AFAPL-TR-65-93

SHOCK TUBE STUDIES OF FUEL-AIR IGNITION CHARACTERISTICS

A. D. SNYDER
J. ROBERTSON
D. L. ZANDERS
G. B. SKINNER

MONSANTO RESEARCH CORPORATION
DAYTON, OHIO

TECHNICAL REPORT AFAPL-TR-65-93

AUGUST, 1965

AIR FORCE AERO PROPULSION LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

NOTICES

Defense Documentation Center release to the Clearinghouse for Federal Scientific and Technical Information (formerly OTS) is not authorized because it contains information of possible application to future weapon systems and consequently is not considered of general interest to the public.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

FOREWORD

This report was prepared by Monsanto Research Corporation, Dayton, Ohio, on Air Force Contract Nrs. AF 33(657)-8193 and AF 33(615)-1317, "Evaluation of Fuels and Lubricants," under Project 3048, Task 304801. This study, Task 9, concerned the shock tube investigation of the ignition characteristics of the hydrogen-air fuel system. A later, extended program of research included the effect of additives on the ignition induction times of hydrogen-air mixtures and the characteristics of hydrocarbon-air ignitions.

The research was sponsored by the Aero Propulsion Laboratory, Fuels and Lubricants Branch, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Messrs. J. R. Fultz and C. J. Johnson as project engineers. Technical monitors were F. D. Stull, and R. R. Craig, Ramjet Component Branch, Ramjet Engine Division of the Air Force Aero Propulsion Laboratory.

The work was performed during the period 1 April 1964 to 26 July 1965 at the Dayton Laboratory of Monsanto Research Corporation. Mr. J. C. Harris was project leader. Dr. G. B. Skinner, the principal investigator, was succeeded by Dr. A. D. Snyder. J. L. Robertson and D. L. Zanders conducted the experimental measurements. The assistance of R. G. Olt and J. R. Moon is gratefully acknowledged. The computational aid by J. E. Sutherland and A. D. Dickinson is also appreciated.

This technical report was submitted by the authors August 1965 and has been reviewed and is approved.

Arthur V. Churchill

ARTHUR V. CHURCHILL, Chief
Fuels, Lubrication and Hazards Branch
Support Technology Division
AF Aero Propulsion Laboratory

ABSTRACT

Ignition induction times of hydrogen-air mixtures were measured after the reflected wave in a single-pulse shock tube as a function of mixture ratio, absolute pressure and temperature. The data have been correlated by a nonlinear regression program resulting in an equation for induction time as a function of these variables. The results support earlier work at this laboratory on argon-diluted hydrogen-oxygen experiments in that at temperatures below 1100°K the ignition delays became very long because of self-inhibition of the reaction through HO_2 formation. The effects of added water vapor and nitric oxide on the ignition characteristics of hydrogen-air mixtures were studied. Both additives resulted in sensitization of the ignition reaction. A detailed investigation of the nitric oxide catalysis indicated that the maximum effect occurred at 0.5 mole percent of additive, where the ignition delay was decreased by a factor of 100 and the ignition temperature by 200°K. Nitrogen dioxide was found to be equally effective, but ammonia exhibited no sensitizing action. The ignition induction times of 0.5 and 1.0 equivalence ratio mixtures of methane-, butane-, and octane-air mixtures were determined from 0.2 to 10 milliseconds at a reflected shock pressure of 60 psia. The data are presented both in tabular and graphical form. All ignition delay data are discussed in light of related studies and potential kinetic mechanisms. Recommendations for future work are presented.

TABLE OF CONTENTS

ILLUSTRATIONS

TABLES

I. SUMMARY

The primary purpose of this work was to furnish ignition induction times for undiluted hydrogen-air mixtures in the low-temperature region as design criteria for future ramjet development. The ignition delay data were determined under the following conditions: equivalence ratios of hydrogen-air mixtures of 0.50, 0.75, and 1.00; pressures of 15, 30, 60, 100 and 130 psia; temperatures from 800-1100°K. The ignition delays were measured from 0.2 to 10 milliseconds. Correlation of the experimental data by quantitative chemical kinetic calculations was beyond the scope of this program. However, the data were examined by employing a nonlinear regression program and found to fit the following equation:

$$\tau = \frac{2.32 \times 10^{-7}\, e^{15,950/T}}{p^{(0.4)}\ \emptyset}\ , \text{ for temperature range } 800\text{-}1100°\text{K}$$

where τ is the induction time in milliseconds, T is the Kelvin temperature, p is the pressure in psia and $\emptyset$ is the equivalence ratio. This equation applies only to hydrogen-air mixtures with fuel concentrations which are less than stoichiometric, and should not be employed for hydrogen-rich mixtures.

An extension of the original program included research to identify the effects on the ignition reaction of contaminants that may be found in different types of combustion facilities. This study included the investigation of the effects of both water vapor and nitric oxide on the ignition characteristics of the hydrogen-air mixtures. While both additives sensitized the reaction, it was found that certain concentrations of nitric oxide in the hydrogen-air mixtures significantly catalyzed the reaction, resulting in a dramatic reduction in ignition induction times. With 0.5 mole percent added nitric oxide, the resultant decrease in induction time is two orders of magnitude or a factor of 100. At constant induction time this is equivalent to a decrease in ignition temperature of 200°C. Similar behavior was observed on addition of nitrogen dioxide, while ammonia was found to be ineffective. The kinetic mechanism of this reaction is not fully understood. At low temperature the formation of the stable HO_2 species represents a slow chain-breaking reaction in that the chain carrier,

hydrogen atom, is removed according to:

$$(1)\ H + O_2 + M \rightarrow HO_2 + M$$

It is felt that the addition of nitric oxide interferes with this chain-breaking step by rapidly reacting with the HO_2 and regenerating a chain carrier by either of two reactions:

$$(2)\ HO_2 + NO \rightarrow OH + NO_2, \text{ or}$$

$$(3)\ HO_2 + NO \rightarrow HNO_2 + O$$

In ramjet applications involving low flight speed regimes and the resulting low inlet temperatures, the chemical kinetic ignition delay times are of such magnitude that the combustion process becomes reaction rate limited rather than mixing limited. The addition of small quantities of nitric oxide or nitrogen dioxide to a hydrogen fueled ramjet could permit flights at a somewhat lower Mach number.

Finally, a preliminary examination was conducted of the ignition characteristics of hydrocarbon gases in air. Ignition delay data were determined for methane, butane and octane at equivalence ratios in air of 0.50 and 1.00 and at a pressure of 50 psia. The ignition induction times increased in the order octane < butane < methane. The effect of a change in mixture ratio on the ignition characteristics was very minor, indicating that this may not be a significant variable in the case of hydrocarbons. The data are compared with published results of related studies.

II. INTRODUCTION

The initial objective of this research was to measure the ignition induction times of several hydrogen-air mixtures after the reflected wave in a single-pulse shock tube under known pressure conditions from 15 to 130 psia and temperatures from 800 to 1100°K.

At higher temperatures, 1100-2600°K, Schott and Kinsey (Ref. 1) had shown that the product of the induction time and the initial oxygen concentration was linear when plotted against reciprocal absolute temperature. Later research at Monsanto Research Corporation (Ref. 2, 3) indicated that in hydrogen-oxygen mixtures diluted by argon, the ignition induction times became very long at temperatures below 1100°K. This is attributed to self-inhibition of the reaction by formation of the species HO_2, which results in the breaking of the chain.

The measurements undertaken in this work were carried out in the low-temperature region with undiluted hydrogen-air mixtures to furnish design criteria for future ramjet development. An extension of the original program included research to identify the effects of contaminants that may be found in different types of facilities on the ignition reaction of hydrogen-air mixtures in the low-temperature regime, and a preliminary investigation of the ignition characteristics of gaseous hydrocarbon-air mixtures.

III. APPARATUS

The shock tube (Fig. 1a) employed for this study is of the single-pulse type first described by Glick, Squire and Hertzberg (Ref. 4). The reaction and driver sections are made from 3-in. stainless steel pipe, the former being 12 ft. long and the latter between 6 and 28 ft. The expansion tank is 3 ft. in diameter and 8 ft. long. Thin plastic diaphragms separate the sections, while "O" ring seals are used throughout, so the sections can be individually evacuated or pressurized.

For measuring the shock speed, SLM pressure transducers spaced 4 ft. apart near the downstream end of the reaction section are used. Two identical trigger circuits amplify the transducer signals, while thyratron elements with manual reset assure that only one signal emits from each amplifier in an experiment. The amplifier signals are used to start and stop a timer accurate to one microsecond and also to start two oscilloscopes. One of these (Fig. 1b) is used to trace a pressure record of the reaction. The other (Fig. 1c) measures the output from a photomultiplier tube mounted 3 inches from the end of the reaction section in front of a quartz window. The oscilloscope traces were recorded by polaroid camera.

Gas mixtures to be studied were made up beforehand by pressure. Burdette breathing air and AIRCO hydrogen were used without further purification. Nitric oxide (Matheson Co., research grade) was used for the NO additions and ordinary tap water was used to study the water vapor effect. Hydrocarbon gases were Matheson research grade.

In a typical run, all sections of the shock tube were first evacuated, and the sample and driver gases were added. Since the "tailored-interface" technique (Ref. 3) 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 diaphragm was ruptured manually by the plunger (h). The second diaphragm, the expansion tank, the auxiliary shock tube (i) and the sampling valve (e) were not required for these studies.

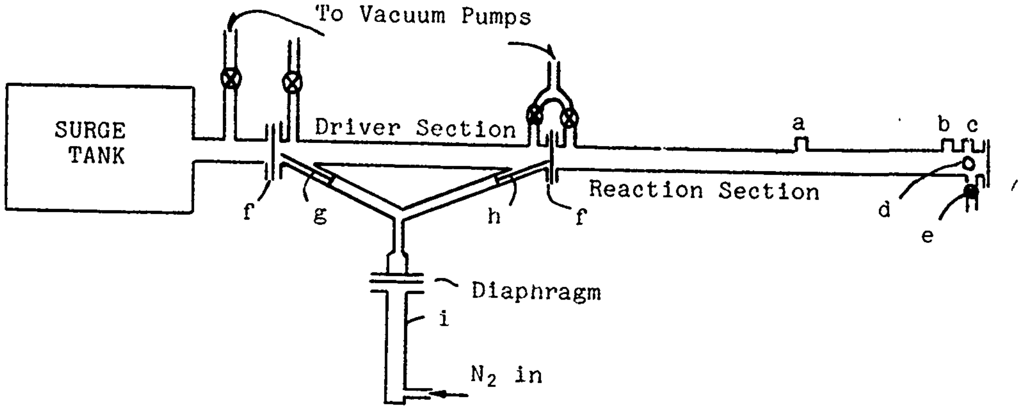

Fig. 1a
Schematic Drawing of Shock Tube

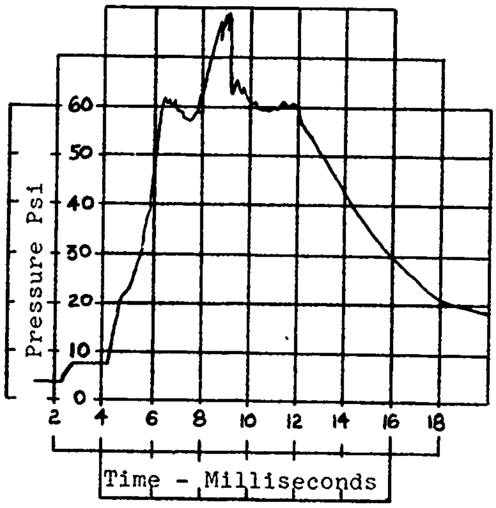

Fig. 1b

Typical Pressure Record

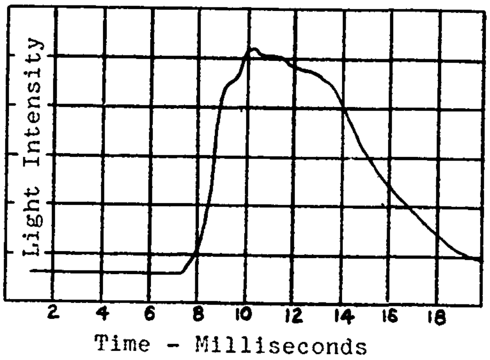

Fig. 1c

Typical Photomultiplier Record

IV. SHOCK TUBE CALCULATIONS

For each experiment the shock speed, pressure record and photo-cell record were obtained. This information was then reduced with the aid of data from Monsanto Research Corporation's Shock Tube Initial Calculation (STIC) computer program, which calculates the temperature and pressure behind the reflected shock wave, using the known thermal functions of the mixture components. This program assumes that the gases behave ideally and that no chemical reaction occurs ahead of the reflected shock wave. It was assumed that the reaction temperature and pressure were actually realized immediately behind the reflected shock wave and that subsequent pressure changes caused changes in temperature given by the isentropic equation:

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

This is reasonable since small changes 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.

The data were processed via a polynomial curve fitting computer program (PØLYFIT) by a standard least squares method. The transformation used was the log of induction times versus temperature.

V. HYDROGEN-AIR IGNITION CHARACTERISTICS

A. Experimental Results

Ignition induction times were measured for hydrogen-air mixtures with equivalence ratios of 0.50, 0.75 and 1.00 at pressures of 15, 30, 60, 100 and 130 psia in the temperature range 800-1100°K. Calculations relating shock speed with the temperature and pressure generated after the incident and reflected shock waves were performed by using an existing computer program which was run on the IBM 7094 computer at Wright-Patterson Air Force Base.

The temperature range over which induction times were measured was determined by the characteristics of the shock tube. Induction times shorter than 0.1 msec and longer than 12 msec could not be determined accurately. Ignition was signaled by a sharp rise in ultraviolet emission from the reacting gas, and by a nearly simultaneous rise in pressure. The pressure rose to no more than double its original value in most cases.

Results of the hydrogen-air investigation are shown in Figures 2-4, in which the ln τ is plotted versus the reciprocal of absolute temperature. To minimize confusion only the least squares lines are plotted. All experimental points are presented in Tables 1-3.

B. Conclusions

The experimental scatter in the data, especially for the stoichiometric mixture at higher pressures, was observed to be much greater than that usually experienced in argon-diluted mixtures and in the 0.5 equivalence ratio results. This was caused by the occurrence of detonations rather than normal combustion, and was evidenced by an extreme "sawtoothed" variation in the pressure record after ignition.

Despite this scatter in experimental data, they were submitted for mathematical correlation on the IBM 7040 computer at the Central Research Department of Monsanto Company at St. Louis, Missouri. Both linear and nonlinear regression analyses were run assuming an equation of the form:

$$\tau = \frac{A\, e^{\beta/T}}{p^{\alpha}\ \phi}$$

TABLE 1

SHOCK TUBE INDUCTION TIMES FOR H_2-AIR
EQUIVALENCE RATIO - 0.50

Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
15	0.55	1711	950.6	1.0520
15	0.60	1698	943.3	1.0601
15	2.2	1660	922.2	1.0844
15	2.9	1646	914.4	1.0936
15	1.9	1641	911.7	1.0969
15	5.8	1639	910.6	1.0982
15	8.2	1619	899.4	1.1119
15	8.6	1600	888.9	1.1250
30	0.10	1885	1047.2	0.9549
30	0.14	1858	1032.2	0.9688
30	0.20	1845	1025.0	0.9756
30	0.40	1825	1013.9	0.9863
30	0.85	1783	990.6	1.0095
30	0.88	1781	989.4	1.0107
30	1.1	1770	983.3	1.0170
30	1.3	1759	977.2	1.0233
30	4.6	1719	955.0	1.0471
30	5.7	1699	943.9	1.0594
30	11.6	1660	922.2	1.0844
60	0.24	1859	1033.0	0.9681
60	0.52	1798	998.9	1.0011
60	0.76	1798	998.9	1.0011
60	6.8	1774	985.6	1.0146
60	1.8	1749	971.7	1.0291
60	1.4	1741	967.2	1.0339
60	2.9	1738	965.6	1.0356
60	1.9	1733	962.8	1.0386
60	7.6	1714	952.2	1.502
60	4.4	1709	949.5	1.0532
60	7.0	1689	938.3	1.0668
60	5.6	1654	918.9	1.0883
100	0.26	1932	1073.3	0.9320
100	0.52	1892	1051.1	0.9514
100	0.80	1841	1022.8	0.9777
100	1.30	1791	995.0	1.005
100	1.85	1748	971.1	1.0298
100	8.4	1569	871.7	1.1472
100	8.2	1568	871.1	1.148
100	11.4	1545	858.3	1.1651
130	0.26	1734	963.3	1.0381
130	0.60	1709	949.4	1.0533
130	0.96	1693	940.6	1.0632
130	1.2	1652	917.8	1.0896
130	0.60	1651	917.2	1.0903
130	0.90	1638	910.0	1.0989
130	1.8	1623	901.7	1.1090
130	1.4	1616	897.8	1.1138
130	2.4	1546	858.9	1.1643
130	5.8	1545	858.3	1.1651
130	2.2	1543	857.2	1.1666
130	10.6	1506	836.7	1.1952
130	7.6	1495	830.6	1.2039

TABLE 2

SHOCK TUBE INDUCTION TIMES FOR H_2-AIR
EQUIVALENCE RATIO - 0.75

Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
15	0.66	1745	969.4	1.0316	60	0.65	1770	983.3	1.0170
15	0.42	1730	961.1	1.0405	60	0.80	1732	962.2	1.0393
15	0.70	1727	959.4	1.0423	60	1.6	1728	960.0	1.0417
15	1.16	1703	946.1	1.0570	60	1.4	1707	948.3	1.0545
15	1.18	1700	944.4	1.0589	60	1.4	1696	942.2	1.0613
15	11.8	1683	935.0	1.0695	60	3.0	1663	923.9	1.0824
15	2.3	1677	931.7	1.0733	60	2.6	1654	918.9	1.0883
15	7.2	1675	930.6	1.0746	60	4.2	1641	911.7	1.0969
15	7.4	1664	924.4	1.0818	60	10.4	1615	897.2	1.1146
15	3.0	1652	917.8	1.0896	60	9.8	1610	894.4	1.1181
15	2.0	1640	911.1	1.0976	60	4.0	1584	880.0	1.1364
30	0.60	1787	992.8	1.0073	100	0.37	1754	974.4	1.0263
30	1.4	1734	963.3	1.0381	100	0.97	1723	957.2	1.0447
30	1.4	1727	959.4	1.0423	100	1.38	1712	951.1	1.0514
30	1.3	1709	949.4	1.0533	100	2.5	1664	924.4	1.0818
30	3.5	1701	945.0	1.0582	100	4.0	1625	902.8	1.1077
30	1.9	1685	936.1	1.0683	100	1.3	1602	890.0	1.1236
30	4.6	1682	934.4	1.0702	100	1.7	1585	880.6	1.1356
30	6.4	1659	921.7	1.0850	100	2.1	1564	868.9	1.1509
30	14.2	1652	917.8	1.0896	100	8.0	1539	855.0	1.1696
30	6.2	1650	916.7	1.0909	100	11.4	1520	844.4	1.1843
30	2.0	1643	912.8	1.0955					
30	11.4	1530	850.0	1.1765					
60	0.32	1823	1012.8	0.9874					

TABLE 3

SHOCK TUBE INDUCTION TIMES FOR H_2- AIR
EQUIVALENCE RATIO 1.0

Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
15	0.38	1741	967.2	1.0339
15	0.52	1715	952.8	1.0495
15	0.60	1703	946.1	1.0570
15	0.50	1693	940.6	1.0632
15	1.75	1679	932.8	1.0720
15	10.4	1664	924.4	1.0818
15	7.0	1664	924.4	1.0818
15	3.60	1659	921.7	1.0850
15	1.70	1653	918.3	1.0890
15	6.0	1652	917.8	1.0896
15	6.2	1643	912.8	1.0955
30	0.55	1766	981.1	1.0193
30	1.0	1751	972.8	1.0280
30	1.35	1736	964.4	1.0369
30	1.6	1726	958.9	1.0429
30	1.9	1717	953.9	1.0483
30	2.4	1707	948.3	1.0545
30	1.8	1687	937.2	1.0670
30	1.8	1678	932.2	1.0727
30	2.4	1668	926.7	1.0791
30	1.4	1655	919.4	1.0877
30	2.0	1639	910.6	1.0982
30	14.6	1596	886.7	1.1278
30	11.0	1542	856.7	1.1673
60	1.25	1756	975.6	1.0250
60	1.45	1752	973.3	1.0274
60	0.35	1750	972.2	1.0286
60	0.65	1749	971.7	1.0291
60	1.90	1736	964.4	1.0369
60	1.35	1710	950.0	1.0526
60	1.25	1692	940.0	1.0638
60	6.2	1690	938.9	1.0651
60	3.25	1687	937.2	1.0670
60	7.2	1665	925.0	1.0811
60	8.4	1662	923.3	1.0831
60	1.4	1646	914.4	1.0936
100	1.05	1696	942.2	1.0613
100	1.05	1693	940.6	1.0632
100	1.05	1678	932.2	1.0727
100	1.2	1663	923.9	1.0824
100	3.0	1637	909.4	1.0996
100	9.2	1636	908.9	1.1002
100	0.60	1622	901.1	1.1098
100	0.40	1611	895.0	1.1173
100	1.0	1594	885.6	1.1292
100	5.0	1583	882.2	1.1335
130	1.2	1678	932.2	1.0727
130	0.80	1651	917.2	1.0903
130	0.48	1649	916.1	1.0916
130	0.30	1635	908.3	1.1010
130	1.4	1606	892.2	1.1208
130	1.4	1596	886.7	1.1278
130	1.65	1566	870.0	1.1494
130	2.0	1562	867.8	1.1523
130	6.6	1519	843.9	1.1850
130	8.4	1499	832.8	1.2008
130	8.6	1487	826.1	1.2105
130	11.4	1454	807.8	1.2379

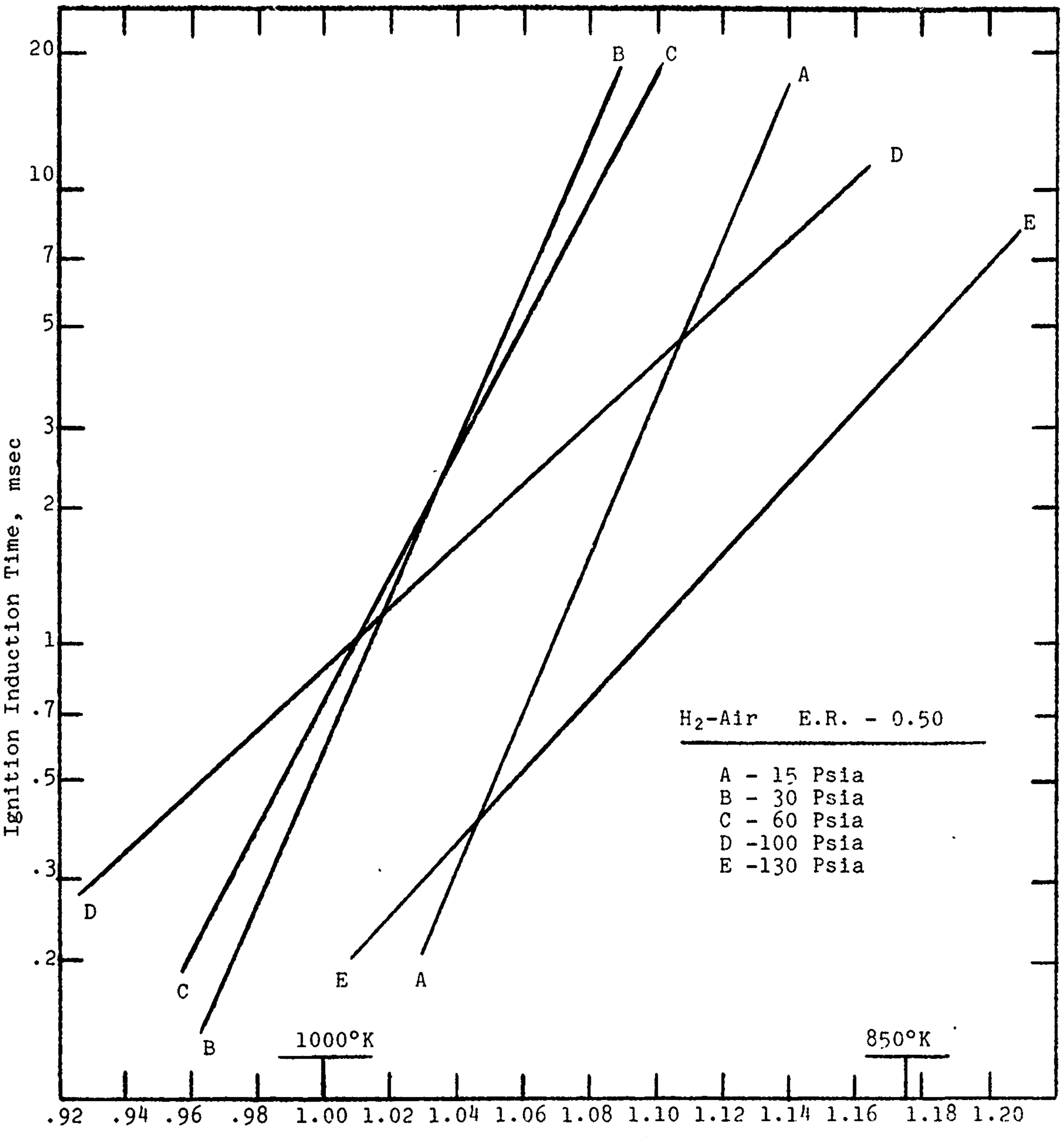

Figure 2. Ignition Characteristics of 0.50 Equivalence Ratio Hydrogen-Air Mixtures

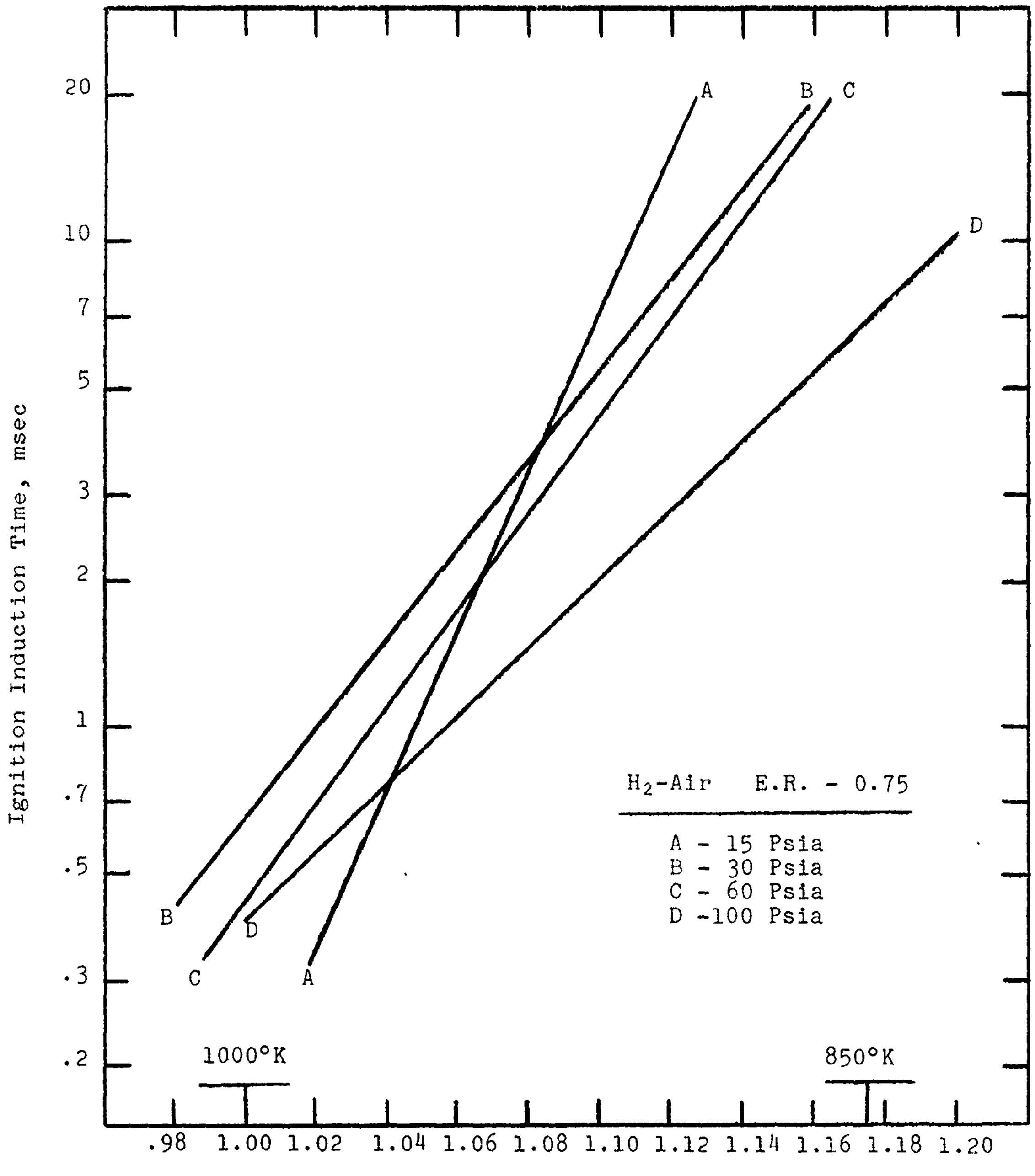

Figure 3. Ignition Characteristics of 0.75 Equivalence Ratio Hydrogen-Air Mixtures

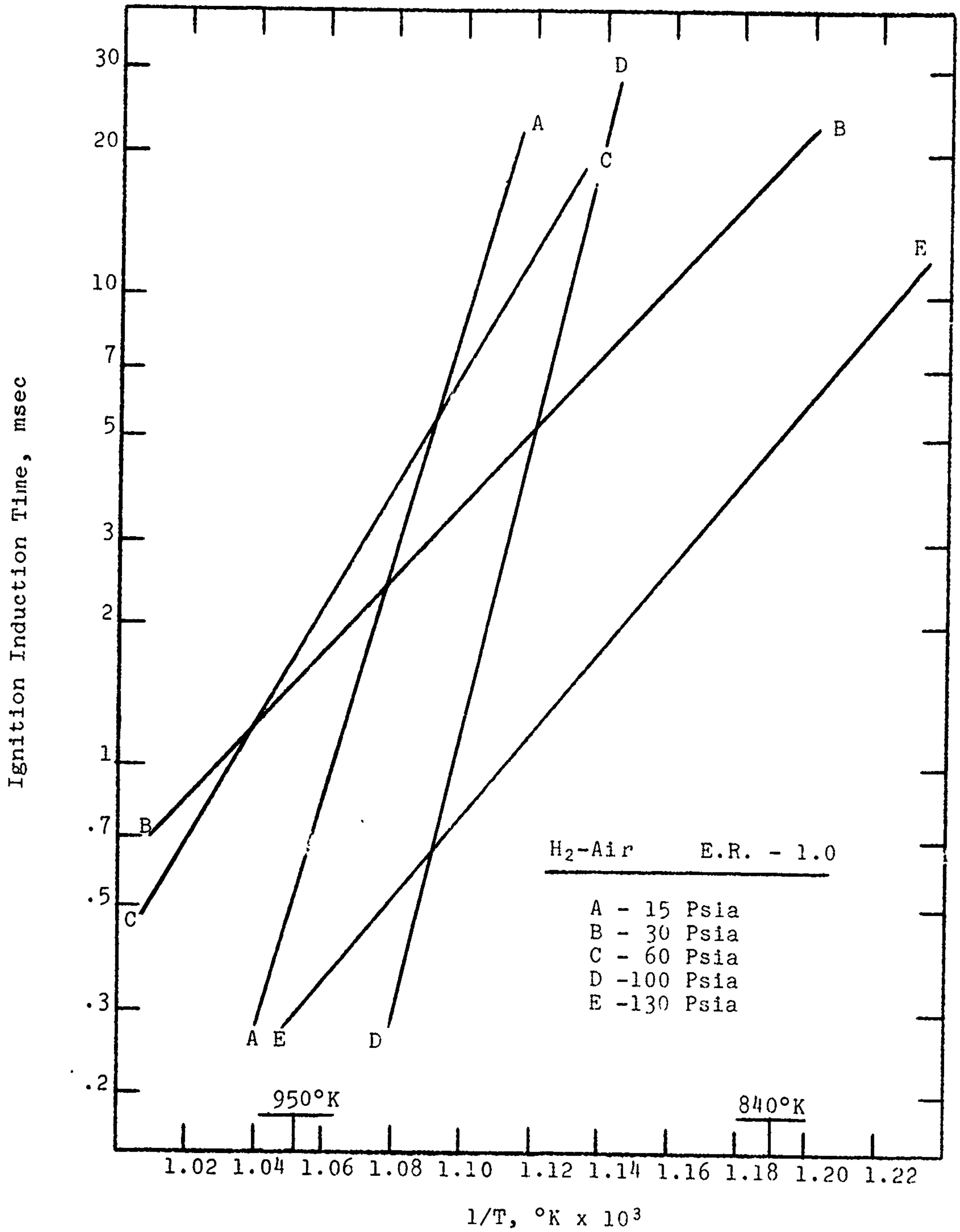

Figure 4. Ignition Characteristics of 1.0 Equivalence Ratio Hydrogen-Air Mixtures

where τ is the induction time in milliseconds

T is the temperature in Kelvin degrees

p is the pressure in psia

ϕ is the equivalence ratio $= \frac{\text{(Fuel/Air) actual}}{\text{(Fuel/Air) stoichiometric}}$

and A, β and α are regression coefficients.

The form of the equation was selected on the basis of experience in the variation of induction time with each of the variables separately, and while it is not general it does contain the dependent variables in a kinetically significant form. Considering the degree of scatter in the stoichiometric mixture data, the regression coefficients were determined with good precision. The following equation resulted:

$$\tau = \frac{2.32 \times 10^{-7}\, e^{15,950/T}}{p^{(0.4)}\, \phi}$$

The 95% confidence limits of the equation indicate that the computed value of τ may differ from a given experimental measurement by a factor of 4.

The inclusion of an additive such as nitric oxide in the hydrogen-air system appears to exhibit a distinct, stabilizing effect on the reaction even though it sensitizes the ignition.

C. Discussion

Our observations agree admirably with the recent study of Voevodsky and Soloukhin (Ref. 5). In this work the transition from the "mild" ignition to the detonation wave is related to the second explosion limit of the classical (Ref. 6), low-temperature and pressure, explosion bulb investigations (Fig. 5). This second limit results from a competition of branching reactions such as:

$$H + O_2 \rightarrow OH + O$$

$$O + H_2 \rightarrow OH + H$$

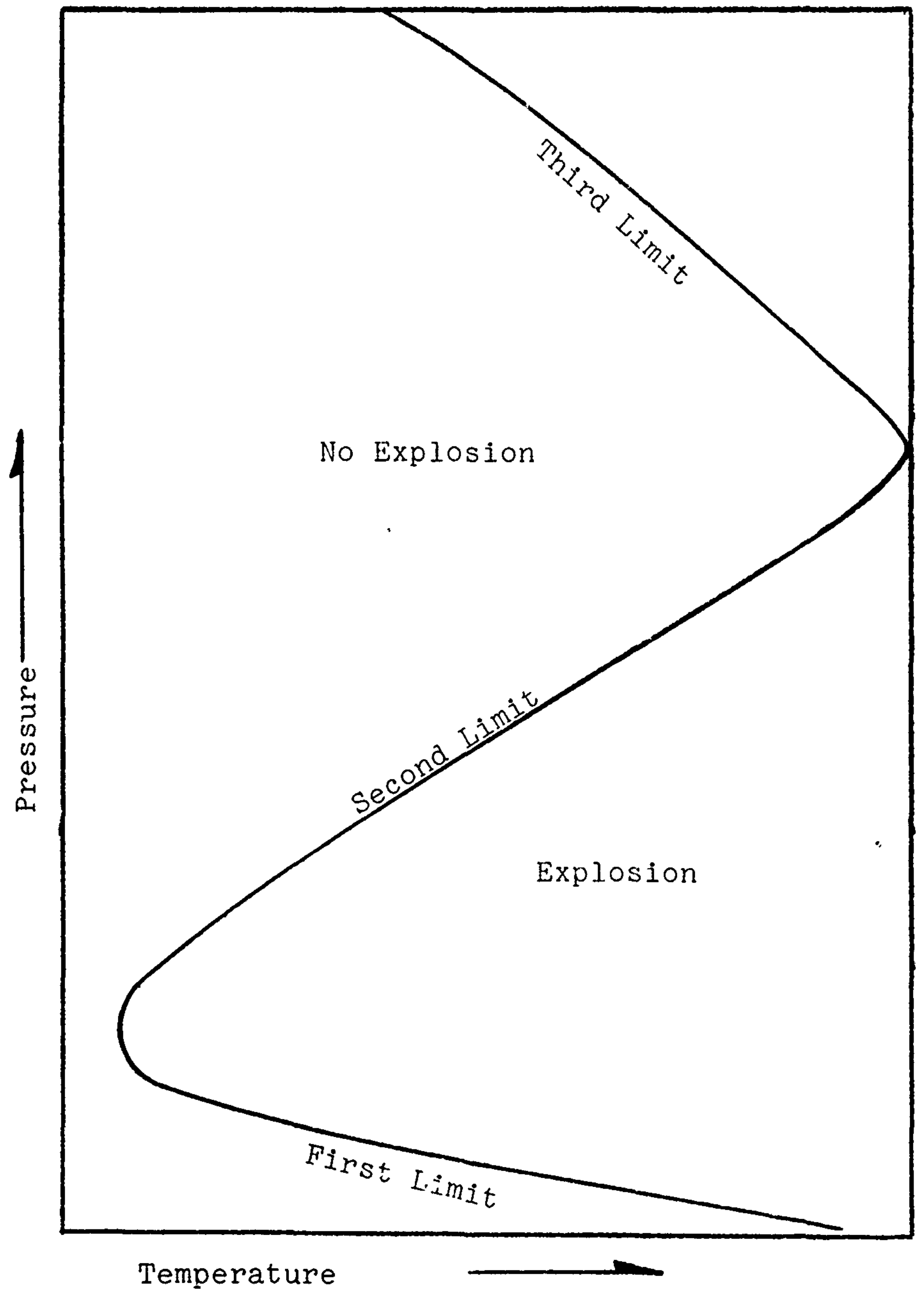

Figure 5. Classical Explosion Limit Curves for H_2-O_2 Mixtures

and the breaking reaction:

$$H + O_2 + M \rightarrow HO_2 + M$$

As the temperature is decreased at constant pressure, the second limit is crossed from an explosive to a non-explosive region. Extrapolated to the shock tube situation this is exemplified by changing from the detonation region, through a transition or intermediate region located near the P-T area of the second limit mixtures, and finally into an area of "normal" ignition.

While there exists a copious quantity of literature on the mechanism and kinetics of the hydrogen-oxygen ignition reaction, no directly related study could be found with which to compare the experimental data reported here.

VI. EFFECTS OF ADDITIVES ON HYDROGEN-AIR IGNITIONS

The first study requested after completion of the hydrogen-air ignition characteristic measurements was to determine the influence of potential contaminants on the previously determined ignition induction times. The contaminants selected would be encountered in an experimental ramjet engine facility where the source of hot combustion air would be either preburning (H_2O contaminant) or arc discharge (NO contaminant).

At the outset of this program it was recommended to the sponsor that an effort be made to sensitize the low-temperature ignition rates of hydrogen-air mixtures through the use of chemical additives. Two candidate accelerators suggested at that time were nitric oxide and nitrogen dioxide. This recommendation was based primarily on the chemical sensitizers which were found to be efficient in reducing the second explosion limit of hydrogen-oxygen in static-bulb experiments (Ref. 6) and on some earlier experience in sensitizing diborane-air explosions (Ref. 7).

A. Water Vapor Additions

Ignition induction times were measured for 0.5 and 1.0 equivalence ratio hydrogen-air mixtures containing 10, 15 and 20 mole percent of water vapor. All experiments were conducted at a reflected shock wave pressure of 30 psia. The data are summarized in Table 4 and the least squares plots are presented in Figure 6. The water vapor exhibited a slight sensitizing effect on the 0.5 equivalence ratio mixture over the entire temperature range studied. At constant ignition induction time, the ignition temperatures were reduced up to 60°K. The additive showed a similar effect on the stoichiometric mixture at high temperature, but the slope of the ignition curve was changed so that in the low temperature region a slight inhibiting effect resulted.

B. Nitric Oxide Experiments

The first experiments conducted employing nitric oxide additive were at the 8 mole percent level in the 0.5 and 1.0 equivalence ratio mixtures at a pressure of 30 psia. The sensitization on addition of the nitric oxide was marked in that the

TABLE 4

SHOCK TUBE INDUCTION TIMES FOR H_2-AIR + H_2O

Percent Additive	Equivalence Ratio	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
10	0.50	30	0.42	1720	955.6	1.0464
			1.6	1711	950.6	1.0519
			0.65	1707	948.3	1.0545
			2.1	1695	941.7	1.0619
			1.4	1689	938.3	1.0657
			0.90	1688	937.8	1.0663
			2.6	1685	936.1	1.0682
			5.4	1677	931.7	1.0733
			6.0	1672	928.9	1.0765
			6.8	1619	899.4	1.1118
10	1.0	30	0.24	1781	989.4	1.0107
			0.74	1727	959.4	1.0423
			0.90	1720	955.6	1.0464
			1.7	1717	953.9	1.0483
			2.1	1712	951.1	1.0514
			0.54	1711	950.6	1.0519
			4.8	1693	940.6	1.0631
			6.8	1681	933.9	1.0707
			0.70	1676	931.1	1.0739
			1.6	1661	922.8	1.0836
			4.4	1658	921.1	1.0856
			6.8	1631	906.1	1.1036
			10.8	1623	901.7	1.1090
15	0.50	30	0.24	1769	982.8	1.0175
			0.42	1753	973.9	1.0268
			0.58	1729	960.6	1.0410
			0.82	1716	953.3	1.0490
			0.80	1682	934.4	1.0702
			1.35	1663	923.9	1.0824
			1.8	1662	923.3	1.0831
			1.0	1638	910.0	1.0989
			7.2	1636	908.9	1.1002
			6.8	1607	892.8	1.1200
			6.0	1606	892.2	1.1208
			4.8	1587	881.7	1.1342
			9.0	1547	859.4	1.1636
			14.6	1510	838.9	1.1920
15	1.0	30	0.10	1850	1027.8	0.9730
			0.44	1788	993.3	1.0067
			0.52	1775	986.1	1.0141
			0.46	1750	972.2	1.0286
			0.60	1741	967.2	1.0339
			0.80	1725	958.3	1.0435
			1.6	1692	940.0	1.0638
			4.2	1691	939.4	1.0645
			4.0	1663	923.9	1.0824
			5.8	1630	905.6	1.1042
			5.0	1608	893.3	1.1194
			12.4	1602	890.0	1.1236
			8.0	1588	882.2	1.1335

TABLE 4 (cont'd)

Percent Additive	Equivalence Ratio	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
20	0.50	30	0.50	1748	971.1	1.0297
			0.50	1727	959.4	1.0423
			1.0	1722	956.7	1.0452
			0.32	1717	953.9	1.0483
			1.75	1678	932.2	1.0727
			1.2	1640	911.1	1.0975
			3.8	1639	910.6	1.0981
			2.2	1627	903.9	1.1063
			6.4	1615	897.2	1.1145
			11.6	1595	886.1	1.1285
			14.8	1518	843.3	1.1858
20	1.0	30	0.28	1792	995.6	1.0044
			0.36	1770	983.3	1.0169
			0.85	1754	974.4	1.0262
			1.2	1744	968.9	1.0320
			1.2	1739	966.1	1.0350
			1.6	1735	963.9	1.0374
			3.95	1713	951.7	1.0507
			2.6	1706	947.8	1.0550
			8.2	1696	942.2	1.0613
			11.0	1678	932.2	1.0727
			6.6	1671	928.3	1.0772
			7.0	1648	915.6	1.0921

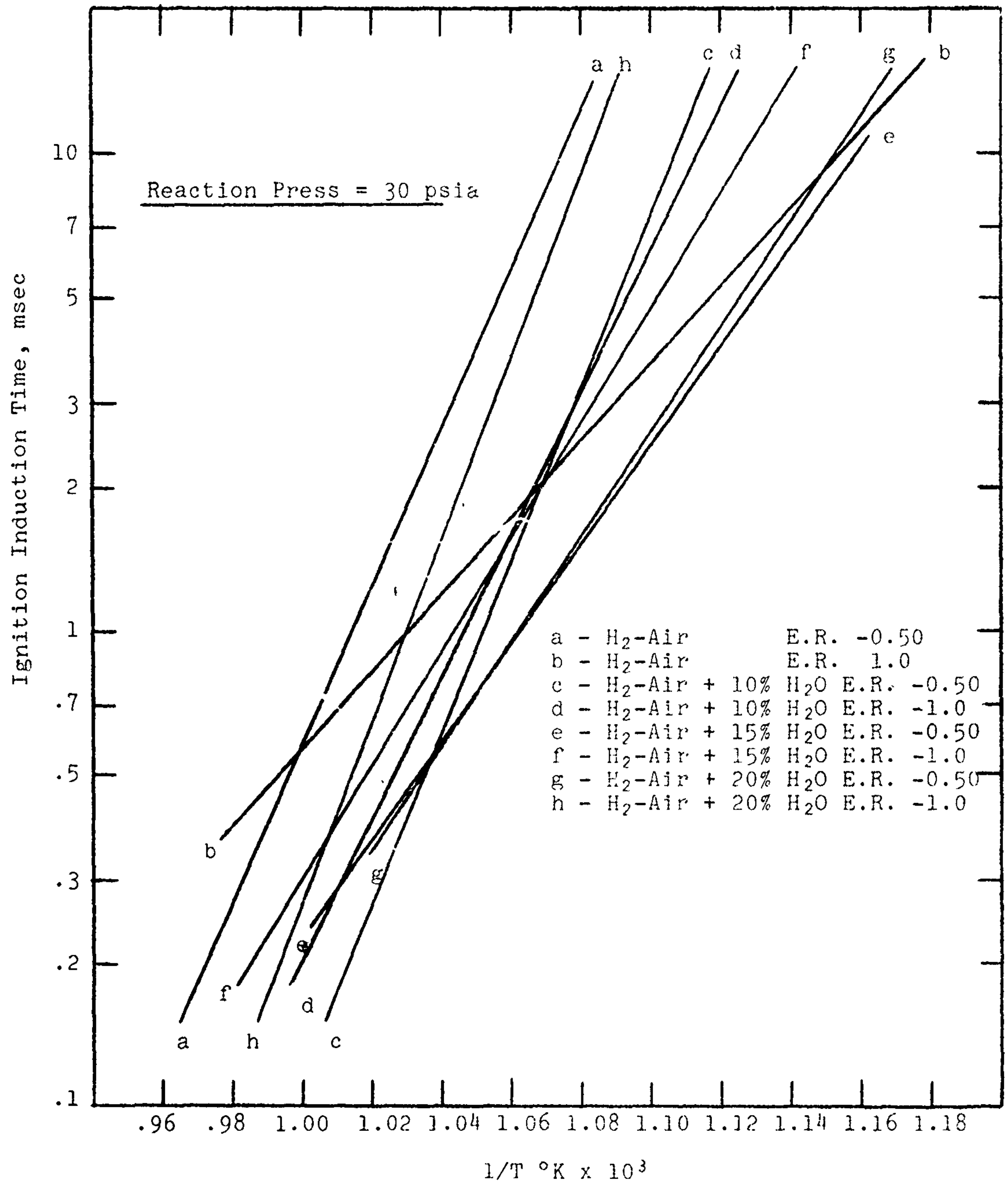

Figure 6. Ignition Characteristics of H_2-Air Mixtures with Added Water

ignition characteristic curve was displaced to lower temperatures and induction times with little change in slope. In the case of the 8 mole percent mixture the ignition delays were shortened by a factor of 5 and 10 for the 0.5 and 1.0 equivalence ratio mixtures, respectively. At constant delay this was equivalent to a decrease in ignition temperature of 70 and 100°K for the two mixtures.

Past experience with nitrogen oxide sensitization of the static hydrogen-oxygen (Ref. 8, 9) and diborane-oxygen (Ref. 7) ignition reactions indicated that the degree of sensitization could reach a maximum at a certain additive level with the effect decreasing at both lower and higher concentrations. Consequently a series of studies was conducted in which the concentration level of NO added to the stoichiometric hydrogen-air mixture was varied and ignition induction time-temperature data were measured at a pressure of 30 psia. The following concentrations were investigated: 0.1, 0.3, 0.5, 1.0, 5.0, and 8.0 mole percent NO.

The data are entered in Table 5 and the ignition induction times are plotted in Figure 7. The experimental scatter of the data in this investigation was extremely small, indicating some stabilization of the ignition reaction by the nitric oxide. It was observed that as the additive concentration was decreased from 8.0 to 0.5 mole percent the ignition induction time-temperature curve was displaced to shorter delay times and lower temperatures with little significant change in slope. When the additive concentration was decreased further to 0.3 and then 0.1 mole percent, the delay times again increased, but in these cases the slope of the ignition curve was definitely decreased.

Two additional additives, nitrogen dioxide and ammonia, that had been found to be effective in the static explosion studies, were examined at the 0.5 mole percent level under the same conditions. These measurements are summarized in Table 6 and the resultant ignition data are plotted in Figure 8. Nitrogen dioxide appeared to be as effective as nitric oxide in sensitizing the ignition reaction, while ammonia exhibited no effect.

Figure 9 presents isothermal plots of the variation in ignition induction time with nitric oxide concentration at temperatures of 800, 900 and 1000°K. In every case the minimum delay

TABLE 5

SHOCK TUBE INDUCTION TIMES FOR H_2-AIR + NO

Equivalence Ratio	Mole Percent NO	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
1.0	0.1	30	0.34	1676	931.1	1.0740
1.0	0.1	30	0.50	1642	912.2	1.0963
1.0	0.1	30	0.84	1616	897.8	1.1138
1.0	0.1	30	1.3	1565	869.4	1.1502
1.0	0.1	30	1.8	1522	845.6	1.1826
1.0	0.1	30	2.4	1493	829.4	1.2057
1.0	0.1	30	3.0	1470	816.7	1.2244
1.0	0.1	30	3.8	1466	814.4	1.2279
1.0	0.1	30	5.4	1415	786.1	1.2721
1.0	0.1	30	6.8	1415	786.1	1.2721
1.0	0.1	30	8.4	1388	771.1	1.2968
1.0	0.3	30	0.14	1639	910.6	1.0982
1.0	0.3	30	0.42	1565	869.4	1.1502
1.0	0.3	30	0.54	1543	857.2	1.1666
1.0	0.3	30	0.52	1542	856.7	1.1673
1.0	0.3	30	1.00	1496	831.1	1.2032
1.0	0.3	30	1.4	1457	809.4	1.2355
1.0	0.3	30	2.4	1424	791.1	1.2641
1.0	0.3	30	2.0	1420	788.9	1.2676
1.0	0.3	30	2.2	1413	785.0	1.2739
1.0	0.3	30	4.8	1357	753.9	1.3264
1.0	0.3	30	6.4	1345	747.2	1.3383
1.0	0.3	30	6.8	1339	743.9	1.3443
1.0	0.3	30	8.2	1328	737.8	1.3554
1.0	0.5	30	0.16	1551	861.7	1.1605
1.0	0.5	30	0.40	1506	836.7	1.1952
1.0	0.5	30	0.62	1480	822.2	1.2162
1.0	0.5	30	0.95	1466	814.4	1.2279
1.0	0.5	30	0.94	1465	813.9	1.2287
1.0	0.5	30	1.4	1449	805.0	1.2422
1.0	0.5	30	1.4	1438	798.9	1.2517
1.0	0.5	30	2.4	1428	793.3	1.2606
1.0	0.5	30	4.6	1393	773.9	1.2922
1.0	0.5	30	5.2	1373	762.8	1.3110
1.0	0.5	30	7.2	1373	762.8	1.3110
1.0	0.5	30	9.0	1355	752.8	1.3284
1.0	1.0	30	0.30	1570	872.2	1.1465
1.0	1.0	30	0.60	1546	858.9	1.1643
1.0	1.0	30	0.55	1537	853.9	1.1711
1.0	1.0	30	0.80	1521	845.0	1.1834
1.0	1.0	30	1.0	1500	833.3	1.2000
1.0	1.0	30	1.2	1478	821.1	1.2179
1.0	1.0	30	1.8	1457	809.4	1.2355
1.0	1.0	30	2.8	1434	796.7	1.2552
1.0	1.0	30	5.0	1422	790.0	1.2658
1.0	1.0	30	4.0	1419	788.3	1.2686
1.0	1.0	30	7.6	1398	776.7	1.2875
1.0	1.0	30	8.6	1382	767.8	1.3024
1.0	5.0	30	0.20	1666	925.6	1.0804
1.0	5.0	30	0.34	1638	910.0	1.0989
1.0	5.0	30	0.40	1638	910.0	1.0989
1.0	5.0	30	0.75	1583	879.4	1.1371
1.0	5.0	30	1.4	1541	856.1	1.1681
1.0	5.0	30	1.4	1538	854.4	1.1704
1.0	5.0	30	2.0	1502	834.4	1.1985
1.0	5.0	30	3.2	1478	821.1	1.2179
1.0	5.0	30	6.4	1440	800.0	1.2500
1.0	5.0	30	6.6	1438	798.9	1.2517
1.0	5.0	30	7.8	1433	796.1	1.2561
1.0	5.0	30	3.2	1420	788.9	1.2676
1.0	8.0	30	0.20	1667	926.1	1.0798
1.0	8.0	30	0.35	1667	926.1	1.0798
1.0	8.0	30	0.30	1656	920.0	1.0870
1.0	8.0	30	0.60	1583	879.4	1.1371
1.0	8.0	30	0.80	1571	872.8	1.1457
1.0	8.0	30	1.4	1545	858.3	1.1651
1.0	8.0	30	0.80	1543	857.2	1.1666
1.0	8.0	30	1.6	1537	853.9	1.1711
1.0	8.0	30	1.2	1528	848.9	1.1780
1.0	8.0	30	1.95	1498	832.2	1.2016
1.0	8.0	30	1.6	1491	828.3	1.2073
1.0	8.0	30	3.2	1489	827.2	1.2089
1.0	8.0	30	5.4	1464	813.3	1.2296
1.0	8.0	30	4.8	1463	812.8	1.2303
1.0	8.0	30	5.2	1460	811.1	1.2329
1.0	8.0	30	6.0	1448	804.4	1.2432
1.0	8.0	30	15.2	1370	761.1	1.3139
0.50	8.0	30	0.25	1714	952.2	1.0502
0.50	8.0	30	0.30	1686	936.7	1.0676
0.50	8.0	30	0.50	1676	931.1	1.0740
0.50	8.0	30	1.2	1610	894.4	1.1181
0.50	8.0	30	1.65	1587	881.7	1.1342
0.50	8.0	30	2.4	1542	856.7	1.1673
0.50	8.0	30	4.4	1512	840.0	1.1905
0.50	8.0	30	6.8	1495	830.6	1.2039
0.50	8.0	30	7.6	1463	812.8	1.2303
0.50	8.0	30	10.0	1452	806.7	1.2396

TABLE 6

SHOCK TUBE INDUCTION TIMES FOR H_2-AIR + NO_2, NH_3
EQUIVALENCE RATIO = 1.0

Additive Concentration	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
0.5% NH_3	30	0.80	1726	958.9	1.0429
	30	2.0	1685	936.1	1.0683
	30	11.4	1602	890.0	1.1236
	30	4.2	1590	883.3	1.1321
	30	14.6	1521	845.0	1.1834
0.5% NO_2	30	0.24	1563	868.3	1.1517
	30	0.50	1500	833.3	1.2000
	30	1.08	1480	822.2	1.2162
	30	1.30	1464	813.3	1.2296
	30	2.2	1436	797.8	1.2534
	30	5.2	1398	776.7	1.2875
	30	6.8	1396	775.6	1.2893
	30	7.2	1390	772.2	1.2950
	30	12.4	1366	758.9	1.3177

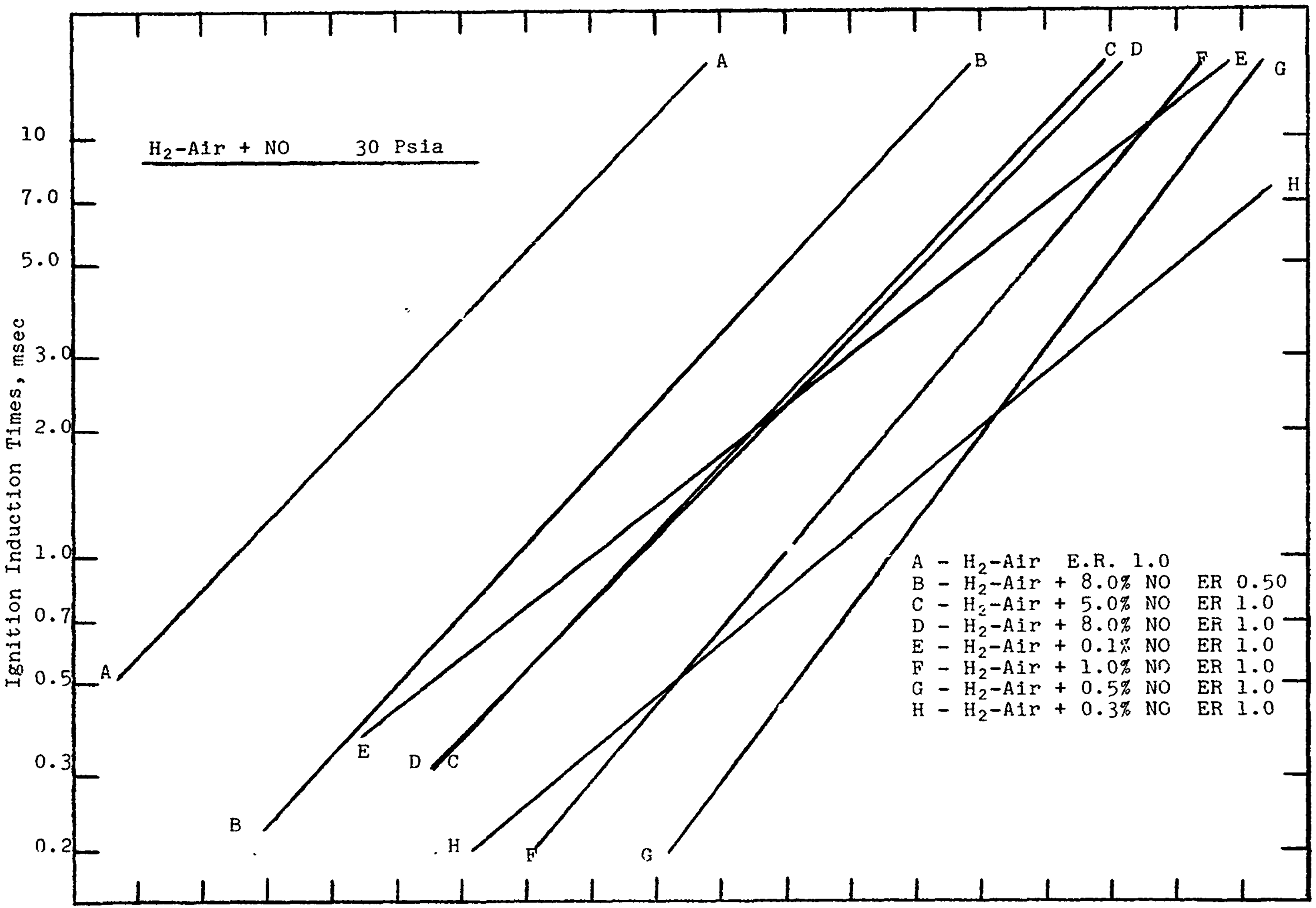

Figure 7. Ignition Characteristics of NO Sensitized Hydrogen-Air Mixtures

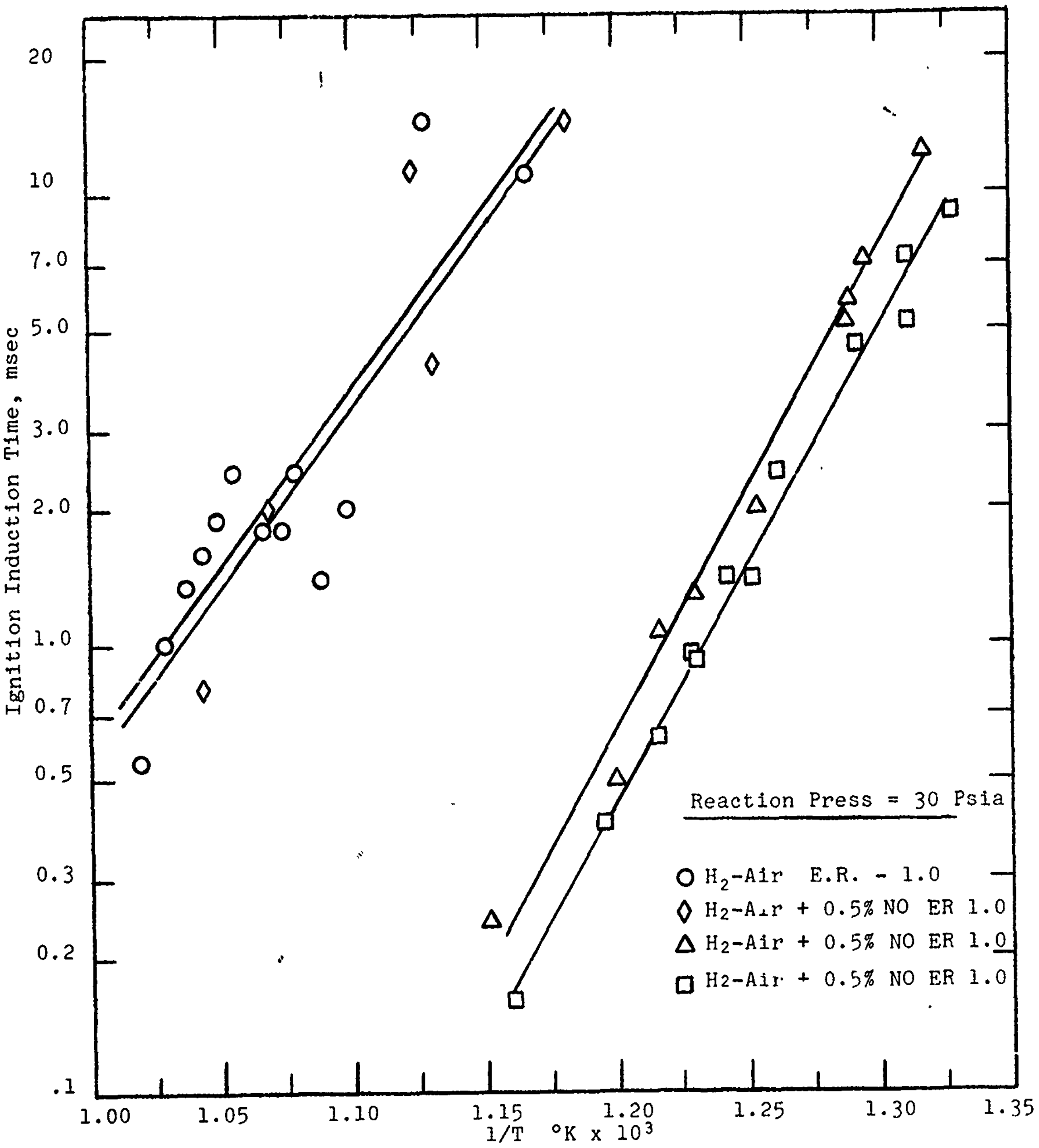

Figure 8. Ignition Characteristics of Hydrogen-Air Mixtures With Various Additives

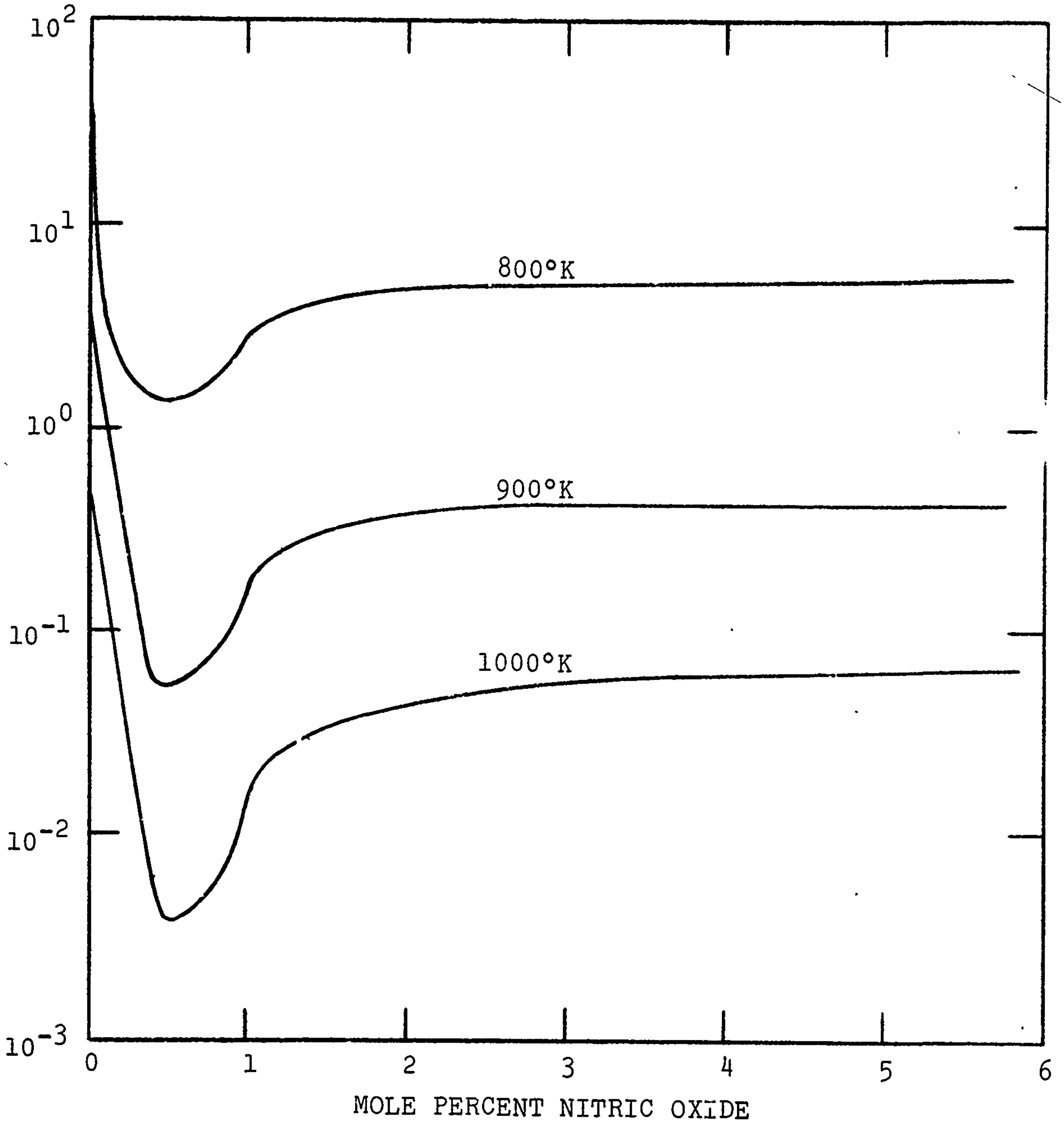

Figure 9. Variation of ignition delay with sensitizer concentration.

occurs near 0.5 mole percent additive, with the induction time increasing to a relatively constant value above 1 mole percent.

Table 7 is a tabular summary of all the additive work. The constants A and B are those derived from the data, assuming that the induction time can be expressed as:

$$\log \tau = A + {}^{B}/T$$

while ΔH gives the "apparent activation energy" for ignition in Kcal/mole. The last column illustrates the ignition temperatures for a constant delay time of 1 millisecond.

It should be stated at this point that since the gaseous mixtures investigated here were all premixed and stored before shock tube experiments were conducted, both NO and NO_2 are in equilibrium with the oxygen in air at the time of the experiment regardless of the oxide additive. At one point we became concerned as to the fate of the small amount of additive in the steel mixture tanks over long term storage. Qualitative infrared adsorption and mass spectrometer studies indicated no significant changes in the mixture over storage times longer than those experienced in these studies.

C. Conclusions

The first evidence of ignition sensitization of hydrogen-oxygen mixtures by nitrogen oxides was observed by H. B. Dixon in 1928. This initiated a long series of research by various investigators. The most recent work is that of Ashmore and co-workers (Ref. 8, 9). This represents the first time that this effect has been shown to occur in the short observation times inherent in shock tube investigations. While the mechanism of the reaction is not fully understood, the original concept that nitrogen oxides were effective by simply increasing the number of branched chains by acting as a low-temperature source of chain propagating species, has not been supported. Most recently Ashmore and Levitt (Ref. 9) have suggested that the sensitization effect could result from the reaction of nitric oxide with the chain-terminating species HO_2 in either of the following reactions:

TABLE 7

IGNITION CHARACTERISTICS
OF
HYDROGEN-AIR-ADDITIVE MIXTURES

Additive Concentration Mole %	A	B	ΔH K cal	T °K @ ti, 1 msec
--------	- 8.374	8,130	37.2	971
0.1, NO	- 6.817	5,990	27.4	878
0.3, NO	- 6.984	5,780	26.5	827
0.5, NO	-12.656	10,280	47.1	812
1.0, NO	-10.688	8,930	40.9	835
5.0, NO	- 8.859	7,670	35.1	865
8.0, NO	- 9.323	8,070	36.9	865
0.5, NO_2	-13.150	10,810	49.5	822
0.5, NH_3	- 8.760	8,440	38.6	963

$$\log t_i = A + {}^{B}/_{T}$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

$$HO_2 + NO \rightarrow HNO_2 + O$$

In both cases the NO effectively removes a chain-breaking species from the reaction mixture and generates a chain-propagating species (OH or O).

The experimental data indicate that NO might have a slightly greater sensitizing effect than NO_2. This might be expected since, in the early portion of the mechanism, NO_2 reacts with the O atom to form nitric oxide and oxygen:

$$NO_2 + O \rightarrow NO + O_2$$

This is tantamount to a competition for oxygen atoms which could delay the branching reaction:

$$O + H_2 \rightarrow OH + H$$

In addition, it appears that NO_2 must be converted to NO in order for the disruption of the chain-breaking steps to occur.

It is not surprising that ammonia was found to be ineffective under the shock tube conditions, since time is not available for its conversion to NO. The same would most probably be true for cyanogen, but this must be verified by experiment.

In recent studies of the hydrazine-nitrogen tetroxide reaction mechanism, Prof. Irvin Glassman and his associates (Ref. 10) have studied the kinetics of the reaction between hydrogen and oxygen in the presence of nitric oxide. The reaction rate is followed at atmospheric pressure under flow conditions in a 2 to 4 inch diameter, one meter long, tube. The reactants are under nitrogen dilution and enter the tube reactor at temperatures between 600 and 1100°K at a flow rate of about 50 feet/second. A series of temperature measurements along the axis of the reactor yield a temperature gradient which can be converted to a reaction rate from which reaction rate constants and activation energies are calculated. The results indicate that nitric oxide catalyzes the hydrogen-oxygen reaction. A maximum sensitization occurs at a given NO concentration. At sufficiently high concentrations, the nitric oxide is found to inhibit. The results, independently arrived at employing a completely different experimental technique, confirm our shock tube observations.

A pertinent summary of the essence of the hydrogen ignition characteristic studies reported here is shown in Figure 10. Curve A represents the behavior found by Schott and Kinsey (Ref. 1) in the higher temperature range of 1100-2600°K. The mixture employed was stoichiometric hydrogen-oxygen under high argon dilution. Curve B represents the low-temperature extension of this curve for ignitions in the temperature range 900-1100°K, as predicted by Skinner and Ringrose (Ref. 2), illustrating the self-inhibiting nature of the HO_2 species in the temperature range where it is sufficiently stable to enter the mechanism. Curve C presents the behavior found in this work for undiluted stoichiometric hydrogen-air mixtures, while Curve D illustrates the sensitizing effect exhibited by 0.5 mole percent nitric oxide on the ignition reaction. The resultant decrease in induction time at constant temperature is about 100 times or 2 orders of magnitude, while at constant induction time the ignition temperature is decreased by about 200°C.

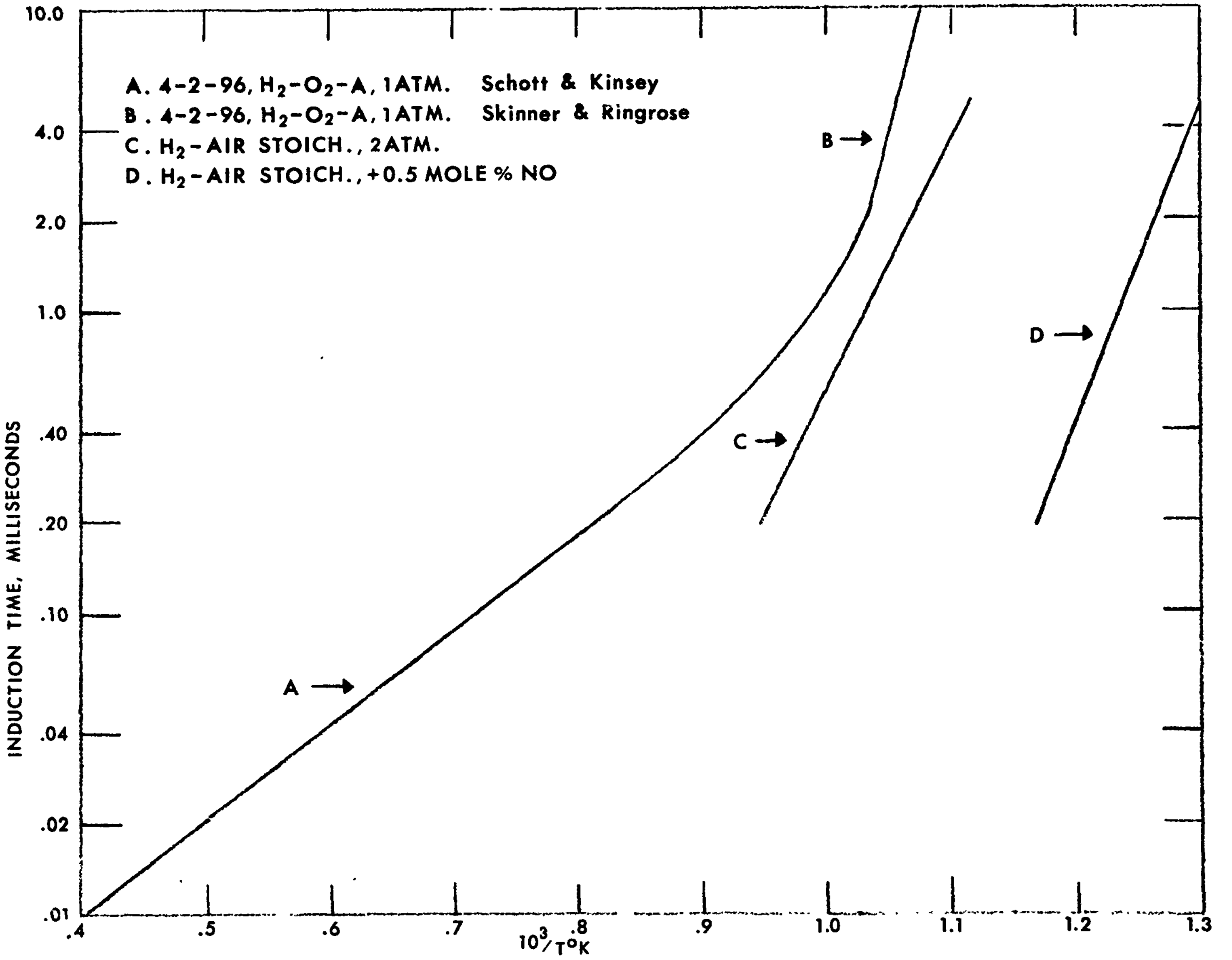

Figure 10. SHOCK TUBE IGNITION CHARACTERISTICS OF HYDROGEN

VII. HYDROCARBON GAS-AIR IGNITION CHARACTERISTICS

A. Experimental Results

A preliminary examination of the ignition induction characteristics of hydrocarbon-air mixtures was undertaken as a logical extension of the hydrogen research. The objective of this work was to furnish chemical reaction induction times as design criteria to test the feasibility of hydrocarbons as fuels in supersonic combustion applications.

This study included measurements on three hydrocarbon-air systems: methane, butane and octane. The ignition induction time-temperature characteristics were determined for 0.5 and 1.0 equivalence ratio mixtures at a reflected shock wave pressure of 60 psia. The methane-air data are presented in Table 8 and are plotted in Figure 11. The temperature range studied was 1250 to 1500°K for ignition delays from 0.2 to 8.0 milliseconds. The butane-air data are presented in Table 9 and plotted in Figure 12. The temperature range in this case was 1070 to 1270°K. Included in this group was a series of measurements to test the effects of 0.3 mole percent added hydrogen on the stoichiometric butane-air ignitions. It is evident that no sensitization of the ignition reaction resulted from hydrogen addition. The octane-air data are presented in Table 10 and plotted in Figure 13. The temperature range of the data was 1030 to 1250°K.

The experimental measurements were highly reproducible and exhibited little scatter compared to the unsensitized hydrogen-air determinations. The general behavior of a decrease in ignition temperature as one progresses along the homologous series of n-paraffins to higher molecular weight is observed here. An interesting result which will require clarification is exhibited in the methane-air system where the ignition induction times for the 0.5 equivalence ratio appear to be shorter than those for the stoichiometric mixture. The usual observation is that the induction time-mixture ratio curve will exhibit a minimum near the point corresponding to the stoichiometric mixture.

B. Discussion

A survey of the literature on hydrocarbon-air ignition induction time measurements indicated that the majority of the

TABLE 8

SHOCK TUBE INDUCTION TIMES FOR CH_4-AIR

Equivalence Ratio	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
0.50	60	0.26	2674	1485.6	0.6731
		0.24	2652	1473.3	0.6787
		0.36	2637	1465.0	0.6825
		0.33	2632	1462.2	0.6839
		0.38	2611	1450.6	0.6893
		0.50	2577	1431.7	0.6984
		0.70	2549	1416.1	0.7061
		0.78	2534	1407.8	0.7103
		0.88	2523	1401.7	0.7134
		1.35	2458	1365.6	0.7322
		1.55	2458	1365.6	0.7322
		1.55	2452	1362.2	0.7341
		2.40	2351	1306.1	0.7656
		4.05	2296	1275.6	0.7839
		7.20	2260	1255.6	0.7964
1.0	60	0.36	2644	1468.9	0.6807
		0.41	2639	1466.1	0.6820
		0.42	2639	1466.1	0.6820
		0.40	2620	1455.6	0.6870
		0.90	2561	1422.8	0.7028
		0.95	2544	1413.3	0.7075
		1.0	2541	1411.7	0.7083
		0.80	2535	1408.3	0.7100
		1.35	2529	1405.0	0.7117
		1.65	2498	1387.8	0.7205
		1.83	2475	1375.0	0.7272
		1.70	2465	1369.4	0.7302
		4.8	2465	1369.4	0.7302
		2.8	2439	1355.0	0.7380
		7.2	2424	1346.7	0.7425
		5.0	2383	1323.9	0.7554
		6.6	2350	1305.6	0.7659

TABLE 9

SHOCK TUBE INDUCTION TIMES FOR C_4H_{10}-AIR

Equivalence Ratio	Percent Additive	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
0.50	None	60	0.18	2281	1267.2	0.7891
			0.16	2276	1264.4	0.7908
			0.36	2213	1229.4	0.8134
			0.42	2201	1222.8	0.8178
			0.54	2147	1192.8	0.8383
			0.64	2140	1188.9	0.8411
			0.78	2110	1172.2	0.8530
			1.20	2091	1161.7	0.8608
			1.65	2057	1142.8	0.8750
			2.45	2028	1126.7	0.8875
			3.6	1990	1105.6	0.9044
			5.2	1966	1092.2	0.9004
1.0	None	60	0.24	2254	1252.2	0.7985
			0.30	2213	1229.4	0.8134
			0.50	2206	1225.6	0.8159
			0.78	2144	1191.1	0.8395
			0.88	2115	1175.0	0.8510
			1.2	2091	1161.7	0.8608
			2.0	2047	1137.2	0.8793
			3.2	2027	1126.1	0.8880
			3.4	1986	1103.3	0.9063
			4.1	1981	1100.6	0.9085
			5.2	1975	1097.2	0.9114
			6.4	1970	1094.4	0.9137
1.0	.3 (H_2)	60	0.28	2241	1245.0	0.8032
			0.30	2229	1238.3	0.8075
			0.44	2206	1225.6	0.8159
			0.52	2198	1221.1	0.8189
			0.73	2168	1204.4	0.8302
			1.15	2112	1173.3	0.8522
			1.55	2089	1160.6	0.8616
			3.0	2041	1133.9	0.8819
			3.15	2019	1121.7	0.8915
			3.13	1995	1108.3	0.9022
			4.1	1968	1093.3	0.9146
			8.0	1966	1092.2	0.9155
			8.6	1934	1074.4	0.9307

TABLE 10

SHOCK TUBE INDUCTION TIMES FOR OCTANE-AIR

Equivalence Ratio	Reaction Pressure (psia)	Induction Time (msec)	Temp °R	Temp °K	1/T °K x 10^3
0.50	60	0.20	2252	1251	0.7992
		0.12	2225	1236	0.8089
		0.40	2171	1206	0.8291
		0.60	2129	1183	0.8454
		0.70	2104	1169	0.8555
		0.88	2077	1154	0.8666
		1.40	2045	1136	0.8802
		4.20	1957	1087	0.9197
		3.90	1937	1076	0.9292
		4.90	1921	1067	0.9370
1.0	60	0.20	2128	1182	0.8458
		0.24	2086	1159	0.8628
		0.48	2065	1147	0.8716
		0.63	2063	1146	0.8725
		0.82	2054	1141	0.8763
		0.95	2009	1116	0.8959
		2.2	2007	1115	0.8968
		3.4	1921	1067	0.9370
		4.35	1874	1041	0.9605
		6.80	1861	1034	0.9672

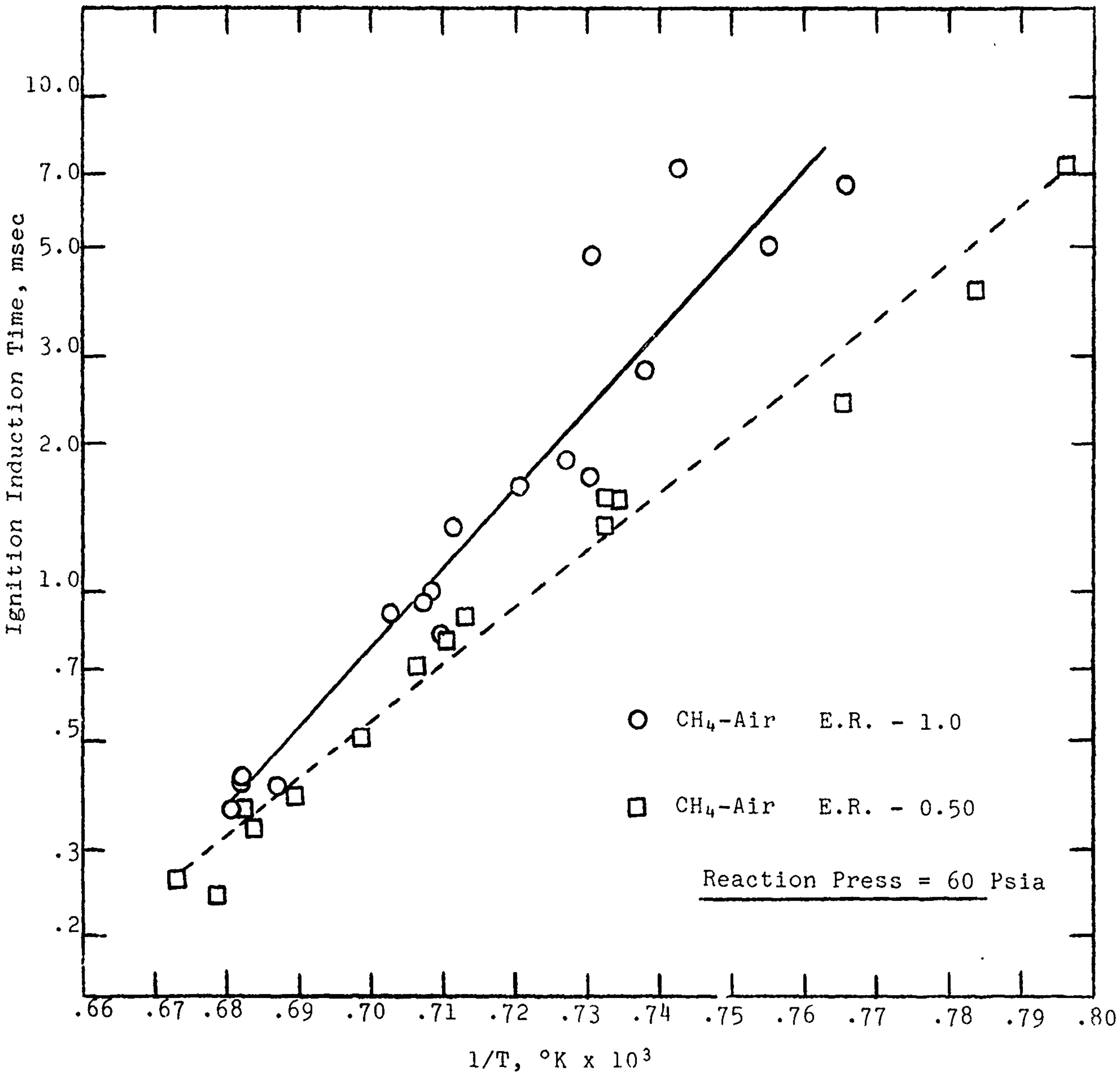

Figure 11. Methane-Air Ignition Characteristics

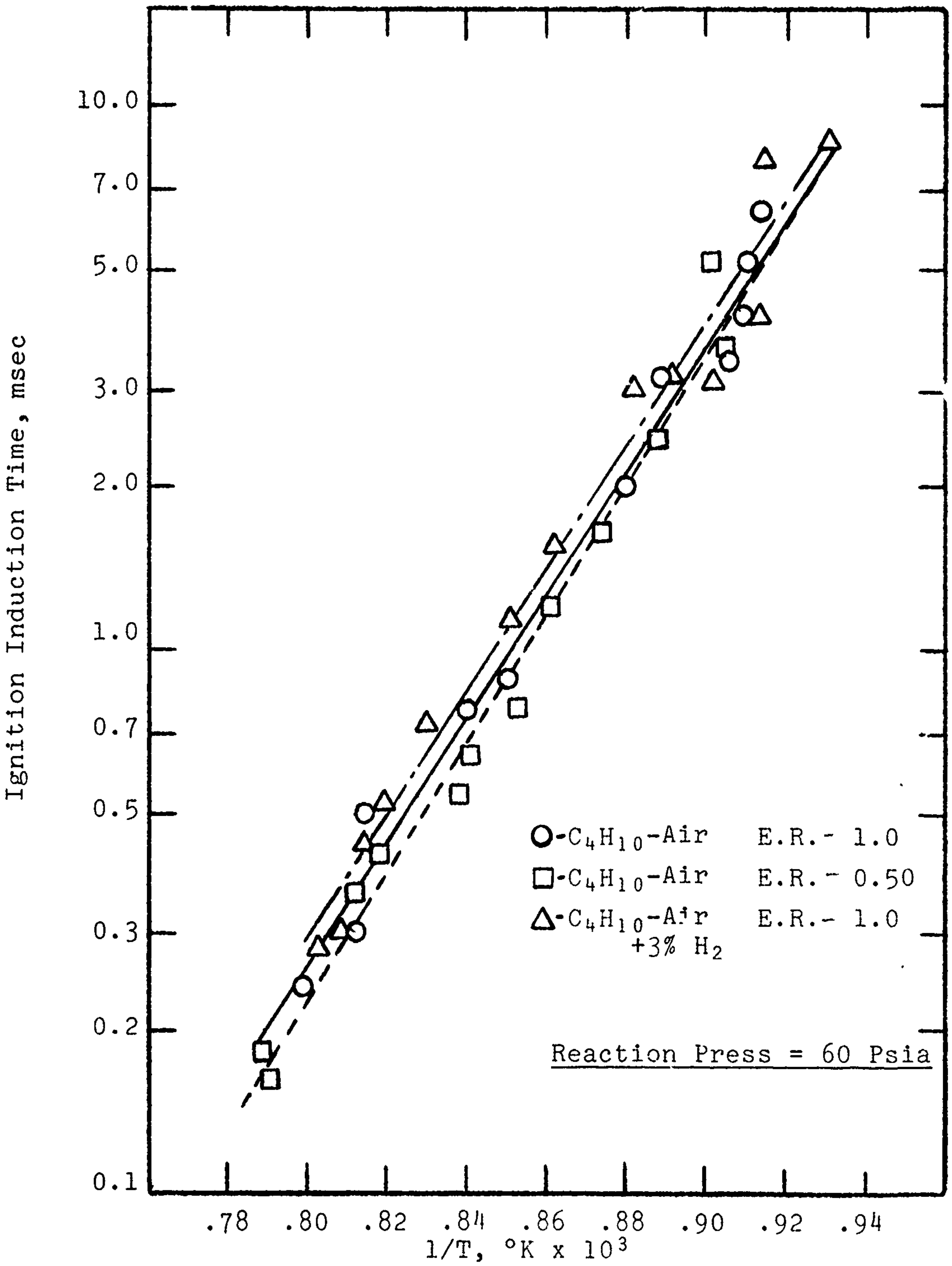

Figure 12. Butane-Air Ignition Characteristics

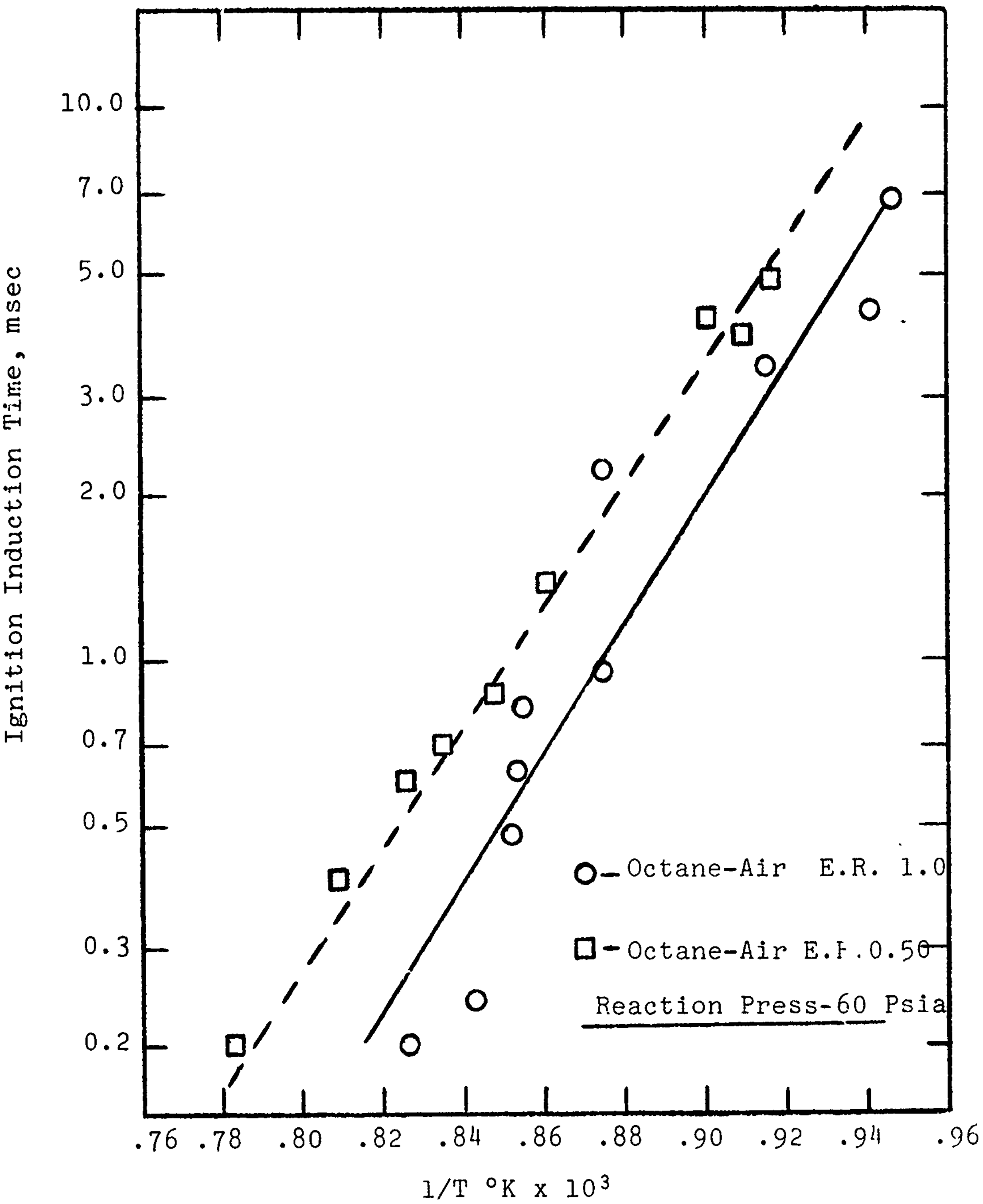

Figure 13. Octane-Air Ignition Characteristics

research can be divided into three general groups: (1) that of Wilhelm Jost and co-workers (Terao, Marginengo, Wagner, Just) from the Institute of Physical Chemistry at the University of Göttingen, (2) the Russian work of Borisov, Kogarko, Voevodsky and Soloukhin, and (3) the work of Mullins at the National Gas Turbine Establishment in England.

The German work is reported from experiments on both adiabatic compression and shock tube apparatuses. The adiabatic compression apparatus is described in Ref. 11, 12. The data are not directly comparable to shock wave ignition induction times, but have been interpreted by Terao (Ref. 13, 14) and compared with his shock tube results on methane, ethane, ethylene and hexane mixtures in air. The adiabatic compression studies included work on hexane, heptane, octane and decane. The shock tube data cover induction times from .01 to 1.0 msec., while the adiabatic compression data cover the range from 2 to 100 msec. Unfortunately all these data are obtained under conditions where two-stage ignition (low-temperature ignition) of the hydrocarbon occurs. Combining the results of all hydrocarbons investigated from C_1 to C_{10}, the ignition temperature range reported for delay times from 0.01 to 20 msec is from 550 to 1000°K. An illustration of the discrepancies between the work reported here and that reported by Terao would be that for stoichiometric methane-air, the ignition delays differ by a factor of 10^4 and ignition temperature by 700°K. Comparing our data on stoichiometric octane with those of Martinengo, the ignition delays differ by a factor of 10^3 and the temperatures by 400°K.

The shock tube ignition data of Kogarko and Borisov (Ref. 15), most recently corrected by the same workers (Ref. 16), are compared with our data in Figure 14 for a number of stoichiometric hydrocarbon-air mixtures. While the agreement illustrated here appears to be very good, it was not expected. The Russian work is carried out in a three-sectioned tube (driver, buffer and sample). The ignition lines are determined by setting a constant sample pressure and varying ignition temperature by increasing the driver pressure. The pressure on ignition along a given line is therefore variable. The majority of the data illustrated here were obtained with an initial sample pressure of 1 atmosphere, resulting in the reflected wave pressure varying from 50 atmospheres at 1100°K to 90 atmospheres at 1500°K (this corresponds to the range of the benzene data). Therefore, to better compare the data, the pressure dependence of ignition delay would have to be determined, since the Russian work is at pressures about 20 times in excess of those employed in our investigations.

The ignition delay measurements of B. P. Mullins (Ref. 17, 18) were made employing the N.G.T.E. (National Gas Turbine Establishment, U. K.) flow method. The apparatus is a standard 3° diffuser spontaneous ignition rig which is fed with electrically heated air. Downstream from the point of fuel injection, seven fused silica windows permit observation of the flame front location from which ignition delay times can be calculated. Mullins measured the ignition delays and the activation energies for a wide range of organic materials. His data on methane and ethane are included in Figure 14 and are seen to agree admirably with the shock tube results.

Hawthorn and Nixon (Ref. 19) have reported ignition delay times for argon-diluted propane-oxygen mixtures. One curve, that for 0.67 equivalence ratio propane-oxygen in 99% argon at 15 psia, is presented in Figure 14. From the data presented one would expect that as the argon dilution is decreased the ignition curve would move toward lower temperatures and shorter delays, and more closely approach the butane-air curve reported in this work. The agreement in this case is again very good.

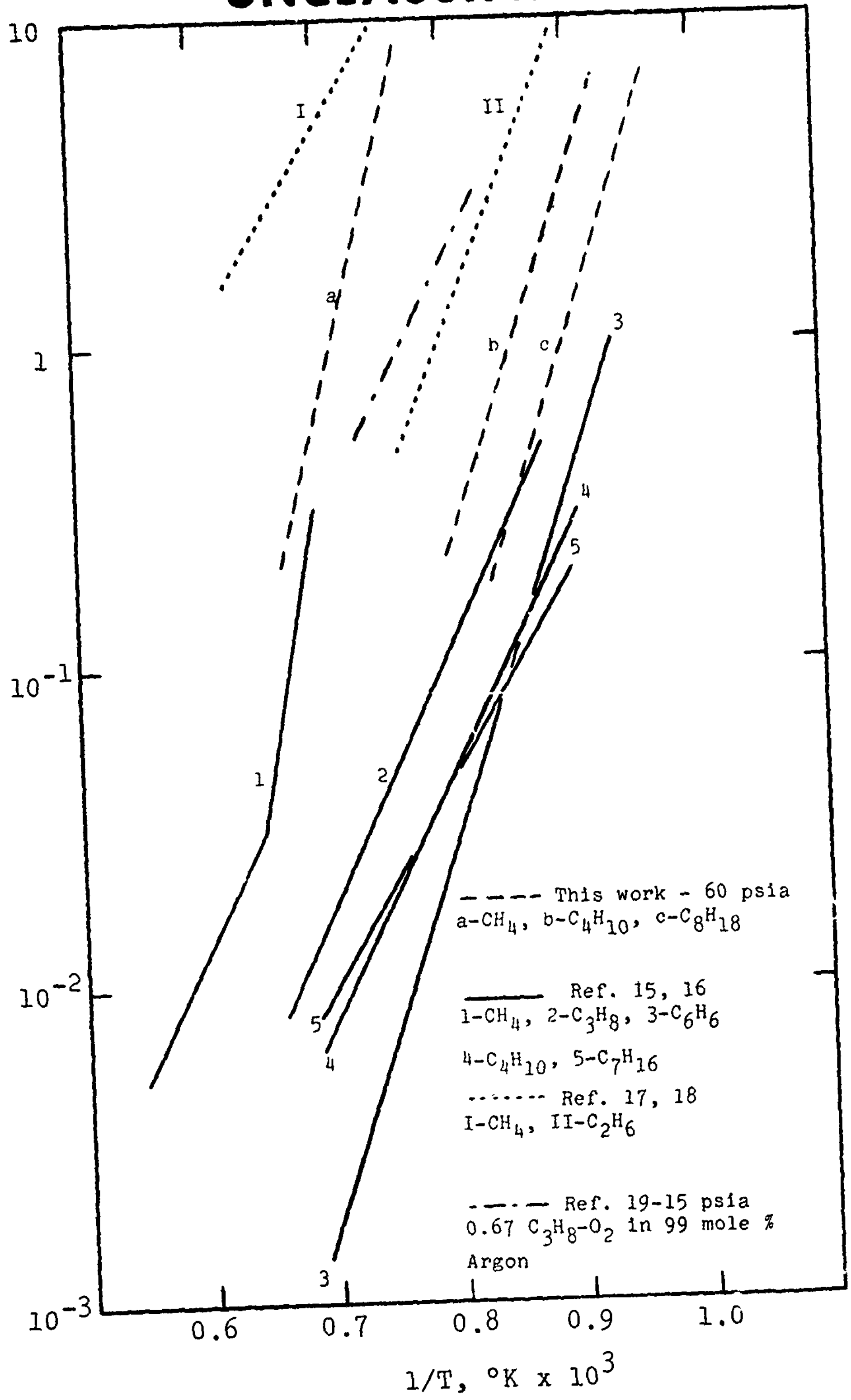

Figure 14 Ignition characteristics of stoichiometric hydrocarbon-air mixtures.

VIII. RECOMMENDATIONS

The application of endothermic hydrocarbon fuels for cooling of advanced aircraft engines will of necessity require compatible supersonic combustion properties of the resultant hydrocarbon product mixture. Figure 14 illustrates the paucity of applicable hydrocarbon-air ignition induction data that exists in the literature. A great deal remains to be done in defining the pressure, temperature and composition dependence of ignition delay times even for the pure hydrocarbons, not to mention the ignition characteristics of the alkenes and alkynes that will result from pyrolysis and dehydrogenation of the original endothermic fuel. The same is true, of course, for model product distributions from these reactions.

It is recommended that the present work be continued so that design criteria will be furnished on the ignition characteristics of the hydrcarbon fuels at composition, pressure and temperature conditions anticipated in the advanced aircraft engines. At a later time, it may be of interest to conduct a research program with the objective to identify chemical additives to sensitize the ignition reactions of these hydrocarbon species.

REFERENCES

1. G. L. Schott and J. L. Kinsey, J. Chem. Phys. 29, 1177- (1958)

2. G. B. Skinner and G. H. Ringrose, J. Chem. Phys. 42, 2190- (1965)

3. G. B. Skinner et al, Monsanto Research Corporation ASD-TDR-62-1042 (1962)

4. H. S. Glick, W. Squire and A. Hertzberg, Fifth Symposium (International) on Combustion, pp 393-, Reinhold Publishing Corp., 1955

5. V. V. Voevodsky and R. K. Soloukhin, Tenth Symposium (International) on Combustion pp 279-, The Combustion Institute, 1965

6. B. Lewis and G. Von Elbe, Combustion, Flames, and Explosions of Gases, pp 29, 68 Academic Press, 1961

7. A. D. Snyder, Ph.D. Thesis Rensselaer Polytechnic Inst., 1957

8. P. G. Ashmore and B. P. Levitt, Seventh Symposium (International) on Combustion pp 45-, Butterworth, 1958

9. P. G. Ashmore and B. J. Tyler, Ninth Symposium (International) on Combustion pp 201-, Academic Press, 1962

10. I. Glassman, personal communication, August 1965

11. A. Martinengo and H. Gg. Wagner, Z. Physik. Chem. (Frankfurt) 20, 206-, (1959)

12. A. Martinengo, H. Gg. Wagner and D. Zunft, Z. Physik. Chem. (Frankfurt) 22, 292-, (1959)

13. K. Terao, J. Phys. Soc. Japan 15, 1113-, (1960)

14. K. Terao, J. Phys. Soc. Japan 15, 2086-, (1960)

15. S. M. Kogarko and A. A. Borisov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 1960, 1255-

16. A. A. Borisov, S. M. Kogarko, and A. V. Lyubimov, Proc. Acad. Sci. USSR, Phys. Chem. Sect. 146, 274-, (1963)

17. B. P. Mullins, Fuel 32, 343-(1953)

18. B. P. Mullins and S. S. Penner, Explosions, Detonations, Flammability, and Ignition pp 192-218, AGARD ograph No. 31, Pergamon Press, 1959

19. R. D. Hawthorn and A. C. Nixon, AIAA Propulsion Joint Specialist Conference, Colorado Springs, Colorado, June 14-18, 1965, AIAA Paper No. 65-594

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Monsanto Research Corporation
Dayton, Ohio

2a REPORT SECURITY CLASSIFICATION
Unclassified

2b GROUP

3 REPORT TITLE SHOCK TUBE STUDIES OF FUEL-AIR IGNITION CHARACTERISTICS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
1 April 1964 to 26 July 1965

5 AUTHOR(S) *(Last name, first name, initial)*
Snyder, A.D., Skinner, G.B., Robertson, J., Zanders, D.L.

6. REPORT DATE
September 1965

7a TOTAL NO OF PAGES
44

7b NO OF REFS
19

8a CONTRACT OR GRANT NO
AF 33 (615)-1317

b. PROJECT NO. 3048

c Task No. 3048-01

d

9a ORIGINATOR'S REPORT NUMBER(S)
MRC-DA-77

9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
AFAPL-TR-65-93

10 AVAILABILITY/LIMITATION NOTICES
Qualified requesters may obtain copies of this report from DDC.

11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY
Air Force Aero Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

13 ABSTRACT Ignition induction times of hydrogen-air mixtures were measured after the reflected wave in a single-pulse shock tube as a function of mixture ratio, absolute pressure and temperature. The data have been correlated by a nonlinear regression program resulting in an equation for induction time as a function of these variables. The results support earlier work at this laboratory on argon-diluted hydrogen-oxygen experiments in that at temperatures below 1100°K the ignition delays became very long because of self-inhibition of the reaction through HO_2 formation. The effects of added water vapor and nitric oxide on the ignition characteristics of hydrogen-air mixtures were studied. Both additives resulted in sensitization of the ignition reaction. A detailed investigation of the nitric oxide catalysis indicated that the maximum effect occurred at 0.5 mole percent of additive, where the ignition delay was decreased by a factor of 100 and the ignition temperature by 200°K. Nitrogen dioxide was found to be equally effective, but ammonia exhibited no sensitizing action. The ignition induction times of 0.5 and 1.0 equivalence ratio mixtures of methane-, butane-, and octane-air mixtures were determined from 0.2 to 10 milliseconds at a reflected shock pressure of 60 psia. The data are presented both in tabular and graphical form. All ignition delay data are discussed in light of related studies and potential kinetic mechanisms. Recommendations for future work are presented.

SUPPLEMENTARY

INFORMATION

CORRECTED COPY

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
Dayton, Ohio 45407

EVALUATION OF FUELS AND LUBRICANTS

Contract Nr. AF 33(615)-1317

Attached is a copy of the Final Report on Contract Nr. AF 33(615)-1317, "Evaluation of Fuels and Lubricants", under Project 3048, Task 304801. This report covers work performed during the period 1 April 1964 to 26 July 1965 at the Dayton Laboratory of Monsanto Research Corporation.

Please do not return this report to MRC. Destroy it when it is no longer useful to you.

MRC No. 2534-9 17 September 1965

Monsanto Distribution

1.	H. K. Nason	St. Louis
2.	K. W. Easley	Washington
3.	R. M. Dickey	Everett
4.	R. J. Wineman	Everett
5.	E. E. Hardy/T. L. Gossage/ C. J. Eby	Dayton
6.	M. B. Moshier	Dayton
7.	Library/Permanent File	Everett
8-11.	Library	Dayton
12.	F. C. Meyer	St. Louis
13-15.	Library	St. Louis
16.	M. R. McCoy	Dayton
17.	J. C. Harris	Dayton
18.	A. D. Snyder	Dayton
19.	D. L. Zanders	Dayton
20.	J. Robertson	Dayton

CORRECTED COPY ATTACHED

dr

October 26, 1965

Errata on "Shock Tube Studies of Fuel-Air Ignition Characteristics"

Recipients of Technical Report AFAPL-TR-6593

Sirs:

Technical Report AFAPL-TR-6593 "Shock Tube Studies of Fuel-Air Ignition Characteristics" was issued with errors in the legend of Figure 8, Page 25.

The correct legend should read:

○ H -Air E.R. -1.0
◇ H -Air + 0.5% NH E.R. 1.0
△ H -Air + 0.5% NO E.R. 1.0
□ H -Air + 0.5% NO E.R. 1.0

A revised Figure will not be issued.

A. D. Snyder

A. D.Snyder
Group Leader,
Physical Chemistry

vb

SUPPLEMENTARY

INFORMATION

CORRECTED COPY

MONSANTO RESEARCH CORPORATION
DAYTON LABORATORY
Dayton, Ohio 45407

EVALUATION OF FUELS AND LUBRICANTS

Contract Nr. AF 33(615)-1317

Attached is a copy of the Final Report on Contract Nr. AF 33(615)-1317, "Evaluation of Fuels and Lubricants", under Project 3048, Task 304801. This report covers work performed during the period 1 April 1964 to 26 July 1965 at the Dayton Laboratory of Monsanto Research Corporation.

Please do not return this report to MRC. Destroy it when it is no longer useful to you.

MRC No. 2534-9 17 September 1965

Monsanto Distribution

1.	H. K. Nason	St. Louis
2.	K. W. Easley	Washington
3.	R. M. Dickey	Everett
4.	R. J. Wineman	Everett
5.	E. E. Hardy/T. L. Gossage/ C. J. Eby	Dayton
6.	M. B. Moshier	Dayton
7.	Library/Permanent File	Everett
8-11.	Library	Dayton
12.	F. C. Meyer	St. Louis
13-15.	Library	St. Louis
16.	M. R. McCoy	Dayton
17.	J. C. Harris	Dayton
18.	A. D. Snyder	Dayton
19.	D. L. Zanders	Dayton
20.	J. Robertson	Dayton

CORRECTED COPY ATTACHED

dr

October 26, 1965

Errata on "Shock Tube Studies of Fuel-Air Ignition Characteristics"

Recipients of Technical Report AFAPL-TR-6593

Sirs:

Technical Report AFAPL-TR-6593 "Shock Tube Studies of Fuel-Air Ignition Characteristics" was issued with errors in the legend of Figure 8, Page 25.

The correct legend should read:

○ H -Air E.R. -1.0

◇ H -Air + 0.5% NH E.R. 1.0

△ H -Air + 0.5% NO E.R. 1.0

□ H -Air + 0.5% NO E.R. 1.0

A revised Figure will not be issued.

A D Snyder

A. D.Snyder
Group Leader,
Physical Chemistry

vb