Chemical Kinetic Analysis of Hydrogen-Air Ignition and Reaction Times

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JULY 1981
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SUMMARY

An analytical study of hydrogen-air kinetics has been performed as part of the scramjet engine research efforts at Langley Research Center. Calculations were made over a range of pressure from 0.2 to 4.0 atm, temperatures from 850 to 2000 K, and mixture equivalence ratios from 0.2 to 2.0. The finite-rate chemistry model included 60 reactions in 20 species of the H₂-O₂-N₂ system. The calculations also included an assessment of the effect of small amounts of the chemicals H₂O, NOₓ, H₂O₂, and O₃ in the initial mixture on ignition and reaction times as well as an assessment of the effect of the variation of the third-body efficiency of H₂O relative to N₂ in certain key reactions on reaction time.

The results indicate that for mixture equivalence ratios between 0.5 and 1.7, ignition times are nearly constant; however, the presence of H₂O and NO can have significant effects on ignition times, depending on the mixture temperature. Reaction time is dominantly influenced by pressure but is nearly independent of initial temperature, equivalence ratio, and the addition of chemicals. Effects of kinetics on reaction at supersonic combustor conditions are discussed, and recommendations are made for further experimental studies of rate constants for key reactions.

INTRODUCTION

The study of the fluid dynamics and combustion processes of hydrogen-fueled supersonic combustion ramjets (scramjets) has been a major part of the hypersonic propulsion research program at Langley Research Center. Most of these studies have been, of necessity, experimental investigations of the overall effects of fuel injection, mixing, and reaction on the flow in subscale engine components. This dependence on empirical results is due to the complexity of the flow around fuel injectors in three-dimensional geometries, which are not readily treated analytically. Most numerical solutions are restricted to two- or three-dimensional parabolic flow with equilibrium or simple finite-rate chemistry models of the H₂-air system. Such numerical solution schemes are applicable only in the parabolic flow region well downstream of the disturbance caused by the transverse fuel injection. Scramjet combustors rely on transverse injection of the fuel in order to achieve rapid mixing and reaction. To begin the calculation therefore requires a prior knowledge of the extent of fuel mixing, ignition, and reaction.

All this information, particularly the ignition-reaction state, may not even be available from experimental data because of the difficulty of freezing the reaction in a sample extracted by a probe from the high-velocity, high-temperature combustor flow. In spite of these problems, however, a sufficient data base has been established to define a scramjet engine concept and to permit fabrication of subscale engine models with integrated inlet, combustor, and nozzle components. The current scramjet is designed for operation over a
flight Mach number range from 4 to 7. The corresponding stagnation tempera-
tures of the captured air are 900 K and 2200 K, respectively, which should be
sufficient for autoignition of hydrogen in the separated flow regions near
fuel injectors. In recent ground tests of subscale engine models (ref. 1),
however, problems were encountered in obtaining ignition and sustaining reac-
tion at test conditions for which ignition and reaction might have been
expected. The need to better understand the chemical mechanism of the igni-
tion and reaction of H₂-air mixtures at conditions typical of a scramjet comb-
bustor led to this study.

The present analytical study uses a computer program (refs. 2 and 3) for
solving chemical kinetics problems in one-dimensional flow, with an H₂-O₂-N₂
finite-rate chemistry model consisting of 60 reactions involving 20 species.
The calculations covered a range of pressures from 0.2 to 4 atm, a range of
temperatures from 850 K to 2000 K, and H₂-air mixtures between 0.2 and 2.0
times the stoichiometric value. In addition, the effects of contaminants such as
NOₓ and H₂O, which may be present in the high-temperature test gases used
in ground test facilities, were investigated. Significant concentrations of
NOₓ molecules are produced in facilities which use an electric arc to heat the
test air; H₂O is produced in combustion-heated facilities as a result of burn-
ing hydrogen in air enriched with oxygen so that the airlike products have the
proper oxygen mole fraction. (In the latter facilities, the test gas product
is sometimes referred to as "vitiated" air.) The effects on ignition times of
potential ignition aids such as H₂O₂ and O₃, which may be added to ground test
facilities, were also considered. In addition, O₃ is naturally encountered in
high-altitude (>30 km) flight. Because the computer program is one-
dimensional, the effects of fuel injection and mixing cannot be included.
However, the present finite-rate calculations of premixed H₂-air flows are
considered important in predicting ignition and reaction in the recirculating
zones near the fuel injectors. In analysis of scramjet combustors, where the
reaction may be limited by the mixing, these results for premixed reactants
provide a lower limit of the times required for reaction.

Many other analytical studies of the chemical kinetics of the H₂-air
system, including vitiated air, have been conducted (e.g., refs. 4 to 19).
However, many of the problems encountered in scramjet testing have not been
addressed explicitly. These include ignition and reaction at low tempera-
tures; varying amounts of water in the vitiated-air test gas; and realistic
equilibrium concentrations of oxygen and hydrogen atoms, hydroxyl free rad-
cals, and oxides of nitrogen in the test stream. For example, in the vitiated
test gas of a ground test facility at conditions representative of Mach 4 and
Mach 7 flight, water mass fractions are about 0.05 and 0.23, respectively. In
an arc-heated facility, NOₓ mass fractions may range between 0.01 and 0.03.
In some of these previous calculations, the chemistry models were too simple
to be applied at low-temperature or high-pressure conditions. In some refer-
ces, the reaction-rate constants were either estimated, because of a lack of
data, or they were approximated from early data that precede the survey by
Baulch et al. in references 20 and 21. This survey (refs. 20 and 21) along
with more recent data (ref. 15) was used to update the rate constants of the
H₂-air mechanism.
The purpose of the present one-dimensional calculations is to define the conditions at which chemical kinetics are important in future ground tests of subscale scramjet-engine models and in analyses of the combustor flow using more sophisticated computer codes. The present calculations include (1) the effects of initial temperature, initial pressure, and the equivalence ratio (degree of stoichiometry) of the H2-air mixture on the ignition and reaction; (2) the effects of contaminants such as H2O, OH, H, and O present in an equilibrium vitiated test gas; (3) the effects of NOx on ignition at low temperature; (4) the effects of H2O2 and O3 used to promote ignition in ground test facilities and the effect of atmospheric O3 that may be encountered in scramjet flight; and (5) the sensitivity of ignition and reaction to the reaction rates of dominant reactions.

SYMBOLS

A

area, m^2

A_j

preexponential constant in rate-constant equation (eq. (19)), \( \text{cm}^3\text{-mol}^{-1}\text{-s}^{-1} \) or \( \text{cm}^6\text{-mol}^{-2}\text{-s}^{-1} \)

a

species production function (eq. (11))

B_j

activation energy in rate-constant equation (eq. (19))

b

enthalpy production function (eq. (12))

(Cp)_i

molar heat capacity of species \( i \), J-mol\(^{-1}\)-K\(^{-1}\)

C_p

specific heat at constant pressure, J-g\(^{-1}\)-K\(^{-1}\)

f, f*

local and stoichiometric hydrogen-to-oxygen mass ratios

H_i

molar enthalpy of species \( i \), J-mol\(^{-1}\)

h

total-mixture static enthalpy per unit mass, J-g\(^{-1}\)

h_c

total-mixture energy per unit mass, J-g\(^{-1}\)

K_j

equilibrium constant

k_{bj}

backward reaction-rate constant

k_j

forward reaction-rate constant

l

number of chemical reactions

M

Mach number; third-body species in certain reactions

M_j

third-body efficiency factor defined by equation (25)

(MW)_i

molecular weight of species \( i \), g-mol\(^{-1}\)
\( m \) mass flow rate, g-s\(^{-1}\)

\( m_{i,j} \) third-body efficiency factor of species \( i \) in reaction \( j \) (see eq. (26))

\( N \) number of species in gas mixture

\( n_j \) temperature exponent in rate-constant equation (eq. (19))

\( P \) pressure, atm (1 atm = 101.325 kPa)

\( R \) universal gas constant, 1.987 cal-mol\(^{-1}\)-K\(^{-1}\) (1 cal = 4.184 J)

\( s_i \) species \( i \) (eq. (18))

\( T \) temperature, K

\( t \) time, s

\( u \) velocity, m-s\(^{-1}\)

\( W_i \) net species production rate (eq. (21))

\( W_m \) mixture molecular weight, g-mol\(^{-1}\)

\( \alpha_i \) mass fraction of species \( i \)

\( \Gamma \) ratio of reaction times

\( \gamma \) specific-heat ratio

\( \lambda \) ratio of ignition times

\( \nu_{ij} \) forward stoichiometric coefficient in general reaction (eq. (18))

\( \nu'_{ij} \) reverse stoichiometric coefficient in general reaction (eq. (18))

\( \rho \) density, kg-m\(^{-3}\)

\( \sigma_i \) concentration of species \( i \), moles per unit mass of mixture, mol-g\(^{-1}\)

\( \tau_{ig} \) ignition time, s

\( \tau_R \) reaction time, s

\( \tau_{TR} \) total reaction time, s
The computer program used for this analysis of a complex reacting gas mixture flowing through an arbitrarily assigned area employs the conservation equations for one-dimensional steady-state flow. The flow is assumed to be isobaric, premixed, inviscid, and adiabatic. Additional information about these equations and the numerical integration procedure used in the computer code may be found in references 2 and 3. The equations employed are:

**Global mass conservation**

\[ \rho Au = \dot{m} \]  \hspace{1cm} (1)

**Continuity for each of the \( N \) species in the mixture**

\[ \frac{d}{dt} (\sigma_i \dot{m}) = W_i Au \]  \hspace{1cm} (i = 1, 2, \ldots, N)  \hspace{1cm} (2)

where \( \sigma_i \) is the concentration of species \( i \), in moles per unit mass of the mixture, and \( W_i \) is the species production rate. Expanding the differentiation of equation (2), using equation (1), and noting that \( \frac{d\dot{m}}{dt} = 0 \) reduces the equation to
\[ \frac{d\alpha_i}{dt} = \frac{W_i}{\rho} \quad (i = 1, 2, \ldots, N) \quad (3) \]

**Conservation of momentum**

\[ \rho \frac{du}{dt} + \frac{1}{u} \frac{dp}{dt} = 0 \quad (4) \]

**Conservation of energy**

\[ h + \frac{u^2}{2} = h_c \quad (5) \]

where \( h_c \) is the total constant energy per unit mass of the gas and the mixture molecular weight is defined as

\[ W_m = \left[ \sum_{i=1}^{N} \frac{1}{\sigma_i} \right]^{-1} \quad (6) \]

**Equation of state**

\[ p = \frac{\rho RT}{W_m} \quad (7) \]

By use of equations (1) to (7), the following differential equations can be derived, with time \( t \) the independent variable:

\[ \frac{du}{dt} = \frac{u}{M^2 - 1} \left( \frac{1}{\bar{A}} \frac{d\bar{A}}{dt} - a \right) \quad (8) \]

\[ \frac{dp}{dt} = -p \left[ \frac{M^2}{M^2 - 1} \left( \frac{1}{\bar{A}} \frac{d\bar{A}}{dt} - a \right) + a \right] \quad (9) \]
\[
\frac{dT}{dt} = -T \left[ (\gamma - 1)M^2 \left( \frac{1}{A} \frac{dA}{dt} - a \right) + b \right]
\]  

(10)

where

\[
a = \frac{RT}{p} \sum_{i=1}^{N} W_i - b
\]  

(11)

and

\[
b = \frac{1}{p} \frac{\gamma - 1}{\gamma} \sum_{i=1}^{N} h_i W_i
\]  

(12)

Other parameters used in these equations are defined as follows:

\[
M^2 = \frac{u^2 w_m}{\gamma RT}
\]  

(13)

\[
\gamma = \frac{c_p}{c_p - (R/W_m)}
\]  

(14)

\[
c_p = \sum_{i=1}^{N} c_i (C_i)
\]  

(15)
\begin{equation}
    h = \sum_{i=1}^{N} \sigma_i H_i
\end{equation}

\begin{equation}
    H_i = (H_i)_T + \int_{T_r}^{T} (C_p)_i \, dT
\end{equation}

Equations (3) and (8) to (10) form a system of \( N + 3 \) equations in \( N + 3 \) unknowns. This equation system is solved by numerically integrating with time for a specified area distribution. The equation set for a specified pressure distribution and for the passage of a normal shock through the gas is given in reference 2.

Chemical Reaction Equations

Each chemical reaction can be written in the general form

\begin{equation}
    \sum_{i=1}^{N} \nu_{ij} s_i \rightarrow \sum_{i=1}^{N} \nu'_{ij} s_i
\end{equation}

where \( s_i \) represents the \( i \)th species. The forward reaction rate is given by

\begin{equation}
    k_j = A_j T^{n_j} \exp(-B_j/RT)
\end{equation}

The backward reaction rate is determined from \( k_j \) and the equilibrium constant \( K_j \):

\begin{equation}
    k_{bj} = \frac{k_j}{K_j}
\end{equation}

The rate of formation of each species \( W_i \) which appears in equation (3) is defined as
\[ W_i = \sum_{j=1}^{k} \omega_{ij} \]

where

\[ \omega_{ij} = \rho^2 (v'_{ij} - v_{ij}) \psi_j \]

is the net rate of formation of species \( i \) by reaction \( j \). The parameter \( \psi_j \) is the net reaction conversion rate introduced in reference 2 as an indication of the amount of change due to each reaction that occurs in the mixture. The form of \( \psi_j \) depends on the type of reaction. Three types of reversible chemical reactions are considered in the computer program:

**Type 1 - Bimolecular shuffle reaction**

\[
s_1 + s_2 \rightarrow s_3 + s_4
\]

with

\[
\psi_j = k_j \left( \sigma_1 \sigma_2 - \frac{\sigma_3 \sigma_4}{k_j} \right)
\]

**Type 2 - Three-body recombination**

\[
M + s_1 + s_2 \rightarrow s_3 + M
\]

(where \( M \) can be any species present) with

\[
\psi_j = k_j \sigma_1 \sigma_2 (\rho - \frac{\sigma_3}{k_j})
\]

In this equation, \( M_j \) is the third-body efficiency factor for the \( j \)th reaction defined as
\[ M_j = \sum_{i=1}^{N} m_{i,j} s_i \]  \hspace{2cm} (25)

and \( m_{i,j} \) is the third-body efficiency factor for species \( i \) in reaction \( j \). This factor is a correction to the preexponential factor \( A_j \) in the rate equation (19) and can be written as

\[ m_{i,j} = \frac{(A_j)_{s_i}}{(A_j)_r} \]  \hspace{2cm} (26)

where \((A_j)_r\) is the value of \( A_j \) for a reference species as third body. For the calculations presented in this paper, all third-body efficiencies are referenced to \( N_2 \). Except as listed at the bottom of table I, all third-body efficiencies are 1.0.

**Type 3 - Two-body dissociation**

\[ M + s_3 \rightarrow s_1 + s_2 + M \]

with

\[ \psi_j = k_j M_j \left( \sigma_3 - \frac{\sigma_1 \sigma_2}{K_j} \right) \]  \hspace{2cm} (27)

For some problems the heat release is an important consideration. In these situations a useful quantity is the net energy conversion rate for the \( j \)th reaction defined as

\[ (\psi_{H})_j = \psi_j (\Delta H_{298})_j \]  \hspace{2cm} (28)

where \((\Delta H_{298})_j\) is the molar heat of reaction at 298 K for the \( j \)th reaction proceeding in the forward direction, from left to right.
Computer Program

The computer program for solving the one-dimensional flow with finite-rate chemical reactions was first presented in reference 2. The system of conservation equations and chemical reactions form a nonlinear, coupled set of differential equations, which are solved by the Adams implicit method (ref. 22). A later modification of the computer code (ref. 3) added the stiffly stable, linear, multistep method of Gear (ref. 23). The incorporation of the Gear method into the program provides a solution technique that is a highly efficient means of altering step size to obtain a stable rapid solution to the large system of stiff equations. This is of particular advantage when the number of chemical species is greater than 15.

Input to the computer program is user oriented. This allows for easy modification to the chemical reaction system, reaction-rate parameters, thermodynamic properties (ref. 24) and general problem specification. Additional details of the input specifications are given in reference 3.

Scope of Present Calculations

The objective of the present study is to parametrically examine the ignition and reaction times of H2-air mixtures at conditions representative of scramjet combustor flows. The ignition time, also known as ignition delay or induction time $T_{ig}$, is the time required for the rapid buildup of the free radicals and atoms with very little heat release. Three definitions of ignition time have been used in previous research: (1) the time for the concentration of OH to reach $5 \times 10^{-9}$ mol/cm$^3$, (2) the time at the end of the constant exponential growth of OH mass fraction, and (3) the time taken to reach a temperature at ignition $T_{ig}$ of

$$T_{ig} = 0.05(T_{eq} - T_o) + T_o$$  \hspace{1cm} (29)

The ignition time given by definition (1) was used only for comparison with the experimental data of reference 15. It was observed that the ignition times given by definitions (2) and (3) are approximately the same over a wide range of pressure and temperature. The ignition-time results from these calculations are therefore presented using equation (29). The total reaction time $T_{TR}$ is defined as the time taken to reach a temperature $T_{TR}$ where

$$T_{TR} = 0.95(T_{eq} - T_o) + T_o$$  \hspace{1cm} (30)

Reaction time is then defined as

$$\tau_R = T_{TR} - T_{ig}$$  \hspace{1cm} (31)
Chemistry model.- The chemical reaction model, given in table I, consists of 60 (r = 60) reactions involving 20 (N = 20) species:

\[
\begin{array}{cccccccc}
O_2 & N_2 & H_2 & O & N & H \\
H_2O & OH & H_2O_2 & NO & NO_2 \\
CO & CO_2 & HNO & HNO_2 & HNO_3 \\
H_2O_2 & O_3 & HCO & Ar \\
\end{array}
\]

Reaction-rate data were taken from references 14, 20, 21, and 25 to 32. These data are some of the latest available for the hydrogen oxidation mechanism and provide improvements to the reaction-rate parameters and third-body efficiency factors for certain key reactions such as

\[
H + O_2 + M \rightarrow HO_2 + M \\
NO + HO_2 \rightarrow OH + NO_2 \\
\]

and

\[
H + OH + M(H_2O) \rightarrow H_2O + M(H_2O)
\]

The impact of the reaction rates and third-body efficiencies of these reactions on ignition and reaction is discussed in the section "Reaction Time."

Parameter variation.- The principal parameters of these calculations are the initial static pressure and temperature and the hydrogen-air mixture composition. Static pressures were varied between 0.2 and 4.0 atm; static temperatures between 850 and 2000 K. The amount of hydrogen in the initial mixture was varied corresponding to equivalence ratios between 0.2 and 2.0. The equivalence ratio \( \phi \) is an indication of the relative stoichiometry of the mixture based on the global reaction for the oxidation of hydrogen:

\[
2H_2 + O_2 \rightarrow 2H_2O
\]

For this reaction the stoichiometric mass ratio of hydrogen to oxygen is

\[
\phi^* = \frac{(\text{moles } H_2)(\text{MW})_{H_2}}{(\text{moles } O_2)(\text{MW})_{O_2}} = \frac{2(2.016)}{1(32)} = 0.126
\]

For an arbitrary mixture of hydrogen and air (or other species) with a mass ratio of hydrogen to oxygen \( f \), the equivalence ratio is defined as
Most of the calculations were made for $\phi = 1.0$.

Chemical additives and contaminants.- In addition to the variation in the state properties, the composition of the air was varied to study the effects of contaminants ($H_2O, NO_x$) present in ground test facilities and chemical additives ($H_2O_2, O_3$) used as potential ignition aids in ground tests of sub-scale scramjet engines. In order to simulate the combustor conditions of a scramjet at Mach 4 to Mach 7 flight, it is necessary to heat the air in ground test facilities. One way to produce a high-temperature test gas is to burn hydrogen in oxygen-enriched air. The test gas produced by such a combustion heater facility (ref. 33) is often referred to as vitiated air, since it has the same oxygen mole fraction as air but is contaminated by a significant concentration of water vapor. The amount of $H_2O$ present in the vitiated test gas is directly related to the desired stagnation temperature (or flight Mach number) that is simulated. For this analysis, the following values of water mass fractions are assumed to form a consistent set with each of the initial temperatures:

<table>
<thead>
<tr>
<th>$T_0, K$</th>
<th>910</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>&gt;1300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{H_2O}$</td>
<td>0.097</td>
<td>0.125</td>
<td>0.145</td>
<td>0.20</td>
<td>0.245</td>
</tr>
</tbody>
</table>

Whereas previous analyses have accounted for vitiation effects by arbitrarily varying the concentration of $H_2O$ and OH free radicals at the same initial temperature, the consistent pairs of water mass fractions and initial temperatures used in the calculations here provide a more realistic means of assessing the effects of vitiated air on ignition and reaction.

Another scramjet ground test facility (ref. 1) uses an electric arc to heat the air and produces significant amounts of nitrogen oxides $NO$ and $NO_2$. It has been estimated that this facility produces total $NO_x$ mass fractions of about 0.01 and 0.03 at conditions simulating Mach 4 and Mach 7 flight, respectively. Calculations were made to ascertain the effects of $NO$ and $NO_2$ mass fractions of 0.01 on the ignition times of the $H_2$-air mixtures.

In addition, the effects of free radicals that may be present in the test gas as a result of dissociation at the high temperatures were examined. The amount of each free radical present was determined by assuming that the air or vitiated air of the mainstream test gas was in chemical equilibrium at the initial pressure and temperature. Thus, for calculations of $H_2$ in equilibrium air, small amounts of $O$, $NO$, and $NO_2$ were included in the initial mixture. For $H_2$ in equilibrium vitiated air, small amounts of $O$, $H$, $OH$, $HO_2$, $NO$, and $NO_2$ were included in the initial mixture. In the following discussion, the results obtained with equilibrium free-stream (EFS) mixtures are referred to.
as H₂-air (EFS) and H₂-vitiated air (EFS) to denote hydrogen mixed with equilibrium air and equilibrium vitiated air, respectively. In the vitiated-air facility, the test gas would likely be in equilibrium at the local temperature and pressure at the combustor entrance. However, the arc-heater facility would produce high levels of NOₓ (mass fractions of 0.01 to 0.03) that would freeze as the flow expanded through the facility nozzle, so that a true equilibrium would not be obtained.

The effect of small amounts (mass fractions of 0.01) of H₂O₂ and O₃ on ignition was examined to assess their potential as ignition aids in ground tests. Calculations were also made with an O₃ concentration of 10 ppmw to approximate the atmospheric levels encountered in flight at an altitude of 30 km. Maximum O₃ concentration in the atmosphere is about 13.5 ppmw at 36 km (ref. 34).

RESULTS AND DISCUSSION

The one-dimensional kinetics computer code (refs. 2 and 3) previously described was used to calculate ignition and reaction times for the range of parameters indicated. Typical output of the computer code is presented in figure 1 in the form of the time variation of species mass fractions through the ignition and reaction zones. Results are given for a stoichiometric H₂-air mixture at an initial temperature of 1000 K and at initial pressures of 0.5 and 2.0 atm in figures 1(a) and 1(b), respectively, and for a stoichiometric mixture of H₂ in equilibrium vitiated air at T₀ = 1000 K and P₀ = 1 atm in figure 1(c). The times of ignition and total reaction are noted on each figure by Tᵢg and T_TR, respectively. The effect of increased pressure to shorten reaction time can be seen by the much smaller difference between T_TR and Tᵢg in figure 1(b), at 2.0 atm, when compared with the difference indicated in figure 1(a), at 0.5 atm.

Ignition Times

The effects of initial pressure and temperature on ignition time of a stoichiometric H₂-air mixture are presented in figures 2(a) and 2(b), respectively. Because of the widespread use of ignition times from reference 4, Tᵢg results as given by reference 4 are plotted for comparison as dashed lines in figure 2(a). In contrast to the constant slope with pressure of the reference 4 ignition times, the present results indicate a drastic nonlinearity in the pressure dependence, particularly at values of T₀ below 1100 K. At T₀ above about 1200 K, the present results indicate a slight retardation of ignition times relative to those given in reference 4. The constant-pressure curves of Tᵢg as a function of the reciprocal temperature in figure 2(b) indicate very long ignition times as T₀ decreases. These effects produced by the present chemical mechanism are primarily due to the formation of the HO₂ molecule through the reaction H + O₂ + N₂ → HO₂ + N₂, which was not included in the kinetics model of reference 4. This reaction is a chain...
terminating reaction which depletes H atoms. Because it is a three-body reaction, it should become more important at higher pressures. Since the reaction rate is weakly dependent on temperature, this reaction is important at low temperatures, where the chain carrier reactions are slower.

The sensitivity of ignition times to the fuel equivalence ratio was checked for H$_2$-air and H$_2$-vitiated air at 1200 K and 1.0 atm. Results of these calculations are given in figure 3 along with previous results for H$_2$-air from references 8, 16, and 19. Also included in figure 3 are data for 1111 K and 1389 K taken from reference 18 in the format presented in reference 17. The present ignition times agree reasonably well with the referenced results, a spread of about 20 percent in $\tau_{ig}$ occurring for $\phi$ between 0.5 and 1.7. In comparison with the data, the present predictions of ignition time at 1200 K show the same trend with increasing $\phi$ and fall between the data for 1111 K and 1389 K. For both H$_2$-air and H$_2$-vitiated air, ignition times predicted by the present chemistry model exhibit only a ±10 percent variation for $\phi$ in the range from 0.5 to 1.7, although the ignition times for H$_2$-vitiated air are longer than for H$_2$-air by about 20 percent. This result supports the conclusion of reference 4 that $\tau_{ig}$ is constant for $\phi$ between 0.4 and 2.0.

In order to test the correctness of the ignition times predicted by the present chemistry model, the theoretical results have been compared with stoichiometric H$_2$-air shock-tube data from reference 15. These comparisons are presented in figure 4(a) for initial pressures of 0.5 and 2.0 atm and in figure 4(b) for initial pressures of 0.27 and 1.0 atm. The agreement between theory and data is quite good, except for $p = 0.27$ atm in figure 4(b). The authors of reference 15 reported that these low-pressure data were the least reliable because of boundary-layer growth in the shock tube.

A cross plot of these reference 15 data at $T_o = 1000$ K is given in figure 5 with theoretical predictions from references 4 and 14 and the present calculations for comparison. The present results agree well with the data except at the low-pressure ($p = 0.27$ atm) datum. The theory of reference 14 includes a sophisticated chemistry model with 25 reactions. It includes hydroperoxyl (HO$_2$) and hydrogen peroxide (H$_2$O$_2$) molecules and shows the proper trend, although it does not agree with the data. Since the chemistry model of reference 4 did not include the HO$_2$ reactions, it would not be expected to agree with the data at high pressures (>1.0 atm), where the HO$_2$ molecule becomes important. The linear relation between $\tau_{ig}$ and $p$ of reference 4 does, however, agree with the data in the narrow range of pressures between 0.5 and 1.0 atm at $T_o = 1000$ K.

Effect of vitiated air.— Some scramjet ground test facilities (ref. 33) rely on the combustion of H$_2$ to produce the desired high-temperature test gas. Because the resulting vitiated-air test gas is contaminated with high concentrations of H$_2$O, the effect of this contaminant and its dissociation products on ignition times has been examined. A comparison of ignition times for stoichiometric H$_2$-air (EFS) and H$_2$-vitiated air (EFS) is presented in figure 6. In figure 6(a), in which the effect of $T_o$ on the variation of $\tau_{ig}$ with $p$ is presented, it can be seen that at $T_o$ less than 1100 K and $p_{ig}$ greater than 0.2 atm, the presence of H$_2$O in the vitiated test gas retards
ignition, particularly at the lower value of $T_o$. At temperatures above 1200 K, the effect of the vitiation is to enhance ignition. The reason for the longer ignition time at $T_o < 1100$ K is that in a vitiated-air stream, the production of $\text{HO}_2$ is accelerated by the reaction $\text{H} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$ because the third-body efficiency of $\text{H}_2\text{O}$ may be as much as 13 times that of $\text{N}_2$. Although some OH radicals are present in the free stream, the foregoing reaction tends to deplete H atoms, an important chain carrier in the ignition region, and cause an increase in ignition times.

At temperatures above 1200 K, ignition is enhanced by the dissociation of $\text{H}_2\text{O}$ in the vitiated free stream and the resulting production of OH radicals, whose concentration ($10^{-5}$ to $10^{-3}$ by mass) is significantly greater than the mass concentration of O and H atoms. The curves of $\tau_{ig}$ versus reciprocal temperature ($1000/T_o$) at constant $p$ in figure 6(b) also illustrate the effect of a vitiated free stream on ignition times. Other calculations (refs. 7 and 16) exhibit similar effects at low $T_o$ over a limited pressure range. Therefore, at low initial temperatures, the ignition characteristics observed in ground tests of scramjet combustors using a vitiated stream are longer than those for tests with air at similar conditions. At the higher initial temperatures, the ignition times are shorter with a vitiated stream.

Effect of equilibrium free stream.—Figure 6 compares the difference between air and vitiated-air free streams when both are in chemical equilibrium. The effect on $\tau_{ig}$ of the free radicals produced by the dissociation of $\text{H}_2\text{O}$ in the vitiated air at chemical equilibrium can be seen from the curves in figure 7. This comparison is made for $\phi = 1.0$ at $T_o = 1300$ K. For $\text{H}_2$-air (solid lines), the presence of O and NO in an EFS ($q_o = 1.3 \times 10^{-8}$, $q_{\text{NO}} = 4 \times 10^{-4}$) has little effect on the ignition times. For the $\text{H}_2$-vitiated air (dashed lines), in which $q_{\text{H}_2\text{O}} = 0.245$, the assumption of EFS at $T_o = 1300$ K produces OH, O, H, and NO ($q_{\text{OH}} = 1.5 \times 10^{-5}$, $q_o = 6 \times 10^{-8}$, $q_H = 1 \times 10^{-11}$, $q_{\text{NO}} = 3.5 \times 10^{-4}$), which reduce ignition times by about 40 percent. Note that for the vitiated air in which the $\text{H}_2\text{O}$ is not dissociated (not in equilibrium), the values of $\tau_{ig}$ for these conditions are larger than for air. These comparisons suggest that care must be exercised when applying theoretical results to insure that the effects of vitiation are properly accounted for. The investigation reported in reference 35 emphasized the necessity of considering free radicals when comparing theory with combustion data for parallel $\text{H}_2$ injection into a vitiated test stream. Reference 8 also indicated a sensitivity of $\tau_{ig}$ to the amounts of H, O, and OH.

Effect of $\text{H}_2\text{O}$.—The presence of $\text{H}_2\text{O}$ in vitiated air has been shown to strongly affect calculated ignition times, particularly at initial temperatures of 1000 K or less. The magnitude of the effect depends on (1) the amount of $\text{H}_2\text{O}$ present in the initial mixture and the corresponding amounts of free radicals such as OH present in an equilibrium free stream, and (2) the third-body efficiency of $\text{H}_2\text{O}$ through its effect on the rate of reaction of $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. Graphical representations of these two influences are presented in figures 8 and 9, respectively. In figure 8, the sensitivity of $\tau_{ig}$ to mass fractions of $\text{H}_2\text{O}$ of 0 (air), 0.145, and 0.245 in an initial mixture at $T_o = 1000$ K, is presented for conditions of EFS (dashed lines) and
with H2O only (solid lines). At a pressure of 0.2 atm the calculated ignition times for all cases range over ±20 percent; however, as the pressure is increased to 1.0 atm, the presence of H2O alone tends to increase $\tau_{ig}$ by a factor of up to 10 for $\alpha_{H2O} = 0.145$ and up to 30 for $\alpha_{H2O} = 0.245$. This increase in $\tau_{ig}$ is due to the depletion of H atoms by the previously mentioned hydroperoxyl (HO2) chain terminating reaction. When equilibrium free stream is used, the ignition times are reduced as pressure increases to 1.0 atm by a factor of about 3, relative to the case with H2O only. This reduction is due to the increased levels of OH.

The sensitivity of ignition times to the third-body efficiency of H2O, i.e., $m_{H2O,4}$ in the reaction $H + O_2 + M \rightarrow HO_2 + M$ at $T_o = 1000$ K is presented in figure 9. The computer program currently uses a value $m_{H2O,4} = 13$ relative to the third-body efficiency of N2. A change in $m_{H2O,4}$ in the preceding reaction causes a corresponding change in the rate of the reaction with H2O as the third body. The effect of increasing and decreasing $m_{H2O,4}$ by a factor of 2 is illustrated in figure 9 for vitiated air (EFS) with $\alpha_{H2O} = 0.145$ at $T_o = 1000$ K. Also shown is the case for air (EFS) with no H2O. At pressures near 0.2 atm, the presence of H2O with its high third-body efficiency has little effect on $\tau_{ig}$ values. As the initial pressure approaches 1.0 atm, the calculated ignition times show a large sensitivity to the value of $m_{H2O,4}$: doubling $m_{H2O,4}$ increases $\tau_{ig}$ by a factor of 10 at 1 atm; halving $m_{H2O,4}$ reduces $\tau_{ig}$ by a factor of 2 and gives values of $\tau_{ig}$ near those of H2-air (EFS). These results emphasize the importance of knowing the efficiency of H2O relative to N2 in modeling the chemistry and in predicting ignition times of H2 in a vitiated air stream at static temperatures of 1000 K or less and pressures near 1.0 atm.

The sensitivity of ignition times to varying concentrations of NO is presented in figure 10 for H2-air and H2-vitiated air at $T_o = 910$ K. For H2-air in figure 10(a) at low pressures (near 0.2 atm), a concentration of NO of as much as 0.01 by mass has little effect on the ignition time, causing a reduction of less than 20 percent in $\tau_{ig}$ for pure air. As the initial pressure approaches 1.0 atm, however, an NO mass fraction of 0.01 reduces $\tau_{ig}$ by a factor of 50. For an NO mass fraction of $10^{-5}$ (10 ppmw), which is the NO concentration in air in equilibrium at 910 K, $\tau_{ig}$ is reduced by about a factor of 4. The experimental results reported in reference 15 indicated reductions in $\tau_{ig}$ by factors of 2/3 and 1/2 at pressures of 0.27 and 0.5 atm, respectively, due to molar concentrations of NOx between 0.005 and 0.01. For a stoichiometric H2-air mixture, the mass fraction of NOx is about 1.5 times the mole fraction. These results, indicated by squares in figure 10(a), agree reasonably well with the present calculations. Data for shock-tube ignition of H2-air at 910 K (ref. 36), denoted by the circles in figure 10(a), also show good agreement with the preset calculations.
Figure 10(b) shows that for H₂-vitiated air, increasing the mass fraction of NO in the initial mixture from $10^{-5}$ (the EFS value) to 0.01 causes significant reductions in $T_{ig}$, particularly at pressures greater than 0.5 atm. For an NO mass fraction of 0.01, the ignition times for both H₂-air and H₂-vitiated air are nearly equal. The chemical mechanism responsible in part for these reductions is the reaction NO + HO₂ $\rightarrow$ OH + NO₂, which produces the active chain carrier OH through the depletion of HO₂. Because HO₂ is formed through a chain terminating reaction that depletes H atoms, it is responsible for the retarding of ignition in vitiated-air mixtures. A more complete mechanism for the effect of NOₓ on H₂-air ignition is proposed in reference 37.

The results in figure 10 indicate a strong influence of NO on ignition times at low temperature and pressures above 0.5 atm.

**Effect of other chemical additives.**—Because of the difficulty of obtaining ignition in a short time (or distance) at the low temperatures (850 to 1000 K) and pressures (0.30 to 1.0 atm) typical of a scramjet combustor, certain chemicals have been considered to prompt ignition. These chemicals, such as H₂O₂ and O₃, would supply OH free radicals and active oxygen atoms which would shorten the ignition time. The oxides of nitrogen or other nitrogen compounds which produce these molecules could be used over a limited range of pressures and temperatures. The reduction in ignition times for stoichiometric mixtures of H₂-air and H₂-vitiated air at 1.0 atm obtained by adding mass fractions of O₃, H₂O₂, NO, and NO₂ of 0.01 is presented in figures 11(a) to 11(d), respectively. The reduction in $T_{ig}$ is given by the parameter $\lambda$ defined as the ratio of $T_{ig}$ with the chemical additive to $T_{ig}$ from figure 6. Chemicals O₃ and H₂O₂ provide substantial reduction in ignition times at all temperatures for both air and vitiated air. Although not presented, reduction of the pressure to 0.5 atm was observed to have little effect on the reduction of $T_{ig}$ for both O₃ and H₂O₂. For the NOₓ additives in figures 11(c) and 11(d), the significant reduction occurs only at the lower temperatures (less than 1100 K). This large reduction in $T_{ig}$ at the low temperatures occurs because of the same chemical mechanism discussed in the previous section—the formation of OH through the depletion of HO₂ reacting with NO.

The effect of atmospheric O₃ encountered in the flight of a scramjet engine also was examined. At altitudes of about 30 km the O₃ concentration is approximately 10 ppmw. Peak O₃ concentration is about 13.5 ppmw at 36 km. The reduction in ignition time for a trace O₃ concentration of 10 ppmw at 1 atm is given in figure 12. Substantial reduction occurs at the lower initial temperatures (less than 1000 K). Lowering the pressure from 1.0 to 0.5 atm did not change the result.

**Reaction Time**

In the present analysis the reaction time is defined as the time difference between the ignition time and the total reaction time required to achieve 95 percent of the equilibrium temperature rise (see eqs. (30) and (31)). The effect of pressure on the variation of reaction time with temperature is presented in figure 13 for stoichiometric mixtures of H₂-air and H₂-vitiated air. In contrast to the ignition time, vitiated air has a negligible effect.
on the reaction time. In the semilog plot of figure 13, the variation of $\tau_R$ with $T_O$ is linear and shows a strong dependence on $p$. The present calculations also indicate that $\tau_R$ is independent of (1) the initial concentration of free radicals and atoms (similar results were reported in refs. 7 and 8); (2) the presence of chemical additives such as NO, $H_2O_2$, and $O_3$; and (3) within $\pm$10 percent, the mixture equivalence ratio in the range 0.5 to 1.5. These reaction times can be correlated, within $\pm$10 percent, by the equation

$$\tau_R = 325p^{-1.6} \exp(-0.8T_O/1000)$$

(34)

A comparison of the correlation given by equation (34) and reaction times from references 4, 7, and 8 is given in figure 14 for a stoichiometric $H_2$-air mixture at $p = 1.0$ atm. The large difference between the present results and the earlier work of reference 4, which gave reaction times as much as 5 times faster than the present theory, can be traced back to the rate constants for three-body recombination exothermic reactions.

Effect of changes in reaction-rate constants.- One reaction which has a major effect on the calculated reaction time is $H + OH + M \rightarrow H_2O + M$. The reaction rate constant $k_3$ for this reaction in the present chemical model is similar to the value recommended in references 20 and 21 with $N_2$ as the third body with an efficiency of 1. However, the rate data of references 20 and 21 exhibited considerable scatter, with a factor of 7 representative of the upper limit change in the rate constant. This factor of 7 was used to increase the rate constant ($k_3$) and reaction times recomputed. No estimate of the lower limit change was attempted. The comparative effect on $\tau_R$ of this change in $k_3$ by a factor of 7 is presented in figure 15 for stoichiometric mixtures of $H_2$-air and $H_2$-vitated air at pressures of 0.5 and 1.0 atm. For each pressure, the upper curves are for the value of $k_3$ given in table I; the lower curves are for a rate constant of 7 times $k_3$. In both cases, the third-body efficiency of $H_2O$ was $m_{H_2O,3} = 6$ (see table I). The effect of the factor of 7 and the high efficiency of $H_2O$ mean that the rate constant for the reaction $H + OH + H_2O + H_2O + H_2O$ will have a coefficient $A_3 = 2.2 \times 10^{23}$ compared with the table I value of $A_3 = 0.52 \times 10^{22}$ for the reaction $H + OH + N_2 + H_2O + N_2$. The result, shown in figure 15, is a reduction in reaction time by a factor of about 3. The calculated values of $\tau_R$ with the faster rate constants agree better with previous results and fall between the $\tau_R$ values from references 4 and 7 (compare fig. 14 with fig. 15(b)).

Effect of third-body efficiency of $H_2O$.- Another way to affect reaction time is to change the reaction rate through the third-body efficiency of $H_2O$ in the reaction $H + OH + H_2O + H_2O + H_2O$. In reference 38 this reaction is considered the dominant path for the production of $H_2O$, with a rate constant of approximately $2.7 \times 10^{17}$ cm$^6$-mol$^{-2}$-s$^{-1}$ at 1650 K. In reference 39, the rate constant had to be $2.4 \times 10^{17} \exp(500/RT)$ cm$^6$-mol$^{-2}$-s$^{-1}$ to agree with their data. In the present chemical mechanism the rate constant, including a third-body efficiency factor of 6 for $H_2O$, is $2.6 \times 10^{21} \tau^{-1.5}$ cm$^6$-mol$^{-2}$-s$^{-1}$. 

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This value is approximately the value recommended by references 20 and 21. A comparison of the three rate constants for the production of H$_2$O is given in the following table:

<table>
<thead>
<tr>
<th>$T_o$, K</th>
<th>Source</th>
<th>$k_3$, cm$^6$-mol$^{-2}$-s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>Ref. 38</td>
<td>$2.7 \times 10^{17}$</td>
</tr>
<tr>
<td></td>
<td>Ref. 39</td>
<td>$2.8 \times 10^{17}$</td>
</tr>
<tr>
<td></td>
<td>Present study</td>
<td>$4.5 \times 10^{16}$</td>
</tr>
</tbody>
</table>

In order to check the sensitivity of $\tau_R$ to a change in this rate of reaction, the third-body efficiency of H$_2$O was varied from 1 to 40, with the latter value corresponding to the rate constants from references 38 and 39. Note that the value of the rate constant for the present calculations includes the factor of 6 for the third-body efficiency of H$_2$O. The effect on $\tau_R$ of varying $m_{H_2O,3}$ from 1 to 40 is presented in figure 16 for $T_o = 1500$ K, $p = 1$ atm, and stoichiometric mixtures of H$_2$-air and H$_2$-vitiated air. These results are represented by the parameter $\Gamma$, defined as the ratio of $\tau_R$ to $\tau_R$ for H$_2$-air from figure 13, with $m_{H_2O,3} = 6$. The spread between the H$_2$-air and H$_2$-vitiated air reaction times disappears when the third-body efficiencies of H$_2$O and N$_2$ are equal ($m_{H_2O,3} = 1$) and increases to a difference of a factor of 2 when $m_{H_2O,3} = 40$, giving a rate constant of $3.0 \times 10^{17}$ cm$^6$-mol$^{-2}$-s$^{-1}$.

It is apparent from the comparisons of figures 15 and 16 that the rate constants for the recombination of H and OH to form H$_2$O will have an important impact on reaction times in scramjet combustors. These results point out the need for more accurate rate data for this reaction with N$_2$ and H$_2$O as third bodies.

**CONCLUDING REMARKS**

An analytical study of the chemical mechanism involved in the ignition and reaction of the H$_2$-air system has been performed at conditions representative of a scramjet combustor. The calculations were made with a one-dimensional kinetics program with an H$_2$-O$_2$-N$_2$ finite-rate chemistry model consisting of 60 reactions in 20 species. An objective of these calculations was to provide information for an assessment of the conditions at which kinetics are important in scramjet combustors. Specifically, the study considered how ignition and reaction times are affected by initial temperature and pressure; fuel equivalence ratio; the presence of contaminants such as H$_2$O, H, OH, and NO$_x$; chemical additives H$_2$O$_2$ and O$_3$; and the reaction rate of key reactions.
Results of the calculations indicated that, within a 20 percent error, ignition time is nearly constant over a range of equivalence ratios from 0.5 to 1.7. Relative to air in chemical equilibrium, the presence of H₂O in the initial mixture (as from a vitiated main stream) increased ignition times at initial temperatures below 1000 K and reduced ignition times by about 33 percent at temperatures above 1200 K. These results were found to be due to the depletion of H atoms by the accelerated production of HO₂ at low initial temperatures through the reaction H + O₂ + H₂O -> HO₂ + H₂O, because the third-body efficiency of H₂O may be 13 times that of N₂. At higher temperatures the dissociation of H₂O produces OH concentrations that counteract the H atom depletion and reduce ignition time. The presence of chemicals such as H₂O₂, O₃, NO, and NO₂, in concentrations (mass fractions) of 0.01 in both H₂-air and H₂-vitiated air mixtures, significantly reduced ignition times at low temperatures (near 910 K). At high temperatures (above 1100 K) NO and NO₂ had little effect on ignition times, whereas H₂O₂ and O₃ still caused a reduction of ignition times by about a factor of 7.

The present calculations indicate that reaction time, defined as the time from the onset of ignition to attainment of 95 percent of the equilibrium temperature, is independent of the concentration of free radicals, chemical additives, and within 10 percent, the equivalence ratio between 0.5 and 1.5. In addition, the presence of H₂O in a vitiated main stream at mass fractions of up to 0.245 had very little effect on reaction time. However, a comparison of rate constants for the reaction H + OH + M + H₂O + M indicates a need for more accurate rate data with N₂ and H₂O as third bodies.

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June 3, 1981
REFERENCES


TABLE I.- HYDROGEN-AIR-REACTION MODEL WITH THIRD-BODY EFFICIENCIES

[Rate constant is given by \( k = AT^N \exp(-\text{Activation energy}/1.987T) \)]

<table>
<thead>
<tr>
<th>REACTION NUMBER</th>
<th>REACTION</th>
<th>REACTION RATE VARIABLES</th>
<th>( A )</th>
<th>( N )</th>
<th>ACTIVATION ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}7500 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( 1{1}790.0 )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 7{.}5000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( 1{0}153.0 )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 2{.}0000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( -560.0 )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 5{.}0000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( -895.0 )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}4100 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( 1{4}968.0 )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}3000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( 1{4}968.0 )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 5{.}4000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>(-596.0 )</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}2000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>( 4550.0 )</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 8{.}0000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>(-1{9}87.0 )</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}3000 \times 1{0}^6 )</td>
<td>(-1{.}0000 )</td>
<td>(-7200.0 )</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( H \rightarrow \cdot H + \cdot O )</td>
<td>( 1{.}9000 \times 1{0}^6 )</td>
<td>(-2{.}0000 )</td>
<td>( 2{4}423.0 )</td>
<td></td>
</tr>
</tbody>
</table>

TABLE II.- THIRD BODY RATIOS ARE 1.3 EXCEPT THE FOLLOWING

| \( \cdot H \) | 11 | \( 4{.}1000 \) | \( \cdot O \) | 12 | \( 1{.}6000 \) | \( \cdot H \) | 13 | \( 1{0}6000 \) | \( \cdot H \) | 14 | \( 2{3}0000 \) |
| \( \cdot O \) | 4 | \( 7{.}0000 \) | \( \cdot H \) | 21 | \( 5{.}0000 \) | \( \cdot H \) | 21 | \( 2{3}0000 \) | \( \cdot O \) | 13 | \( 3{.}0000 \) |
| \( \cdot H \) | 6 | \( 6{.}1000 \) | \( \cdot H \) | 43 | \( 1{3}0000 \) | \( \cdot H \) | 43 | \( 3{.}0000 \) | \( \cdot H \) | 91 | \( 4{.}0000 \) |

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(a) $H_2$-air; $p = 0.5$ atm.

Figure 1.- Species mass fraction as function of time. $\phi = 1.0$; $T_0 = 1000$ K.
(b) $\text{H}_2$-air; $p = 2.0$ atm.

Figure 1.- Continued.
(c) $H_2$-vitiated air; $p = 1.0$ atm.

Figure 1.- Concluded.
Figure 2. - Theoretical ignition times for H$_2$-air.

(a) Effect of pressure.
Figure 2.- Concluded.

(b) Effect of temperature.
Figure 3. - Effect of equivalence ratio on ignition time. $p = 1$ atm.
Figure 4. Ignition times for H₂-air. φ = 1.0.

(a) p = 0.5 and 2.0 atm.
Figure 5.- Ignition times for H$_2$-air as function of pressure. 
$T_0 = 1000$ K; $\phi = 1.0$. 

Ref. 15
Present study
Ref. 4
Ref. 14
Figure 6.— Comparison of ignition times for H₂-air and H₂-vitiated air.
Figure 6.- Concluded.

(b) Effect of temperature.
Figure 7.- Effect of equilibrium free stream on ignition times.
$T_o = 1300 \text{ K}; \ \phi = 1.0$. 

$P, \text{ atm}$

$\tau_{ig}$

$\text{ ms}$

$H_2$-air

$H_2$-vitiated air

Equilibrium free stream
Figure 8.- Effect of H₂O concentration in test stream on ignition times. 
T₀ = 1000 K.
Figure 9.- Effect of rate constants for H + O_2 + H_2O + HO + H_2O on ignition times in an H_2-vitiated air equilibrium free stream. T_0 = 1000 K.
Figure 10.— Effect of NO concentration on ignition times.

(a) H₂-air; T₀ = 910 K.
Figure 10. - Concluded.
Figure 11.- Reduction of ignition times due to chemical additives.

\( p = 1.0 \text{ atm}; \ \phi = 1.0. \)
(b) $\alpha_{H_2O_2} = 0.01.$

Figure 11.- Continued.
Figure 11.- Continued.

(c) $\alpha_{NO} = 0.01$.
Figure 11.- Concluded.

(d) $\alpha_{NO_2} = 0.01.$

Figure 11.- Concluded.
Figure 12.- Reduction of ignition times due to flight contaminant of 10 ppmw $O_3$. $p = 1.0$ atm; $\phi = 1.0$. 
Figure 13.- Reaction times as function of temperature. \( \phi = 1.0 \).
Figure 14. - Comparison of theoretical H$_2$-air reaction times.

$p = 1.0 \text{ atm}; \ \phi = 1.0.$
Figure 15.— Effect of rate constant of $H + OH + M + H_2O + M$ on reaction times for $H_2$-air and $H_2$-vitiated air at $\Phi = 1.0$. 

(a) $p = 0.5$ atm.
Figure 15.— Concluded.
Figure 16.- Effect of third-body efficiency of \( \text{H}_2\text{O} \) in reaction \( \text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M} \) on reaction time. \( T_0 = 1500 \) K; \( p = 1 \) atm; \( \phi = 1.0 \).
An analytical study of hydrogen-air kinetic was performed. Calculations were made over a range of pressure from 0.2 to 4.0 atm, temperatures from 850 to 2000 K, and mixture equivalence ratios from 0.2 to 2.0. The finite-rate chemistry model included 60 reactions in 20 species of the \( \text{H}_2-\text{O}_2-\text{N}_2 \) system. The calculations also included an assessment of how small amounts of the chemicals \( \text{H}_2\text{O}, \text{NO}_x, \text{H}_2\text{O}_2, \) and \( \text{O}_3 \) in the initial mixture affect ignition and reaction times, and how the variation of the third-body efficiency of \( \text{H}_2\text{O} \) relative of \( \text{N}_2 \) in certain key reactions may affect reaction time. The results indicate that for mixture equivalence ratios between 0.5 and 1.7, ignition times are nearly constant; however, the presence of \( \text{H}_2\text{O} \) and \( \text{NO} \) can have significant effects on ignition times, depending on the mixture temperature. Reaction time is dominantly influenced by pressure but is nearly independent of initial temperature, equivalence ratio, and the addition of chemicals. Effects of kinetics on reaction at supersonic combustor conditions are discussed, and recommendations for further experimental studies of rate constants for key reactions are included.