

A Simplified Hydrocarbon Reaction Mechanism for Combustion Applications

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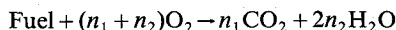
A simplified chemical kinetic reaction mechanism for the combustion of a hydrocarbon fuel is presented and discussed. The observed kinetic behavior of propane combustion as determined in shock tube studies and the calculated kinetic behavior of propane/air mixtures as derived from a detailed propane combustion mechanism were used as a data base for constructing and refining the mechanism. The mechanism contains 13 chemical species and 26 chemical reactions. Numerical studies revealed that the simplified mechanism can reproduce the observed kinetic behavior of propane/air mixtures, including laminar flame speeds, over a wide range of temperatures and pressures. It is anticipated that the mechanism can be used in various combustion applications and provide a more realistic description of the combustion process than can be achieved using global reaction mechanisms.

Introduction

NUMERICAL modeling of combustion processes in air-breathing propulsion systems such as gas turbines, ram-jets, and scramjets has become an important element in many combustion research programs. An essential component in many of these models is a chemical kinetic reaction mechanism describing the oxidation of a hydrocarbon fuel. Even though the kinetics and mechanisms of hydrocarbon combustion have been studied for many years, the reaction and rate coefficient data base is insufficient to assemble reaction mechanisms describing the combustion of conventional jet fuels or ramjet/scramjet fuels.

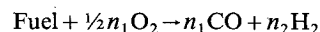
Detailed mechanisms have been assembled and applied for only the simplest of hydrocarbons such as methane, ethane, acetylene, ethylene, methanol, and most recently propane.^{1,2} These detailed mechanisms contain many chemical species and elementary chemical reactions. For example, the propane combustion mechanism proposed by Jachimowski¹ contains 27 chemical species and 83 elementary reactions, while the reaction mechanism proposed by Westbrook and Pitz² contains 41 chemical species and 163 elementary reactions. Current numerical models that attempt to combine a description of the chemistry with other processes such as turbulence, mass transport, fuel vaporization, quenching, etc., encounter serious computational difficulties when detailed chemical mechanisms of this magnitude are used. The problem is usually made manageable by using simplified mechanisms that give a global or overall description of the reaction process. Several such global reaction mechanisms have been proposed and applied.

The simplest global reaction mechanism describing the oxidation of a hydrocarbon fuel is the single-step mechanism,

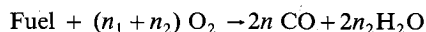


where the coefficients n_1 and n_2 are determined by the nature of the fuel. Another type of simplified mechanism that has been used is the quasiglobal mechanism proposed by Edelman and Fortune.³ In this approach, the consumption

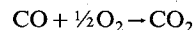
of the hydrocarbon fuel is described by the single global reaction,



The remaining reactions in the mechanism describe in detail the oxidation of the CO and H₂. Intermediate between these approaches is the two-step reaction mechanism in which one global reaction describes the formation of CO and H₂O,



and a second global reaction describes the formation of CO₂



In all these simplified mechanisms, the rates of the global reactions are given by an empirically derived equation usually in the form,

$$R = AT^n [\text{Fuel}]^a [\text{O}_2]^b \exp(-E/RT)$$

The parameters A , n , a , b , and E are commonly determined from experimental data and are usually valid only under the same conditions (pressure, temperature, equivalence ratio) as the experiments. The rate expressions are found to be unreliable at conditions significantly different from those for which they were derived. The proper effects of fuel-air ratio, temperature, and pressure for a wide range of conditions are difficult to include in a single rate expression.

These simplified global reaction mechanisms have been used for various hydrocarbon fuels. Westbrook and Dryer⁴ have reviewed the various applications of the global reaction mechanism approach and pointed out several flaws in the mechanism that can be important in certain combustion applications. For example, single- and two-step reaction mechanisms have been assembled that can reproduce flame speeds over a range of conditions. However, the assumption that the reaction products are CO₂ and H₂O in the case of the single-step model and CO, CO₂, and H₂O in the two-step model results in an overprediction of the heat of reaction and higher adiabatic flame temperatures. Even though the two-step reaction model predicts flame temperatures closer to the correct value, this approach may not be adequate for certain combustion applications. Reitz and Bracco^{5,6} have proposed a formulation of a global kinetics model based on

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the first-order expansion of the reaction rate about local equilibrium that allows H_2 and CO and their equilibria to be included. This approach yields adiabatic flame temperatures in better agreement with the correct values.

While the quasiglobal reaction mechanism is a very appealing alternative to the single- and two-step mechanisms because it can predict the correct adiabatic flame temperature, it has been shown⁵ that it does not adequately describe the various stages characterizing the oxidation of hydrocarbon fuels. Dryer and Westbrook⁷ and Westbrook and Dryer⁸ have shown that the quasiglobal mechanisms can underestimate the consumption of the fuel and overestimate the CO oxidation rate. In addition, the predicted temperature rise can be too rapid. These differences occur in large part because the mechanism does not consider the formation of intermediate hydrocarbon species that are known to have an important role in the oxidation process, particularly with regard to the formation of CO. Hautman et al.⁹ attempted to account for this effect by constructing a multistep global reaction mechanism for the oxidation of C_nH_{2n} ($n > 2$) type hydrocarbons, which included C_2H_4 as an intermediate hydrocarbon. The rate expression for each step in the mechanism was derived from experimental results obtained using a turbulent flow reactor. The mechanism was able to reproduce the experimental flow reactor results adequately, but predicted ignition delay times that were about a factor of two smaller than experimental shock tube data. In addition, since CO, CO_2 , and H_2O are the assumed reaction products, the mechanism will not predict the correct flame temperature at all conditions. Recently, Edelman et al.¹⁰ proposed a multistep quasiglobal reaction mechanism for isooctane and toluene that includes hydrocarbon intermediates. In the isooctane model, ethylene was included as an intermediate, while in the toluene model, acetylene was selected as the intermediate hydrocarbon. The rate expressions for the global reactions were determined by direct comparison of predictions with data obtained from jet-stirred combustor experiments. The ability of the models to predict other data, such as flame speeds, was not reported.

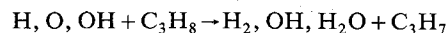
The development and validation of an alternative simplified chemical kinetic reaction mechanism for the combustion of a hydrocarbon fuel are presented and discussed in this paper. In the proposed mechanism, the fuel is assumed to react to form species of lower molecular weight followed by the oxidation of these species by reaction paths analogous to those included in detailed hydrocarbon combustion mechanisms. It is generally accepted that propane is the simplest hydrocarbon having reaction characteristics typical of many conventional fuels including jet and ramjet/scramjet fuels.^{3,4} Therefore, the simplified mechanism was developed largely on the observed and predicted behavior of propane/oxygen mixtures. The results of the observed behavior of propane/oxygen mixtures as determined in shock tube studies and the kinetic behavior predicted by a detailed propane combustion mechanism were used to refine the model. The resulting mechanism was then validated by comparing the calculated results with those predicted by the detailed propane mechanism over a wide range of conditions and also by comparing calculated flame speeds with experimental flame speeds for various propane/air mixtures over a range of conditions.

The Kinetics of Propane Combustion

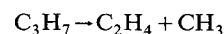
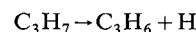
The detailed propane combustion mechanism used in this study is that assembled by Jachimowski.¹ The mechanism contains 27 chemical species and 83 elementary reactions. In the mechanism, the propane is assumed to decompose and react thermally to form lower-molecular hydrocarbon intermediates followed by the reaction and oxidation of these intermediates. The mechanism was shown to reasonably reproduce the observed kinetic behavior of propane/oxygen mixtures as determined in shock tube studies. Results of analytical studies with the mechanism revealed that the oxidation process occurs in several stages with different groups of reactions controlling

each stage. It was also shown that hydrocarbon reactions involved in the formation of the HO_2 radical and the H_2O_2 molecule are very important in controlling the oxidation process during the early stages of the reaction. Without these reactions, the predicted kinetic behavior was not consistent with the experimental results.

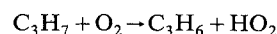
The results of the analytical studies revealed that, during the initial stages of the ignition delay period, propane is consumed primarily by reaction with the radicals H, O, and OH



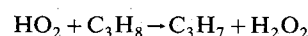
The propyl radical then thermally decomposes into lower molecular weight fragments



and also reacts with molecular oxygen to produce the HO_2 radical

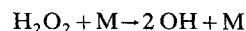


When sufficient levels of the HO_2 radical are produced, the reaction

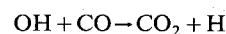


contributes to the formation of the H_2O_2 molecule. During this initial stage, the concentrations of the HO_2 radical and the H_2O_2 molecule increase significantly and exceed the levels of the free radicals H, O, and OH.

During the next stage of the ignition delay period, the H_2O_2 molecule rapidly decomposes to produce the OH radical



The concentration of the free radicals rises very rapidly and the hydrocarbon intermediates are rapidly oxidized through a reaction sequence that produces the CO molecule. During this stage, there is also a rapid increase in the temperature, indicating ignition has occurred. After ignition, the last stage is dominated by the oxidation of CO to CO_2 primarily through the reaction



and to some extent by the formation of H_2O through the recombination reaction



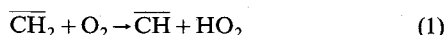
The various reaction stages predicted by the propane mechanism are consistent with the trends reported by Hautman et al.,⁹ who studied the oxidation of propane in a high-temperature flow reactor. Similar staged oxidation occurs for most hydrocarbons at high temperatures.^{9,11,12}

The Simplified Hydrocarbon Combustion Mechanism

The hydrocarbon fuel represented in the mechanism is assumed to contain two hydrogen atoms for each carbon atom, representing a general class of hydrocarbon fuels with the formula C_nH_{2n} . JP-4, which has a reported¹³ average molecular weight of 126, would have the formula C_9H_{18} . The development that follows assumes that the fuel C_nH_{2n} has chemical combustion characteristics essentially identical to propane even though the H/C ratios are different. Because the H/C ratios are different, the concentration profiles of intermediate species cannot be compared directly. Only the overall reaction behavior can be compared. In the mechanism,

the reactivity of the hydrocarbon C_nH_{2n} is described in terms of the reactions of the CH_2 component and is designated by the symbol $\overline{CH_2}$. The hydrocarbon intermediates are represented in turn by the symbols \overline{CH} and \overline{C} . The reaction sequence that describes the consumption of the CH_2 and the formation of the intermediates \overline{CH} and \overline{C} are modeled after reactions in the detailed propane combustion mechanism. The proposed mechanism and the assigned rate coefficient for each reaction are listed in Table 1. The mechanisms contain 13 chemical species and 26 reactions. The rate coefficients for the reverse reactions were calculated using the forward rate coefficient and the appropriate equilibrium constant.

It is generally accepted that, for most saturated-type hydrocarbons, the initiation reaction commonly involves abstraction of a hydrogen atom to yield the HO_2 radical and an alkyl radical. At higher temperatures, thermal decomposition of the fuel can also contribute to the initiation process. In the proposed mechanism, the abstraction reaction was selected as the initiation step,[†]



The rate coefficient assigned to this reaction was set equal to the combined rate coefficients for the analogous propane reactions.¹ In the detailed propane mechanism, separate initiation reactions were used to describe the formation of the normal propyl radical and the isopropyl radical. The combined rate coefficient is the sum of these two rate coefficients.

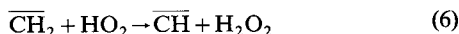
As previously noted in the discussion of the propane combustion mechanism, the fuel is consumed primarily by reactions with the radicals H , O , and OH . Analogous reactions are used in the simplified mechanism



The rate coefficients assigned to these reactions were set equal to the rate coefficients for the analogous propane reactions. In the propane mechanism, the reaction of the propyl radical with the molecular oxygen was determined to be a major source of the HO_2 radical during the initial stages. The analogous reaction was included in the simplified mechanism



Production of the H_2O_2 molecule by a hydrocarbon is represented by the reaction



Rate coefficients initially assigned to reactions (5) and (6) were also set equal to the rate coefficients for the analogous reactions in the propane mechanism.

The primary path for the formation of the lower-molecular-weight hydrocarbon fragments in the propane mechanism is the thermal decomposition of the propyl radicals and the ethyl radical. In the simplified mechanism, this process is modeled by the single reaction



The rate coefficient initially assigned to this reaction was set equal to the combined rate coefficients for the thermal decomposition of the propyl radicals into propylene and atomic hydrogen.

The formation of CO in the simplified mechanism is described by the single reaction



The primary source of CO in the propane mechanism is the HCO radical. The HCO radical is formed primarily during that stage of the reaction when the hydrocarbon intermediates react rather rapidly while large amounts of the radicals H , O , and OH are being generated. The rate coefficient for reaction (8) was arbitrarily set at $1 \times 10^{12} \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{s}^{-1}$. Results of subsequent calculations revealed that the predicted kinetic behavior was not very sensitive to the rate of this reaction for the conditions examined.

The remaining reactions in the mechanism (9-26) describe the kinetics of the $H_2/CO/O_2$ system (see Table 1). The rate coefficients assigned to the reactions are the same rate coefficients that were used in the detailed propane combustion mechanism.¹

Mechanism Refinement and Evaluation

As previously noted, experimental shock tube results and kinetic results predicted by the detailed propane mechanism were used as reference data to refine and evaluate the simplified mechanism. The experimental data selected for comparison were the ignition delay times reported by Burcat et al.¹⁴ Burcat measured ignition delay times in the reflected shock region for various propane/oxygen/argon mixtures. The specific data selected for comparison were the ignition delay times reported for the stoichiometric mixture containing 3.85 mole% C_3H_8 and 19.23 mole% O_2 in argon. The composition of this mixture closely approximates the composition of a stoichiometric propane/air mixture (4.03 mole% C_3H_8 and 20.15 mole% O_2 in N_2). This mixture was also selected because the kinetic behavior exhibited by this mixture (as reflected in the ignition delay time results) suggested that a mechanism change was occurring over the temperature range in which the mixture was studied. Analytical studies with the detailed propane mechanism showed that this behavior can be attributed to the increased importance of the HO_2 radical and the H_2O_2 molecule reactions at the lower temperatures.¹

The other data used to evaluate and refine the mechanism were the ignition delay time curves that were generated from a series of calculations with stoichiometric propane/air mixtures over the temperature range 1000-1600 K for pressures of 0.5-10.0 atm. The ignition delay time is defined as the time required to achieve ignition as signified by the sudden increase in temperature.

To compare the kinetic behavior predicted by the mechanism with the reference data, numerical simulations of the experiments were carried out using the chemical kinetic computer program described by McLain and Rao.¹⁵ To simulate the conditions behind a reflected shock wave (Burcat experiments), the program was operated in a constant-volume mode. Calculations of ignition delay times for comparison with the results obtained using the detailed propane mechanism were carried out at constant pressure. The chemical kinetic computer program treats each reaction as a reversible reaction. Rate coefficients for the reverse reactions were calculated within the program using the forward rate coefficient and the appropriate equilibrium constant as determined from the thermodynamic data for each species. Thermodynamic data for the hydrocarbon species $\overline{CH_2}$, \overline{CH} , and \overline{C} were derived in the following manner. The standard heat of formation of $\overline{CH_2}$ at 298 K, in cal/g, was set equal to the heat of formation of gaseous JP-4, $\Delta H_f = -457.7 \text{ cal/g}$. The heat of formation of gaseous JP-4 was calculated from the reported heat of combustion of gaseous JP-4¹³ assuming the chemical formula C_9H_{18} . The standard entropy for $\overline{CH_2}$ at 298 K, in cal/g/K was set equal to the standard entropy for C_9H_{18} , $S^\circ_{298} = 0.846 \text{ cal/g/K}$ at 298 K.¹⁶ The specific heat

[†]Reactions numbered as in Table 1.

capacity for $\overline{\text{CH}_2}$ as a function of temperature was set equal to the specific heat capacity reported¹⁶ for C_9H_{18} . The standard enthalpy and entropy for the $\overline{\text{CH}}$ and $\overline{\text{C}}$ species were determined by setting

$$\text{H}(\overline{\text{CH}}) \equiv \text{H}(\overline{\text{CH}_2}) + \text{H}(\text{C}_3\text{H}_7) - \text{H}(\text{C}_3\text{H}_8)$$

$$\text{H}(\overline{\text{C}}) \equiv \text{H}(\overline{\text{CH}}) + \text{H}(\text{C}_3\text{H}_6) - \text{H}(\text{C}_3\text{H}_7)$$

and

$$\text{S}(\overline{\text{CH}}) \equiv \text{S}(\overline{\text{CH}_2}) + \text{S}(\text{C}_3\text{H}_7) - \text{S}(\text{C}_3\text{H}_8)$$

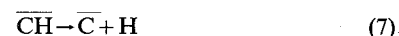
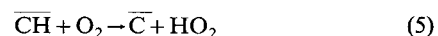
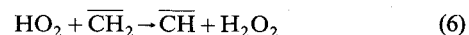
$$\text{S}(\overline{\text{C}}) \equiv \text{S}(\overline{\text{CH}}) + \text{S}(\text{C}_3\text{H}_6) - \text{S}(\text{C}_3\text{H}_7)$$

This is equivalent to setting the heat of reaction and the chemical equilibrium constants for the hydrogen abstraction reactions and for the thermal decomposition reaction in the simplified mechanism equal to the heat of reaction and the chemical equilibrium constants of the analogous propane reactions. Thermodynamic data for the other species in the mechanism were taken from the JANNAF tables.¹⁷ Using this set of thermodynamic data, the calculated adiabatic flame temperatures and equilibrium composition were in good agreement with the calculated results obtained for JP-4.¹⁸

To determine the best procedure for achieving the best possible agreement between the predicted results and the reference data, a sensitivity study was carried out in which the rate coefficients for all of the hydrocarbon reactions [reactions (1-8) in Table 1] were varied and the effect of this variation on the calculated ignition delay times was noted. Most of the sensitivity studies were carried out on the Burcat mixture at an initial pressure and temperature of 8.1 atm and 1150 K and on a stoichiometric $\overline{\text{CH}_2}$ /air mixture at 1 atm and temperatures of 1000 and 1600 K. To simulate the Burcat experiment, a comparable $\overline{\text{CH}_2}$ /O₂/Ar mixture was used. The composition of the comparable mixture was determined by requiring that the ratio of the moles of O₂ to the moles of Ar be the

same as in the experimental mixture while maintaining a stoichiometric $\overline{\text{CH}_2}$ /O₂ ratio. The composition of the comparable mixture was 11.76 mole% $\overline{\text{CH}_2}$, 17.65 mole% O₂, and 70.59% Ar.

Results of the sensitivity study revealed that the calculated ignition delay times were most sensitive to the rate assigned to the reactions



with the rate of reaction (7) (the thermal decomposition of $\overline{\text{CH}}$) having a significant effect on the pressure dependence of the calculated ignition delay times. To achieve agreement between the calculated results and the reference data, the following procedure was used. The rate coefficient for reaction (7) was initially fixed, while the rate coefficients for reactions (5) and (6) were adjusted to achieve a good fit to the Burcat data. The rate coefficient for reaction (7) was then adjusted to achieve a good fit to the calculated ignition delay times for a pressure of 1 atm. The rate coefficients for reactions (5-7) were then alternately adjusted until the best possible fit with all the reference data was achieved.

The rate coefficients for reactions (5) and (6), which provided the best fit, are listed in Table 1. The final expressions give rate coefficient values which are about a factor of three smaller than the initial value for reaction (6) and a factor of eight smaller for reaction (5). No change to the activation energy was required for either reaction. The rate coefficient for reaction (7) that provided the best fit to the reference data is

$$k = \frac{2.86 \times 10^{11} \exp(-34500/RT)}{1 + (8.24/p) \exp(-4100/RT)}, \text{ s}^{-1}$$

Table 1 Simplified hydrocarbon combustion mechanism^a

Reaction						A	N	E
(1)	$\overline{\text{CH}_2}$	+	O ₂	→	$\overline{\text{CH}}$	1.33E+13	0.0	52000.0
(2)	H	+	$\overline{\text{CH}_2}$	→	$\overline{\text{CH}}$	5.40E+13	0.0	7700.0
(3)	O	+	$\overline{\text{CH}_2}$	→	$\overline{\text{CH}}$	4.25E+13	0.0	9700.0
(4)	OH	+	$\overline{\text{CH}_2}$	→	$\overline{\text{CH}}$	3.26E+04	2.75	-776.0
(5)	$\overline{\text{CH}}$	+	O ₂	→	$\overline{\text{C}}$	1.50E+11	0.0	5000.0
(6)	HO ₂	+	$\overline{\text{CH}_2}$	→	$\overline{\text{CH}}$	2.50E+11	0.0	10500.0
(7)	$\overline{\text{CH}}$	→	$\overline{\text{C}}$	+	H		See text	
(8)	$\overline{\text{C}}$	+	OH	→	CO	1.00E+12	0.0	0.0
(9)	CO	+	OH	→	CO ₂	1.68E+07	1.3	-656.0
(10)	CO	+	O	→	CO ₂	2.50E+15	0.0	4370.0
(11)	HO ₂	+	CO	→	OH	1.00E+11	0.0	10000.0
(12)	H	+	O ₂	→	OH	1.42E+14	0.0	16400.0
(13)	OH	+	H ₂	→	H ₂ O	3.16E+07	1.8	3030.0
(14)	O	+	H ₂	→	OH	2.07E+14	0.0	13750.0
(15)	OH	+	OH	→	H ₂ O	5.50E+13	0.0	7000.0
(16)	H	+	OH	→	H ₂ O	2.21E+22	-2.0	0.0
(17)	H	+	H	→	H ₂	6.53E+17	-1.0	0.0
(18)	H	+	O ₂	→	HO ₂	3.20E+18	-1.0	0.0
(19)	HO ₂	+	OH	→	H ₂ O	5.00E+13	0.0	1000.0
(20)	HO ₂	+	H	→	H ₂	2.53E+13	0.0	700.0
(21)	HO ₂	+	H	→	OH	1.99E+14	0.0	1800.0
(22)	HO ₂	+	O	→	OH	5.00E+13	0.0	1000.0
(23)	HO ₂	+	HO ₂	→	H ₂ O ₂	1.99E+12	0.0	0.0
(24)	HO ₂	+	H ₂	→	H ₂ O ₂	3.01E+11	0.0	18700.0
(25)	H ₂ O ₂	+	OH	→	HO ₂	1.02E+13	0.0	1900.0
(26)	M	+	H ₂ O ₂	→	OH	1.21E+17	0.0	45500.0

^aThe rate coefficients are given in the form $k = AT^N \exp(-E/RT)$; units are in seconds, moles, cubic centimeters, calories and degrees Kelvin.

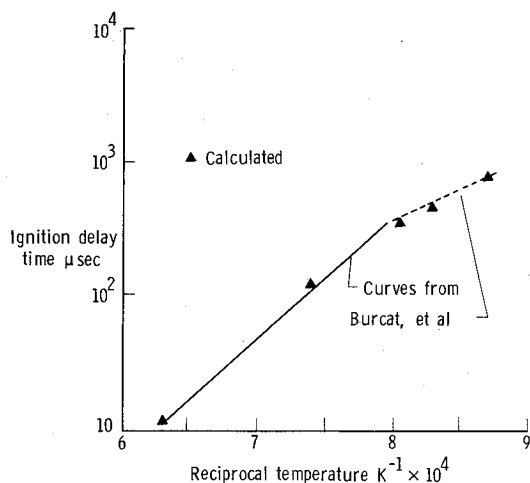


Fig. 1 Calculated ignition delay times compared with experimental data reported by Burcat et al.¹⁴ for the 3.85 mole% C_3H_8 /19.23 mole% O_2 /76.92 mole% Ar mixture ($P = 8$ atm).

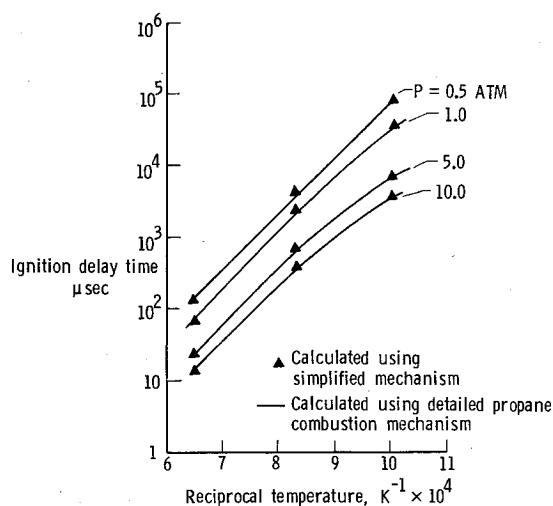
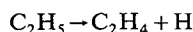


Fig. 2 Calculated ignition delay times as a function of temperature and pressure for a stoichiometric fuel/air mixture.

where the pressure is in atmospheres. Surprisingly, the rate coefficient values given by this expression are within a factor of two of the values given by the rate coefficient expression for the reaction



in the detailed propane mechanism. The comparisons between the calculated results and the reference data are given in Figs. 1 and 2.

Figure 1 compares the calculated ignition delay times and the experimental curves derived by Burcat that are least-square fits of the experimental data for the temperature ranges 1250–1587 and 1150–1250 K. The ignition delay times predicted by the simplified mechanism are in very good agreement with experimental results over the entire temperature range. In Fig. 2, the calculated results are compared with the ignition delay times obtained from the detailed propane mechanism. The agreement is good over the entire temperature range for all pressures. Even though the mechanism was refined only by comparison with data from stoichiometric mixtures, the predictions for fuel-lean and fuel-rich mixtures are also in very good agreement with the results from the detailed propane mechanism as shown in Figs. 3 and 4. In addition, a com-

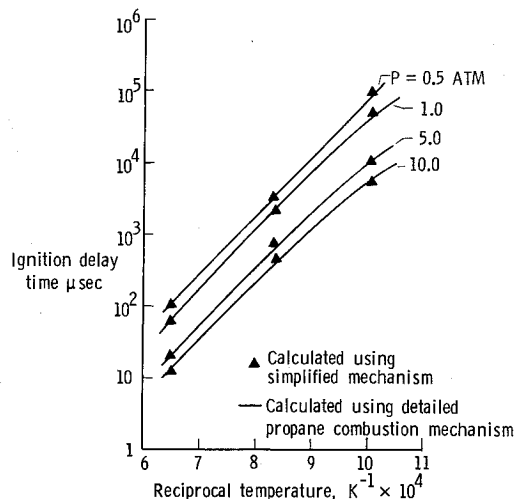


Fig. 3 Calculated ignition delay times as a function of temperature and pressure for a lean ($\phi = 0.5$) fuel/air mixture.

parison of the calculated results from the simplified mechanism and the detailed propane mechanism showed that the temperature profiles and heat release rates are in reasonably good agreement.

Comparison with Other Experimental Data

The ability of a reaction mechanism to predict flame speeds correctly is an important requirement in many combustion applications. As an additional test of the predictive capability of the simplified mechanism, the mechanism was incorporated into a numerical flame model that calculates laminar flame speeds. Results of these calculations were compared with experimental data reported for various propane/air mixtures over a rather wide range of pressures and temperatures. The numerical model used for these calculations is the premixed one-dimensional flame (PROF) code developed originally by Kendall and Kelly¹⁹ for premixed, laminar, laterally unconfined flame problems. The PROF code models the axial diffusion of heat and species, as well as the chemical kinetic processes that occur within a one-dimensional flame. The code treats each reaction as a reversible reaction and calculates the rate coefficient for the reverse reaction using the forward rate coefficient and the appropriate equilibrium constants.

The governing equations in the flame model are developed by integrating the steady two-dimensional species, mass, and energy equations across a plane perpendicular to the axis. This results in a set of one-dimensional equations in terms of bulk gas properties. Transport equations in the code use binary coefficients D_{ij} , which are approximated by the relation

$$D_{ij} = \bar{D}/F_i F_j$$

where \bar{D} is a reference self-diffusion coefficient and F_i and F_j the diffusion factors. Pressure and temperature dependence of D_{ij} is incorporated into \bar{D} so that F_i and F_j are independent of temperature and pressure. The reference species is molecular oxygen for which

$$\bar{D} = 1.72 \times 10^{-5} T^{1.659} p^{-1}, \text{ cm}^2 \cdot \text{s}^{-1}$$

where the pressure and temperature are in atmospheres and degrees Kelvin. The diffusion factor for a species i can be determined using the relation

$$F_i = (M_i/26)^{0.461}$$

where M_i is the molecular weight. This relation was developed by correlating a set of F_i determined for various species in the carbon/nitrogen/oxygen/hydrogen system with the molecular weight. This correlating equation was used to determine the diffusion factors for all the species in the simplified mechanism. Since the results of the numerical modeling studies were to be compared with experimental data for propane/air mixtures, the diffusion factors for the hydrocarbon species CH_2 , CH , and C were calculated using the molecular weights for C_3H_8 , C_3H_7 , and C_3H_6 , respectively. Results of subsequent calculations in which the diffusion factors for CH_2 , CH , and C were varied by $\pm 50\%$ revealed that the calculated flame speeds were not very sensitive to the assigned factors, except for very rich mixtures, $\phi \geq 2.0$.

Experimental data on laminar flame speeds in mixtures of propane with air are shown in Figs. 5-8, together with the calculated results. In Fig. 5 the calculated results are compared with experimental data on laminar flame speeds for various propane/air mixtures at atmospheric pressure and an unburned gas temperature of 298 K. The data band in this figure includes the flame speed results reported by Metghalchi and Keck,²⁰ Singer,²¹ Gibbs and Calcote,²² and Dugger.²³ The agreement between the calculated and experimental results is quite good. The results shown in Fig. 6 illustrate the effect of the initial unburned gas temperature on the flame speed for a stoichiometric propane/air mixture at 1 atm. The predicted results are in very good agreement with the experimental results. Although not shown in Fig. 6, for richer mixtures ($\phi > 1.5$), the mechanism predicts a rather slow decrease in the

flame speed. For example, at $\phi = 2.5$, the reported¹³ rich flammability limit for propane, the flame code predicts a flame speed of 9 cm/s. In rich mixtures, the effect of hydrocarbon reactions should become more important. Therefore, the rather slow decrease in the predicted flame speed suggests that the hydrocarbon reaction chemistry in the simplified model is inadequate for very rich mixtures, $\phi > 2$.

An important factor in many combustion applications is the effect of pressure on the flame speed. Metghalchi and Keck²⁰ measured flame speeds in propane/air mixtures in the pressure range 0.4-40 atm and temperature range 298-750 K. The measurements were made using a constant-volume spherical combustor bomb that could be heated to 500 K. A thermodynamic analysis was used to calculate the laminar flame

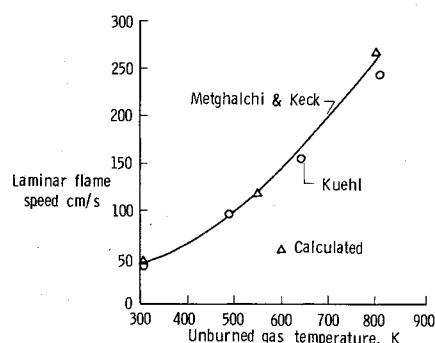


Fig. 6 Comparison of calculated and measured flame speeds for stoichiometric propane/air as a function of temperature at $P = 1$ atm.

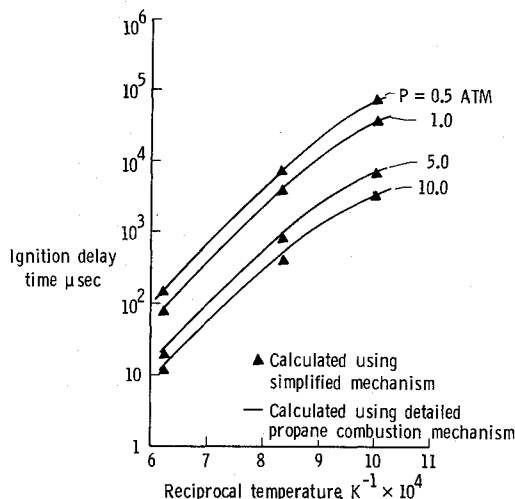


Fig. 4 Calculated ignition delay times as a function of temperature and pressure for a rich ($\phi = 1.5$) fuel/air mixture.

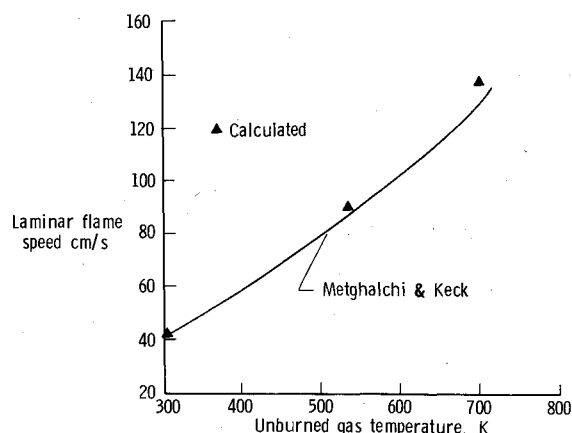


Fig. 7 Comparison of calculated and measured flame speeds for stoichiometric propane/air at $P = 0.4$ atm.

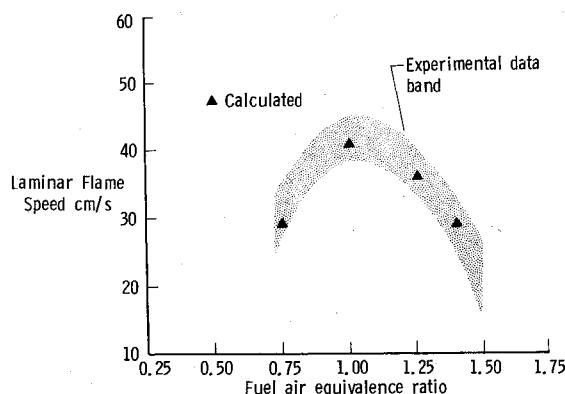


Fig. 5 Comparison of measured and calculated flame speeds in propane/air mixtures at $T = 298$ K and $P = 1$ atm.

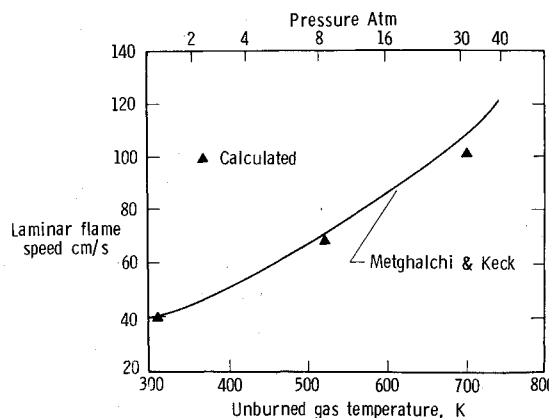


Fig. 8 Comparison of calculated and measured flame speeds for stoichiometric propane/air mixtures.

speeds from a pressure-time history of the combustion process. Some of the experimental results are given in Figs. 7 and 8. The results in Fig. 7 show the effect of the initial mixture temperature on the flame speed for a stoichiometric propane/air mixture at 0.4 atm pressure. The predicted results are in good agreement with the experimental results over the temperature range examined. However, the results suggest that at higher temperatures the simplified mechanism will slightly overestimate the flame speed. In Fig. 8, predicted flame speeds are compared with experimental results obtained at pressures between 1 and 40 atm and temperatures between 300 and 750 K. The predicted flame speeds are in good agreement with the experimental results. The largest difference occurs at the highest temperature and pressure where the calculated flame speed is about 10% smaller than the measured value. Based on the results of these comparisons, the dependence of flame speed on pressure is accurately predicted over a wide pressure range.

Conclusions

The most significant result of the study presented in this paper is the demonstration that a reasonably accurate simplified combustion model can be assembled that can reproduce the kinetic behavior of a hydrocarbon fuel under various combustion conditions. The fact that a rather simplified hydrocarbon mechanism could reasonably reproduce the heat release rates, ignition delay times, and flame speeds suggests that the important chemistry in the mechanism is the $\text{CO}/\text{H}_2/\text{O}_2$ reaction system and that the hydrocarbon reactions merely inhibit this chemistry by controlling the availability of the free radicals for the oxidation of the CO and H_2 . Even though the proposed mechanism was constructed to reproduce the combustion behavior of propane, it should be a useful surrogate mechanism for most hydrocarbon-based fuels with combustion characteristics similar to propane. It is anticipated that the proposed mechanism, when incorporated into numerical combustor models, will provide a more realistic description of the combustion process than can be achieved using a global reaction mechanism. In addition, the proposed mechanism can be used in numerical combustion experiments to examine the adequacy of using the simpler single- or two-step reaction mechanism for modeling hydrocarbon flames in turbulent combustors.

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