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The Carbon Dioxide Chaperon Efficiency for the Reaction $H + O_2 + M \rightarrow HO_2 + M$ From Ignition Delay Times Behind Reflected Shock Waves

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At the low static temperatures and high pressures used to study supersonic combustion of hydrogen with vitiated air, the progress of the reaction is inhibited by the three-body reaction

$$H + O_2 + M \rightarrow HO_2 + M \tag{4}$$

The amount of inhibition is a function of the pressure, temperature, and chaperon efficiency of the third-body species (M). Ignition delay times calculated with the kinetic model of reference 1 for stoichiometric hydrogen-air (1 atm, 960 K), with and without water vapor demonstrate the magnitude of this effect. The model showed that the addition of 10 percent water vapor to the hydrogen-air mixture increased the ignition delay time from 0.31 to 14.2 msec. Experimentally determined values for the chaperon efficiency of water range from 18.4 to 71. Since vitiated air can contain as much as 30 percent water vapor, there is a definite need for a better determination of the chaperon efficiency for water.

Recently, Stein, Yetter, and Dryer (ref. 2) reported preliminary results, obtained using a flow tube reactor, for their study of the chaperon efficiency of carbon dioxide and water. The value reported for carbon dioxide was much larger than present literature values and should be confirmed before one accepts their water value. The purpose of the present work was to use the shock tube, an excellent tool for studying this reaction at high temperatures, to determine the chaperon efficiency for carbon dioxide and to compare the results with those of Stein. This was determined by modeling the experimental ignition delay times for two mixtures of hydrogen, oxygen, carbon dioxide, and argon (4/2/0/94 and 4/2/10/84) behind reflected shock waves.

EXPERIMENTAL DETAILS

The shock tube consisted of a single piece of square, stainless-steel tubing, 5.7 m long, 64 mm i.d. on a side with 13 mm-thick walls. The entire length of the tube was ground to constant inside dimension and then honed to a highly polished finish. The assembled tube could be evacuated to a pressure of about 1 µm and had a leak rate of less than 0.2 µm/min. A liquid nitrogen cold trap in the vacuum line prevented the back-migration of pump oil into the shock tube.

Gas mixtures (table I) were prepared by the method of partial pressures in 34.4-liter stainless steel tanks. The gases used to prepare the mixtures had stated purities of 99.99 percent for hydrogen, 99.98 percent for oxygen, 99.8 percent for carbon dioxide, and 99.998 percent for argon. All samples were prepared to a total pressure of 40 psia. The concentrations of all species were known to better than 1 percent. Soft aluminum diaphragms separated the high-pressure driver (helium) gas from the test gas. These diaphragms were pressurized to 90 percent of their burst pressure and then pierced with a piston. The driver gas pressure was held constant at 60 psia, which insured that the opening process for the diaphragm was the same in all tests. The shock strength was varied by changing the mean molar mass of the driver gas with the addition of argon.

The temperature and pressure behind the reflected shock wave were calculated from the measured velocity of the incident shock wave, with the shock program of Gordon and McBride (ref. 3). Since the reaction temperature must be calculated, it is very important to measure the initial temperature and the shock velocity as accurately as possible. The shock tube wall temperature was measured by an insulated thermocouple to better than 0.5°. The test mixture was assumed to rapidly achieve this temperature. The shock velocity was measured with two quartz pressure transducers (stated rise time μsec) located 7 and 83 mm from the reflecting surface. A measurement made this close to the reflecting surface eliminates concern about shock attenuation. The amplified outputs form these transducers were displayed on a digital oscilloscope (see fig. 1 for sample traces). Data points were recorded every 0.2 μsec. A useful feature of this scope is that the scale can be magnified to allow each point to be viewed. This enabled the incident shock velocity to be measured to better than 0.1 percent.

The ignition delay time was measured by monitoring the pressure history behind the reflected shock wave. The quartz pressure transducer located 7 mm from the reflecting surface was used for this measurement. A nylon holder was designed to completely isolate the pressure transducer from the metal walls of the shock tube. This produced a very quiet pressure history and allowed the measurement of the time when the pressure first started to rise (fig. 2).

RESULTS AND DISCUSSION

Ignition Delay Times

The ignition delay time measured in these experiments was defined as the time interval between shock reflection and the initial rise in the ignition pressure. The pressure change at the time of the initial rise is estimated to be about 2 percent. A typical pressure history is shown in figure 2. The gas composition (4 percent H_2, 2 percent O_2, 94 percent Ar) was selected because it produced delay times greater than 100 μsec in the desired temperature range. This is important, since previous work (ref. 4) suggests that even at a location 7 mm from the reflecting surface, a small but significant error results for delay times less than 100 μsec. Ignition delay time measurements for temperatures over 1300 K could not be used as they were quite difficult to measure. This was because the amplitude of the experimental ignition pressure steadily decreased as the reaction temperature increased. The lower temperature limit was imposed by the maximum available test time behind reflected shock waves (fig. 3). Ignition delay times measured for the two gas mixtures are recorded in table II and plotted in figures 4 and 7.

Schott (ref. 5) showed that the ignition delay time for all of these data could be scaled as (delay time)x(oxygen concentration). Since all of our data were obtained from gas mixtures containing 2 percent oxygen, (delay time)x (pressure) was plotted against reciprocal temperature. The dashed line of figure 4 represents incident shock wave data of Schott calculated for our gas mixture by the equation

$$\log ([O_2]\tau) = -10.647 + 3966/T$$

His incident shock wave data are about 20 percent lower than the present reflected shock wave data. This is exactly the behavior one would expect when incident shock wave data have not been corrected for boundary layer effects. Belles and Brabbs (ref. 6) showed that the residence time would be 4 to 16 percent longer when corrections for the boundary layer are applied.

Kinetic Mechanism

Ignition delay times were calculated with the chemical kinetic computer code of Radhakrishnan and Bittker (ref. 7) and the kinetic mechanism in table III. The hydrogen oxidation mechanism consists of 20 reversible reactions among 8 reacting species. Reverse rates were calculated via the equilibrium constant and the forward rates. All rate constants are listed as expressed in the references and any variations in the rates are shown in the adjustment factor column. The computed ignition delay time was defined as the time at which the pressure increases 2 percent; this corresponds to our best estimate of the experimental pressure at the measured ignition delay time.

The kinetic model was fitted to the high-temperature data by varying the rates of reactions (2), (3), and (7):

$$H + O_2 \rightarrow OH + O \qquad (2)$$

$$O + H_2 \rightarrow OH + H \qquad (3)$$

$$H_2 + O_2 \rightarrow OH + PH \qquad (7)$$

(See table III.) The rate for reaction (2) was increased 20 percent, which is well within the experimental error of the data. This increase in the rate of reaction (2) brought it to within 10 percent of Baulchs' recommended value (ref. 8) and into agreement with the value recommended by Just (ref. 9). Jachimowski (ref. 10) studied initiation reaction (7) and determined a value of $1.7\text{x}10^{13}$ exp (-48150/RT) for the rate constant. According to him, the rate constant was good to within a factor of 3. Thus, the factor of 2 adjustment for this reaction is well within his error. At the low temperature end of the data, the model was fitted by small adjustments in reactions (4) and (12):

$$H + O_2 + M \rightarrow HO_2 + M \qquad (4)$$

$$H + HO_2 \rightarrow OH + OH \qquad (12)$$

Reaction (12) is the primary path by which HO_2 radicals are consumed in the low pressure region. This rate constant was increased by 20 percent.

Once a fit to the data was established, the kinetic mechanism was simplified by removing reactions that were found to be unimportant when fitting the present data. It was at this time that we encountered one of the pitfalls associated with mechanism simplification. The new mechanism modeled the present data very well, but completely missed the high-pressure data of Skinner (ref. 11), and in some cases ignition did not occur. This was because the reaction pathway

$$HO_2 \rightarrow H_2O_2 \rightarrow OH \rightarrow H$$

was omitted in the reduced mechanism. This pathway is very important in the high-pressure region where the rate of production of HO_2 via reaction (4) is much faster than the rate of branching via reaction (2). This illustrates how reducing a detailed kinetic mechanism to only the important reactions for a limited range of experimental data can render the mechanism useless for other test conditions.

The set of rate constants used for reactions (13) to (19) was taken from Dixon-Lewis (ref. 12) rather than Lloyd (ref. 13) because of the difference in the recommended value for reaction (17).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (17)$$

The activation energy Lloyd assigned to the reaction was shown by Troe (refs. 14 and 15) to be incorrect. Since some of the other reactions are dependent on the rate of this reaction, the rate constants assigned to reactions (13) to (19) were taken from reference 12. The best fit to the high-pressure data required a 20-percent increase in the rate constant for reaction (19):

$$H_2O_2 + M \rightarrow OH + OH + M \qquad (19)$$

Comparison of Kinetic Model with Experimental Data

A comparison of ignition delay times predicted by the kinetic model and those measured for the present hydrogen-oxygen mixture and for the high-pressure data of Skinner are shown in figures 4 and 5. Both sets of data are modeled very well by the kinetic mechanism. One may wonder whether a kinetic mechanism developed from shock-tube measurements of gas mixtures highly diluted with argon can be used for modeling practical gas systems. The stoichiometric hydrogen-air ignition delay time data of Slack (ref. 16) allows one to test the appropriateness of such an approach to kinetic modeling.

Slack measured ignition delay times for stoichiometric hydrogen-air over the temperature range 1450 to 850 K and at four pressures (2.0, 1.0, 0.5, and 0.27 atm). The comparison of the ignition delay times predicted by our proposed model and Slack's data is shown in figure 6. Ignition delay times were calculated with nitrogen and oxygen third-body efficiencies of 1.5 and 1.3. The best fit to the data was obtained for an efficiency of 1.3, which is the value recommended by Baulch (ref. 8). The model predictions are in good agreement with the data for the three highest pressures and for temperatures above 950 K. The disagreement between the model predictions and the 0.27-atm data is somewhat surprising. At this pressure ignition is determined by reactions (2), (3), and (7), which are all well known. It is believed that these data may be affected by either vibrational relaxation of nitrogen or the maximum test time behind very low pressure shock waves. The lack of agreement between the model predictions and the data below 950 K is the same behavior that Hitch reported (ref. 17). They studied three hydrogen-air kinetic mechanisms and found that all three models predicted longer delay times in this temperature region than Slack measured. This prompted us to inspect these data points more closely. Two observations became apparent. First, the 0.5- and 1.0-atm data do not show the large increase in delay time with small decrease in the temperature that are shown by Slack's 2.0-atm and our 1.1-atm data. Second, the longest delay times measured are about 1 msec. A possible explanation for this behavior is that these measured delay times are being affected by the maximum available test time.

The maximum test time behind a reflected shock wave is the time interval between shock reflection and the arrival of the reflected disturbance produced by the interaction between the reflected shock wave and the contact surface. This reflected disturbance can be either a shock wave or a rarefaction wave. Figure 3 shows that the reflected disturbance for our experimental setup is a shock wave. This shock wave can easily cause a reacting mixture to ignite. The maximum test time calculated for our test apparatus is 3.1 msec, which compares well with the average experimental value of 3.3 msec. For the apparatus used by Slack, we calculated a test time of 1.2 msec for a 15-ft test section and 1.0 msec for a 12-ft one. This makes it quite possible that his low-temperature data were affected by this disturbance and that these data points may not be a true indication of the ignition delay time.

Carbon Dioxide Chaperon Efficiency

The chaperon efficiency for carbon dioxide was determined by modeling the ignition delay times obtained for the hydrogen-oxygen mixture containing 10 percent carbon dioxide. The calculation with the detailed mechanism is a straightforward procedure, as the third-body efficiency of carbon dioxide is the only adjustable parameter. For completeness the reactions of carbon dioxide with H atoms and OH radicals must be added to the hydrogen-oxygen mechanism.

$$CO + OH \rightarrow CO + H \qquad (21)$$

$$CO + HO \rightarrow CO + OH \qquad (22)$$

Note that the rate constants actually used are for the reverse of these two reactions because they are better known. Model predictions for a chaperon efficiency of 1.0 for carbon dioxide showed that the CO_2 molecule was not inert. The delay times calculated were about 2 percent longer than those calculated for the hydrogen-oxygen mixture. This difference was produced by the slight inhibiting affect of reaction (21), which competes with reactions (2) and (4) for H atoms. The best fit to the hydrogen-oxygen-carbon dioxide data was for a chaperon efficiency of 7.0, which is shown in figure 7. The carbon dioxide chaperon efficiency of 7.0±0.2 relative to argon is in good agreement with the value of 7.3 found by Lewis and Von Elbe (ref. 18) and is slightly larger than the value of 5.0 recommended by Baulch (ref. 8). However, it is much smaller than the value of 14 relative to nitrogen or 21 relative to argon suggested by Stein. Model predictions for this value of the chaperon efficiency are shown in figure 7.

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TABLE I. - INITIAL MIXTURE COMPOSITION

Mixture	Hydrogen	Oxygen	Carbon dioxide	Argon
1	4.01	2.03		93.96
2	4.01	2.03	10.00	83.95

TABLE II. - IGNITION DELAY TIMES

(a) H_2 = 4.01 percent; O_2 = 2.03 percent; Ar = 93.96 percent

Temperature, K	Pressure, atm	Delay time, μsec
1316	1.272	107
1198	1.224	199.5
1147	1.264	259
1093	1.163	387
1072	1.125	516
1049	1.081	636
1049	1.081	607
1024	1.034	811
1000	1.089	1044
994	1.077	1067
998	1.065	1099
970	1.032	1285
962	1.107	1748
959	1.102	1763
956	1.060	1678
950	1.049	2021
948	1.078	1859
945	1.073	1983
932	1.044	2738
932	1.044	2622
929	1.039	2896

(b) H_2 = 4.01 percent; O_2 = 2.03 percent; Ar = 83.96 percent; CO_2 = 10.00 percent

Temperature, K	Pressure, atm	Delay time, μsec
1248	1.113	180
1243	1.034	180
1207	1.155	217
1146	1.115	320
1110	1.050	443
1073	1.127	480
1070	1.120	563
1067	1.170	564
1029	1.145	832
1026	1.113	817
1026	1.113	925
997	1.050	1363
996	1.101	1139
980	1.063	1588
969	1.109	2151
961	1.114	2292
955	1.124	2577

TABLE III. - HYDROGEN-OXYGEN REACTIONS

Reaction	Rate coefficient[a]				Reference
	Adjustment factor	A	n	E	
1 $OH + H_2 \leftarrow H_2O + H$	----	$2.1x10^{13}$	0	5 100	19
2 $H + O_2 \leftarrow OH + O$	1.2	$1.38x10^{14}$	0	16 400	20
3 $O + H_2 \leftarrow OH + H$	1.1	$2.96x10^{13}$	0	9 800	19
[b]4 $H + O_2 + M \leftarrow HO_2 + M$	0.95	$2.1x10^{18}$	-1.0	-------	23
5 $H_2 + M \leftarrow H + H + M$	----	$2.2x10^{14}$	0	96 000	8
6 $O_2 + M \leftarrow O + O + M$	----	$1.8x10^{18}$	-1.0	118 020	22
7 $H_2 + O_2 \leftarrow OH + OH$	2.0	$1.7x0^{13}$	0	48 150	10
[b]8 $H_2O + M \leftarrow H + OH + M$	----	$2.2x10^{16}$		105 140	8
9 $O + H_2O \leftarrow OH + OH$	----	$6.8x10^{13}$		18 365	8
10 $H + HO_2 \leftarrow H_2 + O_2$	----	$1.4x10^{13}$		-------	12
11 $O + HO_2 \leftarrow OH + O_2$	----	$5.0x10^{13}$		1 000	13
12 $H + HO_2 \leftarrow OH + OH$	1.2	$1.7x10^{14}$		1 070	12
13 $OH + HO_2 \leftarrow H_2O + O_2$	----	$8.0x10^{12}$		2 980	12
14 $H + HO_2 \leftarrow O + H_2O$	----	$1.7x10^{13}$		1 070	12
15 $H_2 + HO_2 \leftarrow H_2O_2 + H$	----	$6.0x10^{11}$		18 500	12
16 $OH + H_2O_2 \leftarrow H_2O + HO_2$	----	$6.1x10^{12}$		1 430	12
17 $HO_2 + HO_2 \leftarrow H_2O_2 + O_2$	----	$2.0x10^{12}$		-------	12
18 $H + H_2O_2 \leftarrow OH + H_2O$	----	$7.8x10^{11}$		-------	12
19 $M + H_2O_2 \leftarrow OH + OH$	1.2	$1.2x10^{17}$		45 510	12
20 $O + H + M \leftarrow OH + M$	----	$7.1x10^{18}$	-1.0	-------	1
21 $CO + OH \leftarrow CO_2 + H$	----	$4.17x10^{11}$	0	1 000	19
22 $CO + HO_2 \leftarrow CO_2 + OH$	----	$5.75x10^{13}$	0	22 930	21

[a] $k = AT^ne^{-E/RT}$ $cm^3mole^{-1}sec^{-1}$ or $cm^6mole^{-2}sec^{-1}$.

[b] Third body efficiencies relative to Ar = 1:
Reaction (4) $O_2 = N_2 = 1.3$; $H_2 = 3.5$; $CO_2 = 7.0$; $H_2O = 21.3$
Reaction (8) $O_2 = N_2 = H_2 = 4.2$; $H_2O = 16.7$; $CO_2 = 7.5$.

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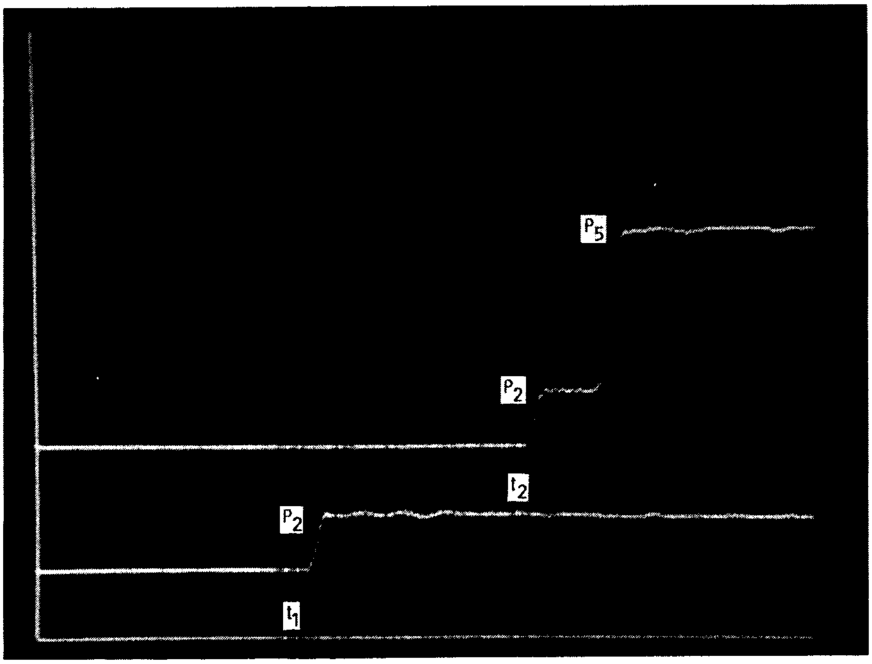

FIGURE 1. - SHOCK VELOCITY MEASUREMENT OF INCIDENT SHOCK WAVE. OUTPUT FROM QUATZ PRESSURE TRANSDUCERS LOCATED 83 AND 7 MM FROM THE END WALL. TIME FOR SHOCK WAVE TO TRAVEL 76 MM (t_1 TO t_2), 116.8 μSEC; TIME PER POINT, 0.2 μSEC

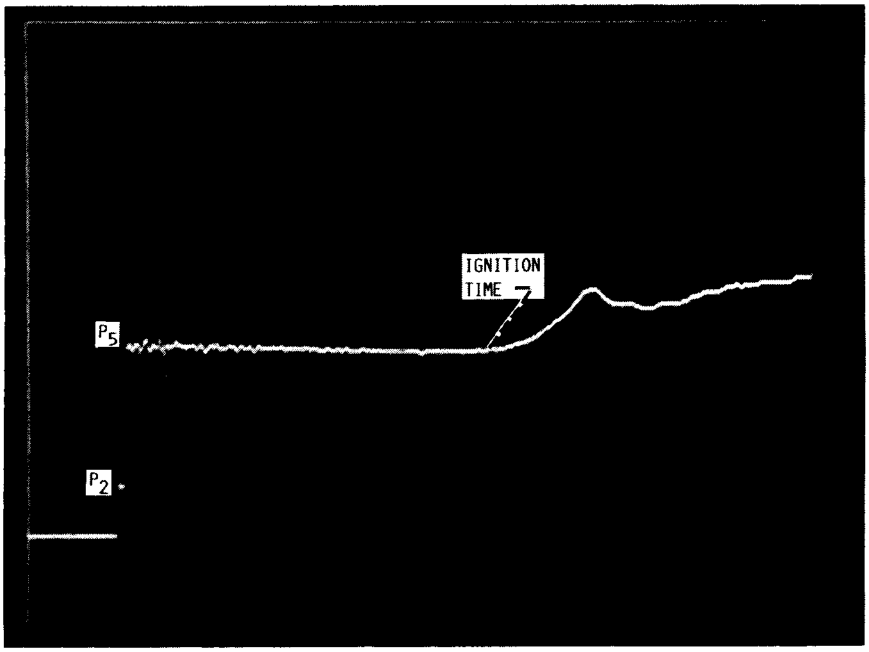

FIGURE 2. - IGNITION DELAY TIME MEASUREMENT BEHIND REFLECTED SHOCK WAVE. TIME ZERO IS THE TIME AT WHICH THE REFLECTED SHOCK ARRIVES AT THE FRONT EDGE OF THE PROBE (END OF P_2). IGNITION TIME IS MEASURED FROM TIME ZERO TO THE BEGINNING OF THE GRADUAL RISE IN PRESSURE; P_5 IS REFLECTED SHOCK PRESSURE.

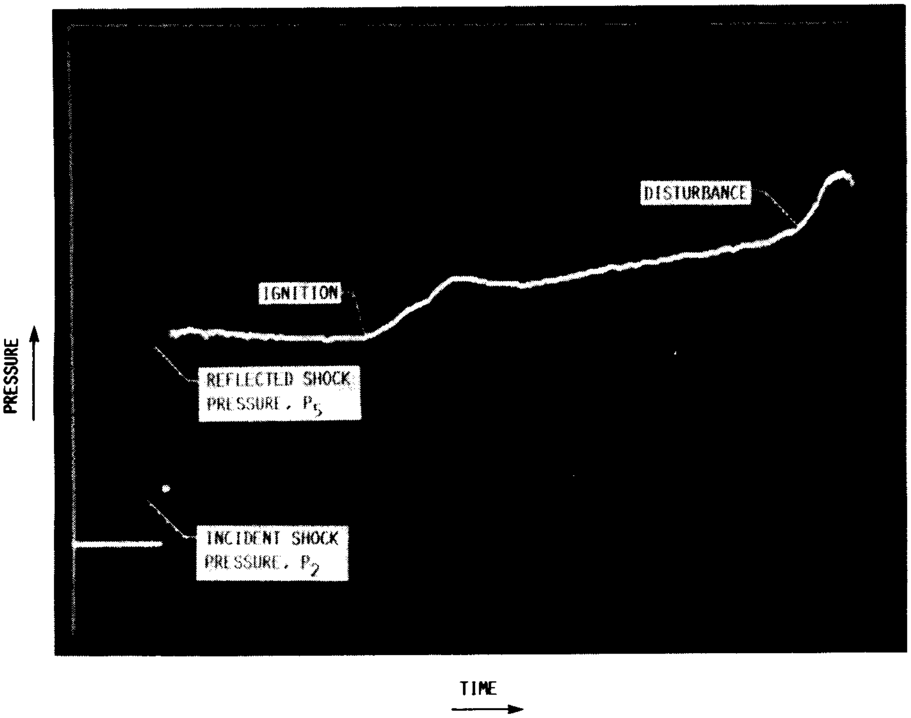

FIGURE 3. - MAXIMUM TEST TIME FOR EXPERIMENTAL SETUP. THE DISTURBANCE WHICH PROPAGATES INTO THE TEST GAS IS A SHOCK WAVE, WHICH RESULTED FROM THE INTERACTION BETWEEN THE REFLECTED SHOCK WAVE AND THE CONTACT SURFACE. MAXIMUM TEST TIME, 3.3 μSEC.

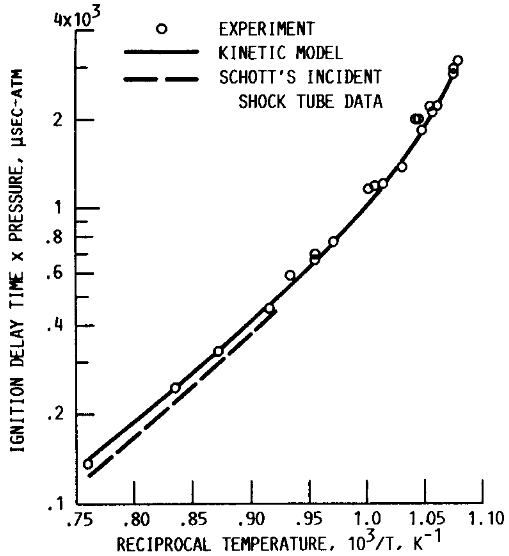

FIGURE 4. - PRODUCT OF IGNITION DELAY TIME AND PRESSURE PLOTTED VERSUS RECIPROCAL TEMPERATURE FOR 4 PERCENT H_2 - 2 PERCENT O_2 - 94 PERCENT AR MIXTURE.

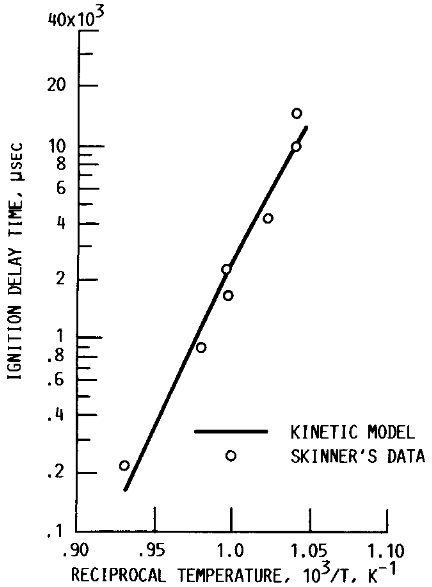

FIGURE 5. - IGNITION DELAY TIMES MEASURED BY SKINNER AT P = 5.0 ATM FOR 8 PERCENT H_2 - 2 PERCENT O_2 - 90 PERCENT AR MIXTURE.

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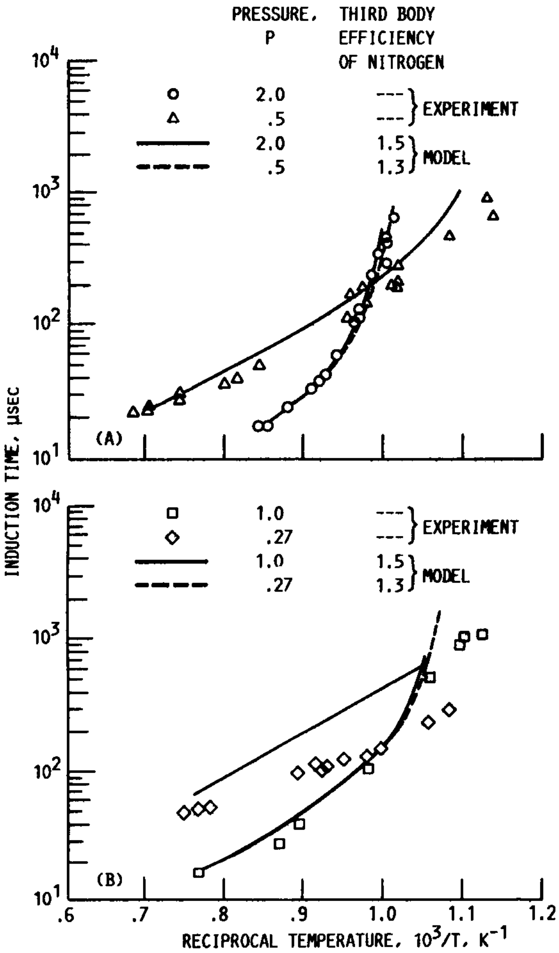

FIGURE 6. - COMPARISON OF KINETIC MODEL WITH STOICHIOMETRIC HYDROGEN-AIR IGNITION DELAY TIMES MEASURED BY SLACK.

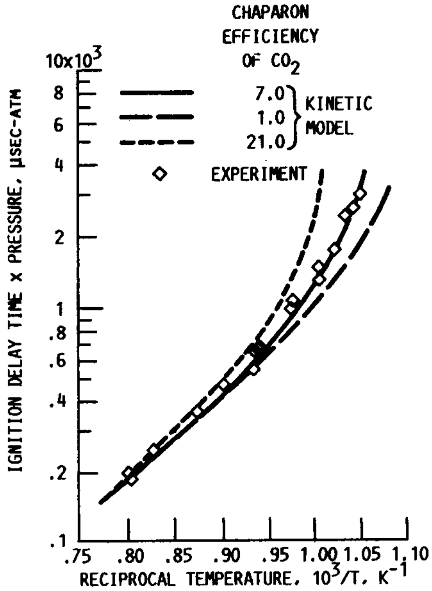

FIGURE 7. - PRODUCT OF IGNITION DELAY TIME AND PRESSURE VERSUS RECIPROCAL TEMPERATURE FOR 4 PERCENT H_2 - 2 PERCENT O_2 - 10 PERCENT CO_2 - 84 PERCENT AR MIXTURE. BEST FIT TO THE DATA BY THE KINETIC MECHANISM WAS FOR M(CO_2 = 7.0).

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16. Abstract

Ignition delay times for stoichiometric hydrogen-oxygen in argon with and without carbon dioxide have been measured behind reflected shock waves. A 20-reaction kinetic mechanism models the measured hydrogen-oxygen delay times over the temperature range 950 to 1300 K. The chaperon efficiency for carbon dioxide determined for the hydrogen-oxygen-carbon dioxide mixture was 7.0. This value is in agreement with literature values but much less than a recent value obtained from flow tube experiments. Delay times measured behind a reflected shock wave were about 20 percent longer than those measured behind incident shock waves. The kinetic mechanism successfully modeled the high-pressure data of Skinner and the hydrogen-air data of Slack. It is suggested that the lowest temperature points for the hydrogen-air data of Slack are unreliable and that the 0.27-atm data may illustrate a case where vibrational relaxation of nitrogen is important. The reaction pathway $HO_2 \rightarrow H_2O_2 \rightarrow OH \rightarrow H$ was required to model the high-pressure data of Skinner. The successful modeling of the stoichiometric hydrogen-air data demonstrated the appropriateness of deriving kinetic models from data for gas mixtures highly diluted with argon. The technique of reducing a detailed kinetic mechanism to only the important reactions for a limited range of experimental data may render the mechanism useless for other test conditions.

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Hydrogen/oxygen kinetics; Shock waves; Ignition delay times; Hydrogen/air; Modeling

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