000      2.8500

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    3.97E-06    3.97E-06    3.96E-06    3.95E-06    3.92E-06    3.89E-06
      O2                    9.94E-07    9.93E-07    9.93E-07    9.91E-07    9.86E-07    9.81E-07
      H2O                   4.53E-12    3.65E-11    2.58E-10    1.65E-09    7.10E-09    1.32E-08
      H                     1.36E-14    1.06E-13    7.36E-13    4.23E-12    1.19E-11    1.36E-11
      O                     8.45E-15    6.57E-14    4.56E-13    2.62E-12    7.34E-12    8.40E-12
      OH                    4.98E-16    3.47E-15    2.38E-14    1.37E-13    3.88E-13    4.49E-13
      HO2                   5.30E-14    4.14E-13    2.88E-12    1.69E-11    5.11E-11    6.29E-11
      BR                    1.91E-13    1.55E-12    1.10E-11    6.81E-11    2.34E-10    3.10E-10
      HBR                   2.16E-11    2.25E-10    1.69E-09    1.09E-08    4.60E-08    8.32E-08
      C2F4BR                4.26E-12    3.47E-11    2.39E-10    1.40E-09    4.42E-09    6.11E-09
      C2F4B2                1.99E-07    1.99E-07    1.98E-07    1.93E-07    1.74E-07    1.54E-07
      C2F4                  8.79E-12    9.64E-11    7.31E-10    4.78E-09    2.09E-08    3.87E-08
      H2O2                  8.31E-13    8.42E-12    6.28E-11    4.06E-10    1.77E-09    3.32E-09


ELAPSED TIME (MSEC)          3.0000

                                  CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

      H2                    3.88E-06
      O2                    9.79E-07
      H2O                   1.60E-08
      H                     1.34E-11
      O                     8.24E-12
      OH                    4.43E-13
      HO2                   6.35E-11
      BR                    3.20E-10
      HBR                   9.86E-08
      C2F4BR                6.53E-09
      C2F4B2                1.46E-07
      C2F4                  4.62E-08
      H2O2                  4.01E-09

         *   INDUCTION TIME (MAX OH CONC)
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                    MONSANTO RESEARCH CORPORATION - SHOCK TUBE INDUCTION TIME CALCULATIONS

                                              INITIAL
                                   SPECIES  CONCENTRATIONS
                                              (MOLES/CC)

                                   H2         8.000E-02
                                   O2         2.000E-02
                                   ARGON      8.960E-01
                                   C2F4B2     4.000E-03

                  REACTION TEMPERATURE    1300.0 (DEG. K.)        PRESSURE     5.00 (ATMOSPHERES)

ELAPSED TIME (MSEC)          0.1000      C.2000      0.3000      0.4000      0.5000      0.6000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  3.75E-06    3.75E-06    3.75E-06    3.75E-06    3.74E-06    3.74E-06
        O2                  9.37E-07    9.37E-07    9.37E-07    9.37E-07    9.37E-07    9.35E-07
        H2O                 2.66E-12    1.27E-11    5.09E-11    1.94E-10    7.17E-10    2.46E-09
        H                   2.CCE-14    8.96E-14    3.52E-13    1.33E-12    4.76E-12    1.49E-11
        O                   1.50E-14    6.74E-14    2.65E-13    9.98E-13    3.58E-12    1.12E-11
        OH                  1.C5E-15    3.97E-15    1.50E-14    5.59E-14    2.00E-13    6.03E-13
        HO2                 3.06E-14    1.39E-13    5.47E-13    2.07E-12    7.48E-12    2.40E-11
        BR                  2.28E-13    1.10E-12    4.41E-12    1.68E-11    6.18E-11    2.07E-10
        HBR                 9.38E-12    6.35E-11    2.87E-10    1.14E-09    4.28E-09    1.47E-08
        C2F4BR              2.37E-12    1.14E-11    4.52E-11    1.71E-10    6.13E-10    1.91E-C9
        C2F4B2              1.87E-07    1.87E-C7    1.87E-07    1.87E-07    1.85E-C7    1.79E-07
        C2F4                3.62E-12    2.66E-11    1.23E-10    4.94E-10    1.86E-09    6.50E-09
        H2O2                2.40E-13    1.57E-12    7.04E-12    2.79E-11    1.05E-10    3.63E-10

                                                      *
ELAPSED TIME (MSEC)          0.7000      0.8CC0      0.8700      0.9000      1.0000

                                   CONCENTRATION IN (MOLES/CC) AT SPECIFIED TIME INTERVALS

        H2                  3.72E-06    3.68E-06    3.66E-06    3.65E-06    3.62E-06
        O2                  9.32E-07    9.27E-07    9.23E-07    9.21E-07    9.16E-07
        H2O                 6.93E-09    1.47E-C8    2.09E-08    2.36E-08    3.21E-08
        H                   3.26E-11    4.51E-11    4.65E-11    4.60E-11    4.20E-11
        O                   2.45E-11    3.36E-11    3.43E-11    3.39E-11    3.11E-11
        OH                  1.39E-12    1.95E-12    2.02E-12    2.01E-12    2.51E-12
        HO2                 5.61E-11    8.54E-11    9.38E-11    9.52E-11    9.53E-11
        BR                  5.17E-10    8.17E-10    9.C2E-10    9.14E-10    9.02E-10
        HBR                 4.07E-08    8.29E-08    1.13E-07    1.25E-07    1.61E-07
        C2F4BR              4.30E-09    6.55E-09    7.42E-09    7.65E-09    8.06E-09
        C2F4B2              1.65E-07    1.42E-C7    1.27E-07    1.20E-07    1.03E-07
        C2F4                1.85E-08    3.86E-C8    5.34E-08    5.93E-08    7.68E-08
        H2O2                1.C3E-09    2.21E-09    3.16E-09    3.56E-09    4.86E-09

     *   INDUCTION TIME (MAX OH CONC)
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