REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED Non-Peer Reviewed Reprint

4. TITLE AND SUBTITLE Interpreting Shock Tube Ignition Data	5. FUNDING NUMBERS DAAD19-01-1-0597

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Stanford University, Mechanical Engineering Department Building 520, Duena Street Stanford CA, 94305-3032	8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSORING / MONITORING AGENCY REPORT NUMBER 41100. 4 - EG

11. SUPPLEMENTARY NOTES
   The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS Ignition Times, ignition time correlations, Shock Tubes, n-heptane, iso-octane		15. NUMBER OF PAGES 23
		16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

Paper 03F-61

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Abstract

Chemical kinetic modelers make extensive use of shock tube ignition data in the development and validation of combustion reaction mechanisms. These data come from measurements using a range of diagnostics and a variety of shock tubes, fuels, and initial conditions. With the wide selection of data available, it is useful to realize that not all of the data are of all the same type or quality, nor are all the data suitable for simple, direct comparison with the predictions of reaction mechanisms. We present here a discussion of some guidelines for the comparison of shock tube ignition time data with reaction mechanism modeling. Areas discussed include: definitions of ignition time; ignition time correlations (with examples taken from recent n-heptane and iso-octane measurements); shock tube constant-volume behavior; shock tube diameter and boundary layer effects; carrier gas and impurity effects; and future needs and challenges in shock tube research.

Introduction

Chemical kinetic modelers have made extensive use of shock tube ignition data in the development and validation of combustion reaction mechanisms. These data are available for many different fuels and a range of reaction conditions. With the wide selection of data that are available, it is useful to realize that not all the data are of all the same type or quality, nor are all the data suitable for simple, direct comparison with the predictions of reaction mechanisms. What is needed is to match accurate and well-defined experimental shock tube data with the predictions of an appropriate computational model.

One zeroth-order approximation model (ZOAM) regularly applied to reflected shock wave ignition time data is the following: use published T_5, P_5 (reflected shock wave initial temperature and pressure), and X_i (initial mole fractions of mixture components); use a constant volume or density constraint (zero velocity, $U_5=0$) combined with the assumption of no heat transfer or mass diffusion in the computation; and compare published ignition times or species concentration time histories to computed values.

A higher-order, fuller description of the shock wave experiment would include the temporal and spatial variations in the test gas control volume caused by boundary layer growth, attenuation of the incident shock wave, and energy release of the combustion test gas mixture. At some point in the progress of a reflected shock experiment in a high concentration mixture, a transition to detonation can occur that would make the interpretation of shock tube data even more complicated.

Thus every aspect of the ZOAM is open to interpretation and needs to be well defined to be useful. Initial state conditions in the ZOAM need to be chosen from the spatially and temporally varying values: $T_5(t,x)$, $P_5(t,x)$, $V_5(t,x)$, and published T_5 and P_5 need to be defined in this context, particularly if averaging or extrapolation is employed, as is common. Any vibrational non-equilibrium and relaxation processes that occur, primarily in the carrier gases also affect initial conditions. And while it is expected that the initial mole fractions of the reactants are uniform over the reflected shock regime (i.e., $X_i(t=0,x) = X_i(t=0)$), reactants that can rapidly decompose during the passage of the lower temperature and pressure incident shock may have some spatial variation. Finally the ignition time τ_{ign} needs to be clearly and properly defined. In many ignition experiments the exponential branching process is sufficiently slow that the "rapid ignition process" may take substantially more time than ~1% of the induction time and a more unequivocal ignition time definition is needed. At the other extreme, variations in ignition time can occur along the length of the shock tube control volume, especially during very energetic ignition events, and an ignition time measurement location needs to be defined.

The information that could be used to improve the ZOAM approximation is generally not presented in the literature. This information could take the form of $T_5(t,x)$, $P_5(t,x)$, $V_5(t,x)$ (velocity) and $X_i(t,x)$ time histories during the entire ignition event, or include detailed fluid mechanical/chemical models that more accurately predict and describe the actual flow state and condition throughout the test gas volume. All this information points to a movement away from the ZOAM to a fuller description of shock wave ignition experiments. However, validation tests of these fuller descriptions have rarely if ever been done and are likely to be facility specific; hence the ZOAM is likely to remain important.

Uncertainties in the predictive ability of the zeroth-order model can vary widely. The zeroth-order approximation model is expected to be most accurate under the following conditions: short test times (less than 500 μs), large diameter shock tubes (greater than 10 cm), low initial fuel and oxidizer concentrations (such that the pressure change and energy release during ignition are small), an inert diluent gas such as argon (more uniform shock tube performance than with diatomic gases such as nitrogen), and pre-shock pressures, P_1, greater than some modest minimum pressure (of order 10 torr.)

However, experimentally, low initial fuel concentrations can be difficult to produce and measure accurately. As well, much of the previous ignition-time work was done on relatively small diameter shock tubes with pressure transducers as the indicating diagnostic. This diagnostic gives useful ignition times only for high concentrations (of order 1% fuel or greater). The requirements of engine (IC, HCCI, CI and SI) modelers also present a different set of problems. Engine modelers would like ignition time data for conditions near to those of practical devices. These conditions, with temperatures as low as 700 K, pressures as high as 100 atm and stoichiometric mixtures of fuel and air (1-2% fuel, 20% O_2, 79% N_2) can result in ignition times of several to tens of milliseconds, and represent an extension from the conditions where shock tube operation is best described with the ZOAM.

This is not to say that shock tubes are unsuited for measurements in these regimes. Shock tubes are excellent devices to perform these studies and measure ignition times. What is necessary is an improved interpretation of the results of these measurements as well as improved understanding of the capabilities of shock tubes and more complete characterization of (facility-specific) shock tube behavior and flow properties. As a first step in this direction, we propose in this paper to provide some guidelines for the use of shock tube ignition data in the development and validation of combustion reaction mechanisms. Primarily we will be concerned with understanding the uncertainties associated with shock tube ignition data, as well as the assumptions used in modeling these data.

The use of shock tubes in chemical kinetic rate investigations has been discussed before, e.g. see Belford and Strehlow (1969) [1], Bowman and Hanson ([2] and Lifshitz (2001) [3], as well as in detonation studies, e.g. see Schultz and Shepherd (2000) [4].

What is Ignition Time?

Reaction models allow us to make a direct comparison of the different definitions of ignition time. Fig. 1 shows the model predictions for four types of ignition time indicators for five different initial conditions that span a wide region of the initial condition parameter space for iso-octane/O_2/N_2 ignition mixtures.

Several observations about the suitability of these ignition predictors can be made. As seen on a semi-log plot, the CH* (excited state) emission has a continuous and complex behavior, and lacks an unambiguous single feature. The CH* emission signal has been simulated by assuming that it is proportional to the production rate of CH* which is formed by the reaction $C_2H + O \rightarrow CH^* + CO$ and then rapidly quenched. When measured using a linear scale, however, there is usually a single strong peak that can be identified with the ignition time. Pressure is a good indicator of ignition at high fuel concentrations (except in some cases where the stoichiometry is substantially different than unity and the ignition process is substantially drawn out in time.) In the two low concentration ignition cases, 2% O_2, $\phi=1.0$ and 0.2% O_2, $\phi=0.25$, however, there is a small, almost immeasurable pressure rise, which renders this ignition indicator unsuitable for low concentration mixtures. The CH* and OH (and intermediate species C_3H_6) mole fraction histories all show clear evidence of a change owing to ignition for all cases, yet there is no unique way to define ignition time. For example, the ignition delay time could reasonably be defined as occurring either at the time of maximum rate of change or of the peak value of some species or variable such as [OH], [CH] or pressure, or could be based on an extrapolation of the maximum slope to the zero signal level.
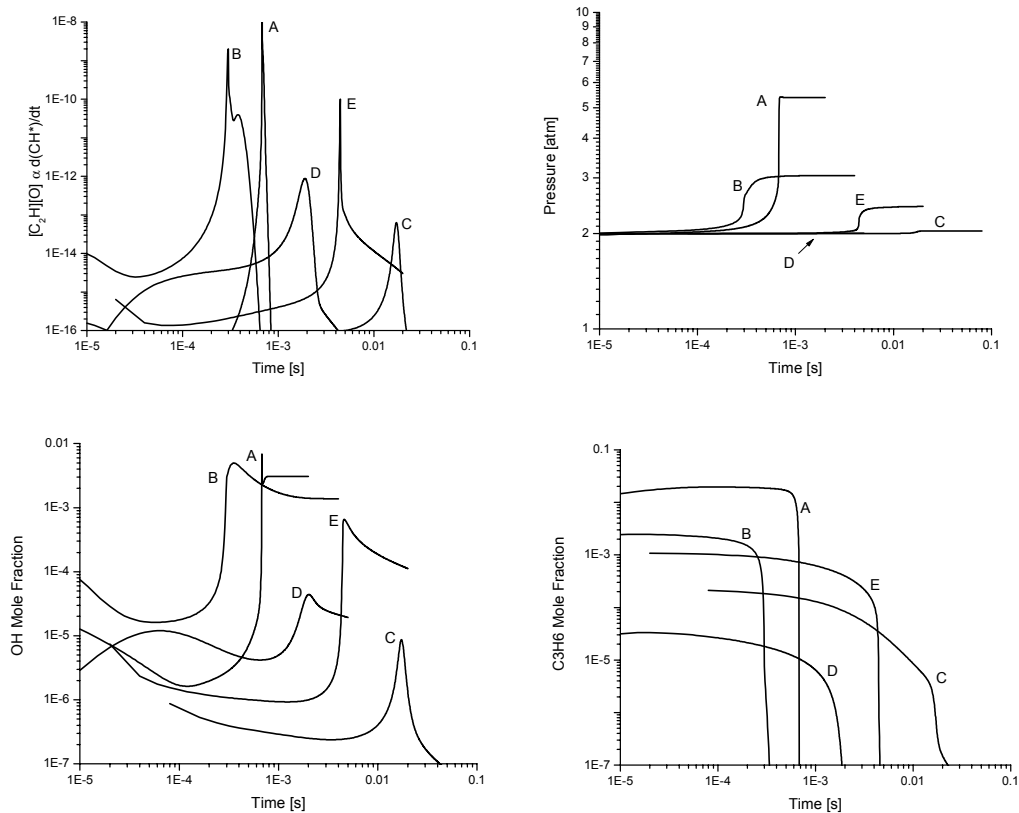
Fig. 1. CH* production, pressure, OH and C_3H_6 mole fraction time histories for a variety of iso-octane/O_2/N_2 ignition mixtures at initial reflected shock conditions of 1400 K, 2 atm: {A, 20% O_2, ϕ=2.0}, {B, 20% O_2, ϕ=0.25}, {C, 0.2% O_2, ϕ=2.0}, {D, 0.2% O_2, ϕ=0.25}, {E, 2% O_2, ϕ=1.0}. Modeling using the Davis and Law (1998) [6] iso-octane oxidation mechanism.

Table 1 shows a comparison of the different ignition times derived from several different indicators: CH* emission, pressure change, OH or C_3H_6 species concentration. The variation of ignition times using these definitions, except in case B, is typically less than 2% from the average, indicating that any of these methods can be used to identify ignition time and that they are reasonably interchangeable, over the range of reaction conditions studied. In very lean mixtures such as case B, 20% O_2, ϕ=0.25, a more specific definition may be needed, though the scatter is still typically less than 10%. What is especially important to note is that while there is reasonable agreement amongst the methods, some methods, such as pressure measurement, cannot be used over a wide range of conditions because of signal-to-noise ratio issues.

Case	X_{CH*} peak	X_{OH} peak	$(dX_{C3H6}/dt)_{max}$	$(dP/dt)_{max}$
A	683	680	688	675
B	300/380[+]	364	340	292
C	17330	17440	16960	17200**
D	1910	2020	1907	1900**
E	4470	4620	4640	4460

Table 1. Ignition times from Fig. 1. [+] first/second peak; ** very small change in P. All times given in microseconds. Initial conditions of cases described in Fig. 2.

Several issues remain. First is the issue of limited shock tube test time. Though methods are available to extend reflected shock test time by tailoring driver gas mixtures, larger uncertainties in temperature exist in shock tube measurement with test times greater than about 2 ms, and for relatively small shock tube diameters or insufficient driver length, this upper test time limit may be as short as 500 µs or less. Long measured ignition times, of order several ms, should be considered as lower limits of the true constant volume ignition time, as boundary layer effects will degrade the constant volume assumption by increasing the test gas temperature significantly at longer times. This effect is described in more detail in a later section.

A related issue is the minimum measurable ignition time. For combustion temperatures, reflected shocks travel at a speed of about 0.5 mm/µs, and for optical measurements through windows of the order of 6-12 mm diameter, this finite shock transit time can cause an experimental convolution of the signal of at least 12 µs if the viewing area is not limited by the probe beam diameter or the collection slit width. Piezo-electric pressure transducers typically have active diameters of approximately 4 mm and response frequencies of 400 kHz, giving similar experimental convolutions if they are mounted on the shock tube side wall, and are prone to ringing if placed on the shock tube end wall. This ringing prevents identification of ignition times that are shorter than several crystal ringing cycles. Blast wave effects found in high concentration mixtures cause modifications to ignition times measured away from the endwall. Corrections to ignition time measurements can be of the order of 10-40 µs for sidewall measurement locations 20 mm from the endwall. See Petersen et al. [5] for details of this calculation. Shock tube endwall emission measurements of ignition time can eliminate this particular problem. We have found through experience that measured ignition times shorter than 50 µs have larger uncertainties and are less suitable for reliable study.

Another issue is multi-stage ignition. The ignition process in large fuels such as n-heptane and iso-octane proceed through a series of decomposition and oxidation steps to small, and more stable intermediates, e.g. H_2, C_2H_4, C_2H_2, C_3H_6, followed by the final oxidation steps of these small stable species. Example evidence of the rapid formation of the stable intermediate C_3H_6 in iso-octane ignition modeling is presented in Fig. 1. An ignition time based solely on the disappearance of the initial reactant, in this case iso-octane, would suggest an ignition time of the order of 10-100 µs, while an ignition time

based on the largest step in pressure, the final removal of C_3H_6, or the rapid formation of OH radicals would be two orders of magnitude longer.

Depending on the initial conditions, the ignition-indicating diagnostic (pressure, OH, etc.) may vary too slowly because of the smoothing effect of these multi-stage processes to offer an obvious ignition time. In these cases an overall ignition time would need to be arbitrarily defined. This ignition time should have a kinetic basis, for example, time to half the maximum change in pressure or to half the maximum species concentration, rather than a laboratory basis, such as time for the CH* emission signal to reach 1 volt, etc., which would be difficult to relate to kinetic modeling.

Are Ignition Time Correlations Useful?

A review of the shock tube literature for a common fuel will usually bring to light a variety of ignition time studies. Shown in Fig. 2 are example data from five groups who studied ignition times in n-heptane/O_2/Ar mixtures. For ease of comparison, these data have been normalized using the correlation of Burcat et al. (1991) [7]. These studies used a variety of ignition time markers including: pressure rise and OH* and CH* emission. The reaction conditions vary over a range of temperature, pressure, equivalence ratio and fuel or oxygen concentration.

What is clearly evident in the results obtained in these different studies is that they can vary as much as one order of magnitude above and below the correlation suggested Burcat et al. What is the reason for this? Is this caused by use of a correlation that is not valid for the conditions of the other studies? (As will be evident from the modeling discussion below, current correlations can still give a fair first approximation to the ignition times, even outside their data set.) Is this caused by differences in the definition of ignition time amongst the studies? (Apparently not, based on the example (Fig. 1, Table 1) discussed above.) Is this caused by errors in the experimental methods of the different workers? (This type of error is really only detectable through comparisons based on correlations.) Is this caused by differences in the shock tubes? (The performance of particular shock tubes, which is often related to their diameter, may not be suitable for ignition time studies.) Answers to these questions are needed before these data can be used for quantitative comparison with computational models. Resolution to these questions will hopefully enable the modeler to use shock tube ignition time data to constrain the predictions of their reaction mechanism to better than the nearly two orders of magnitude variation evident in this plot.

The development of correlations for ignition time data is necessary for several reasons. Firstly, some modelers require ignition time correlations to embed in their engine programs or reactive flow combustion codes rather than use full or reduced kinetic modeling to describe the chemical processes. Correlations also guide the experimentalist in the design of data sets, by reducing the number of experimental conditions needed to fully examine the ignition behavior of a particular fuel. Additionally, ignition time correlations are essential to allow comparison of findings from different studies that might have been conducted with different reaction conditions. Such comparisons are

necessary as can be seen from Fig. 2, because some data sets fall far from the consensus and may not be consistent with other data sets, and may yield misleading results if used in model validation. Comparisons such Fig. 2 also typically provide a means of assessing the degree of data scatter in individual studies.
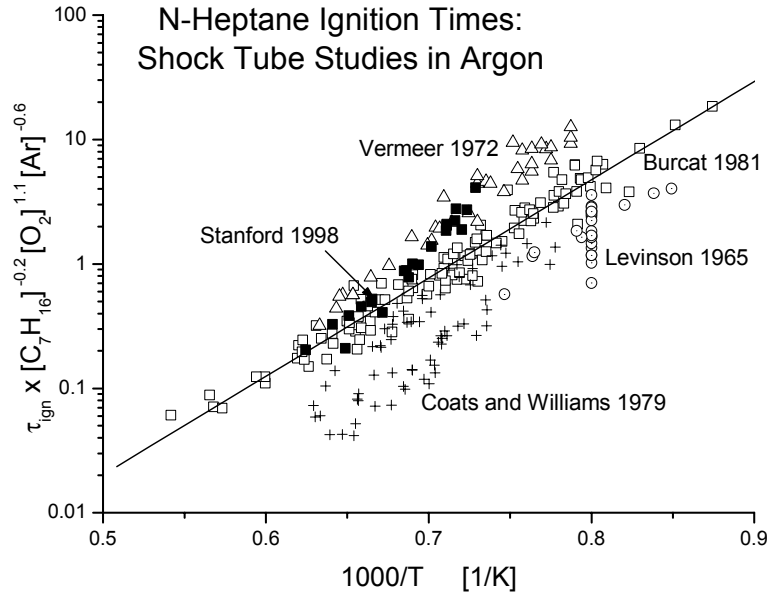

Fig. 2. n-Heptane ignition times. All times correlated using scaling of Burcat et al. (1991): τ_{ign} varying as $[C_7H_{16}]^{0.2} [O_2]^{-1.1} [Ar]^{0.6}$.

Correlations can take many forms. Over the range of conditions that Burcat et al. measured n-heptane ignition times, the authors correlated ignition times using an expression of the form:

$$\tau_{ign} = C [C_7H_{16}]^P [O_2]^Q [Ar]^R \exp(E_{AB}/RT) \hspace{3cm} \text{Eqn. 1.}$$

This form, an improvement over earlier expressions without a dependence on bulk carrier gas concentration, describes the behavior of n-heptane ignition times using five parameters, and assumes that the ignition times vary as power laws in the concentrations of fuel, oxygen and argon, respectively, and exponentially as (1/T). See Lifshitz (2001) [3] for a discussion about this form of correlation.

Recent work in our laboratory by Horning et al. (2002) [8] found that for n-alkanes, ignition times could be correlated well with an expression, also with five parameters, of the form:

$$\tau_{ign} = C P^N X_{O2}^M \phi^S \exp(E_{AH}/RT) \hspace{3cm} \text{Eqn. 2.}$$

and in particular for n-heptane:

$$\tau_{ign} = 6.67 \times 10^{-12} \, P^{-0.61} \, X_{O2}^{-0.68} \, \phi^{0.96} \, \exp(44{,}600/RT) \qquad \text{Eqn. 3.}$$

where τ_{ign} is in s, T is in K, P is in atm, and E_A is in cal/mol.

The key advantage of this form of the correlation is that it mimics several current n-heptane oxidation mechanisms in the dependence of ignition time on P, X_{O2} and E_A at temperatures above 1100 K. Over the limited equivalence ratio range, $\phi = 0.5$ to 2.0, a power law relation provides a good simple description of the dependence of ignition time with equivalence ratio. For a wider equivalence ratio range, $\phi = 0.2$ to 4.0, a different form of the correlation is preferred, one that duplicates the experimental and model predictions of a weak power law dependence at small ϕ, where oxygen chemistry plays a more important role in determining ignition time, and a strong power law dependence at large ϕ, where fuel pyrolysis and oxygen scavenging chemistry plays an important role. The Horning et al. correlation takes advantage of the predictions and knowledge derived from a fuller kinetic model of the ignition process. (See Horning et al. (2002) for a comparison of the ignition time predictions of several models and their relationship with this correlation.)

For the case of iso-octane, Davidson et al. (2002) [9] found ignition time dependences that were similar to those Horning observed in n-heptane for pressure, equivalence ratio, and activation energy, but found a stronger dependence on fuel or oxygen mole fraction at large concentrations. The correlation proposed by Davidson et al. for the high concentration data is

$$\tau_{ign} = 4.50 \times 10^{-10} \, P^{-0.56} \, \exp(-232 \, X_{Fuel}) \, \phi^{1.62} \, \exp(44{,}780/RT). \qquad \text{Eqn. 4.}$$

Another form of the correlation that captures the very low concentration iso-octane data, gives similar high concentration predictions, and is related to the Horning et al. correlation is given by:

$$\tau_{ign} = 1.65 \times 10^{-10} \, P^{-0.66} \, X_{O2}^{-0.34} \, \phi^{1.13} \, \exp(43{,}050/RT) \, \exp(-129 \, X_{fuel}). \qquad \text{Eqn. 5.}$$

These two examples, the non-power law variation of n-heptane ignition time with equivalence ratio and the non-power law variation of iso-octane ignition time with fuel concentration, demonstrate that a simple power law correlation for ignition time measured over a very wide range of conditions may not always capture the needed chemistry and phenomena. Correlations using power laws are widespread in the literature, and for data sets of limited extent in pressure, equivalence ratio, fuel concentration and temperature, may still be a very good choice. A comparison with detailed kinetic model predictions is usually warranted to understand the useable regime of conditions for a correlation.

Comparing Correlations and Kinetic Modeling

As discussed in the previous section, it is critical when comparing ignition time data with correlations and kinetic models to know how complete the experimental coverage of the (T, P, X_{O2}, ϕ) parameter space is for a particular fuel and buffer gas: M=Ar or N_2. In the following discussion we will continue to use as examples the n-heptane ignition times by Horning et al. (2002) and iso-octane ignition times by Davidson et al. (2002).

Horning et al. measured n-heptane ignition times using endwall CH* emission over a range of conditions that included 1329-1676 K, 1.15-5.69 atm, 0.2-1.75 % n-heptane, 2.2-19.7 % oxygen and equivalence ratios between 0.5 and 2.0. The measured ignition times for these experiments fell between 100 and 500 µs and minimized any error associated with boundary-layer-generated temperature non-uniformity in the relatively large diameter (15.3 cm) shock tube. Similarly Davidson et al. measured iso-octane ignition times over a range of conditions that included 1177-2009 K, 1.18-8.17 atm, 100ppm – 1% iso-octane, 0.125 to 12.5% oxygen and equivalence ratios of 0.25 to 2.0. Work by Niemitz et al. (1988) [10] extends this range to 1.6% iso-octane and 20% oxygen.

The extent of parameter space that these data cover in ϕ-X_{O2} space is indicated in Fig. 3. In both cases, coverage of the ϕ-X_{O2} space is good, but it is evident when presented in this manner that further measurements at high oxygen concentrations (20%) and equivalence ratios of 0.25 and 2.0 may be warranted. The extent of the coverage in pressure and temperature space is less important for these conditions (1100-2000 K and 1- 8 atm) because both the experimental data and current models show simple power law variation of the ignition times with pressure and exponential variation with inverse temperature, and hence extrapolation to other conditions can be made more confidently.

We can compare the experimental ignition time data (in the form of a correlation) with the predictions of a kinetic model for a wide range of conditions by using a three-dimensional representation over the ϕ-X_{O2} space. In the top frame of Fig. 4 the ignition time predictions from the Davidson et al. iso-octane shock tube correlation are shown along with the constant volume model predictions using the Pitsch et al. (2001) [11] reduced reaction mechanism. This three-dimensional plot shows the variation of ignition time with oxygen mole fraction (from 100 ppm to 20%) and equivalence ratio (from 0.25 to 2.0) for initial conditions of 1400 K and 2 atm. The bottom frame shows similar results from the Horning et al. n-heptane data and the Pitsch et al. (2000) [12] reduced reaction mechanism. The advantage of this representation is that a direct comparison of correlation (and hence data) and model can be made over wide range of conditions.
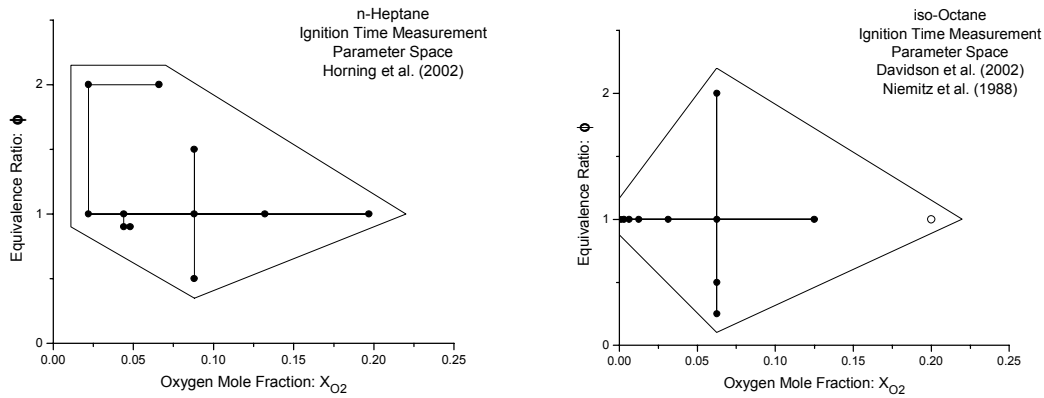
Fig. 3. Extent of parameter space covered by experimental data of Horning et al. for n-heptane ignition time measurements and Davidson et al. iso-octane data. Open circle in iso-octane chart is data of Niemitz et al. (1988).

We see that the Pitsch et al. iso-octane model (47 species, 134 reactions) captures the major features of the iso-octane data correlation: the variation with stoichiometry and the strong variation with oxygen mole fraction. This particular correlation suggests that at large oxygen mole fraction 20% and large equivalence ratio 2.0 that the ignition time shortens dramatically. This region of mixture space in Fig. 3 has not been tested experimentally, but the Pitsch et al. model does suggest that it will still be shortened somewhat.

In the case of n-heptane, the ignition time correlation is very simple (power law in both oxygen mole fraction and equivalence ratio). But the kinetic model of Pitsch et al., though able to generate approximately correct ignition times, does not show the same simple trends over the whole surface. Anomalous non-monotonic variation with oxygen concentration at lean equivalence ratios is evident, for example. The present experimental database for lean mixtures is currently not extensive enough to support or contradict the variation found in the model. This approximate representation of the ignition time correlation (and hence data) is typical of a strongly reduced reaction mechanism, in this case, 44 species and 112 reactions. At large oxygen mole fraction 20% and small equivalence ratio 0.25, the correlation and the model diverge significantly. This mixture regime has also not been tested experimentally based on the n-heptane parameter space coverage of Fig. 3.

One observation directly evident from the above presentation format is that at a high oxygen mole fraction of 20% and equivalence ratios of approximately 1, the correlations and models predict that the iso-octane ignition times will be shorter than the n-heptane ignitions. This trend is not expected based on assumed role of iso-octane in reducing knock (i.e. extending ignition times) in gasoline engines.

This observation that the iso-octane and n-heptane ignition times are similar is not new. In Westbrook, Warnatz and Pitz (1988) [10] there is evidence (their Fig. 1) that the ignition time of iso-octane is comparable with that of n-heptane under certain high

concentration conditions. Westbrook et al. (2002) [13] have also shown in rapid compression machines that it is possible to have non-monatonic behavior in the relationship between octane number and knocking, higher octane number fuels producing more knocking than lower octane number fuels in some cases. The differences in the chemical kinetic history experienced in shock tubes and rapid compression machines and in practical engines is also discussed in a review by Westbrook et al. (2000) [14].
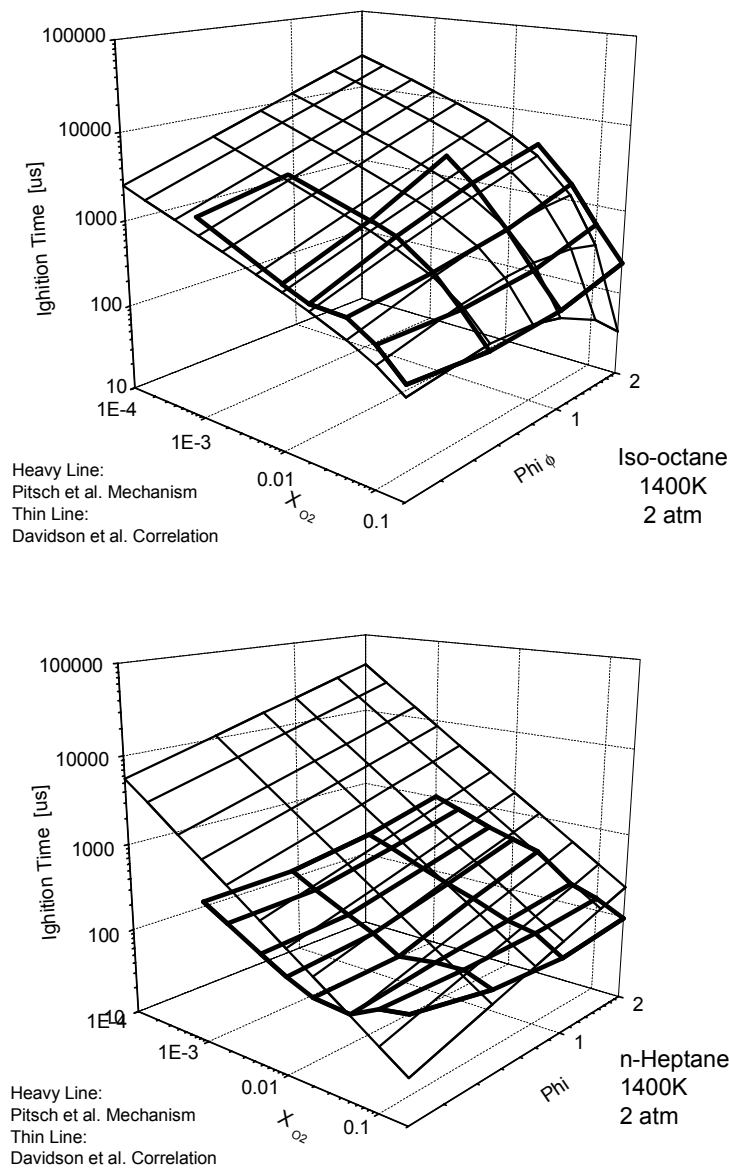

Fig. 4. Three-dimension comparison of correlations and models for n-heptane and iso-octane ignition times.

An extensive shock tube ignition time study can offer more than just a series of discrete targets for kinetic modelers. Multi-dimensional representations of the data can expose global trends which themselves can be used as kinetic targets for model validation

and refinement. Correlations offer a very simple way to do this, making significant similarities and differences and important trends in the experiment and the model more evident.

Shock Tube Constant Volume Behavior

In comparing modeled ignition data with experimental data, the model calculations are usually done with a constant volume or constant density constraint. One measure of the validity or suitability of this assumption is a comparison of modeled and experimental pressure jump and plateau pressures during and after ignition.

Example shock tube pressure traces for a range of fuel concentrations are shown in Fig. 5. These traces have several identifiable features. The first plateau is the filling pressure P_1, the second plateau is the pressure behind the incident shock P_2. The pressure transducer in these experiments was placed 2 cm from the end wall of the shock tube, resulting in a short interval, of order 65 μs where this incident shock pressure can be measured. The third plateau is the reflected shock pressure P_5. The rapid rise in pressure at ignition in the highest concentration examples, 0.5% and 0.25% fuel, seen in both the model and data of the upper frames of Fig. 5, is the constant volume ignition pressure increase. The ragged form of the experimental pressure data after this time is evidence of a blast wave or detonation that occurs after this pressure jump. In the lower concentration examples, the post-ignition plateau pressures are similar to P_5 and the ignition pressure jump is barely noticeable. At times longer than 2 ms in all of these traces, the pressure begins to fall because of the interaction of the driver rarefaction wave with the reflected shock region.

If the shock tube were an ideal constant volume reactor, then even with the energy release process occurring during ignition, the modeled pressure and measured pressure would achieve the same levels during the initial ignition pressure jump and the final resting plateau. The ignition pressure jump is determined by the energy release rate of the ignition process, and the final resting pressure is determined by the energy that is released. A comparison of the experimental and modeled ignition pressure jumps is shown in Fig. 6. At higher fuel concentrations, the pressure jump is substantially less than that predicted by the constant volume model, which is indicative of a failure of the constant volume constraint during the last stages of these energetic ignition events.
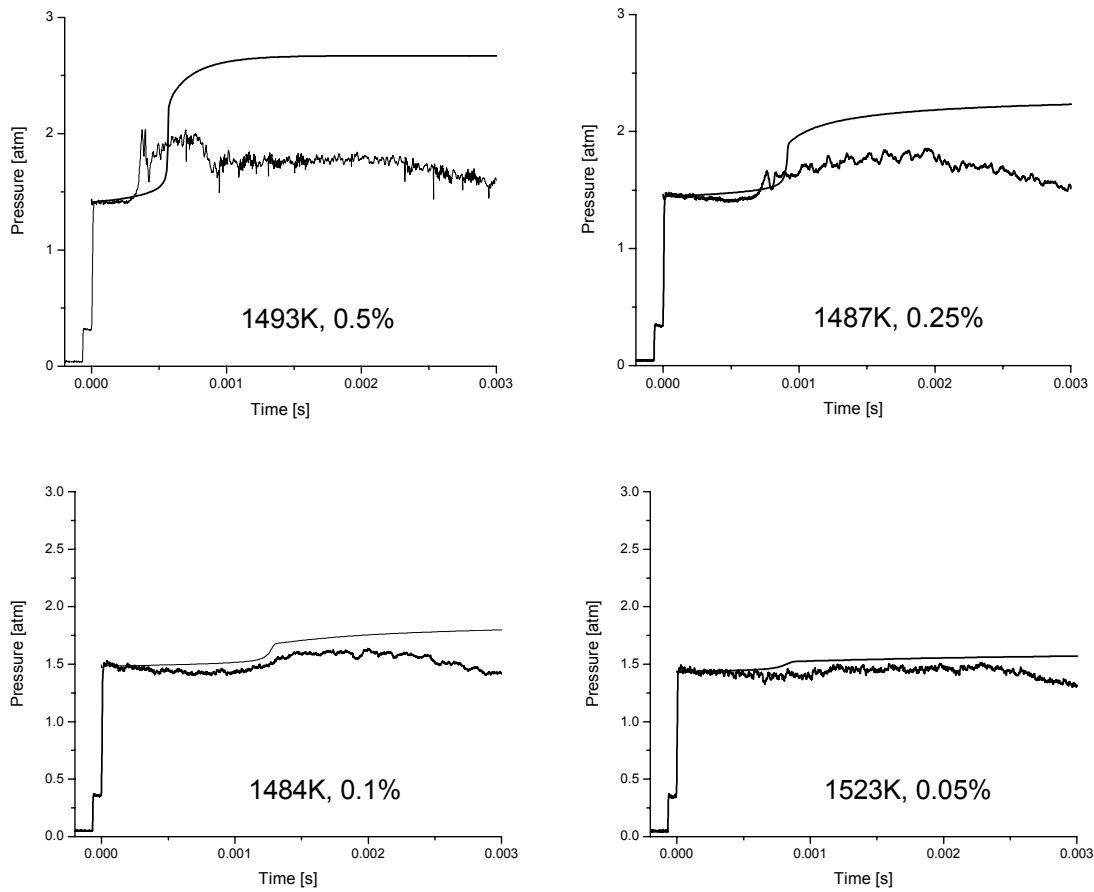
Fig. 5. Side wall pressure measurements and modeling during ignition events in iso-octane/O_2/Ar for a variety of fuel concentrations; 0.5% to 0.01%. Initial shock conditions: ~1500K, ~1.4 atm, ϕ=1.0. Modeling using Davis and Law (1998).
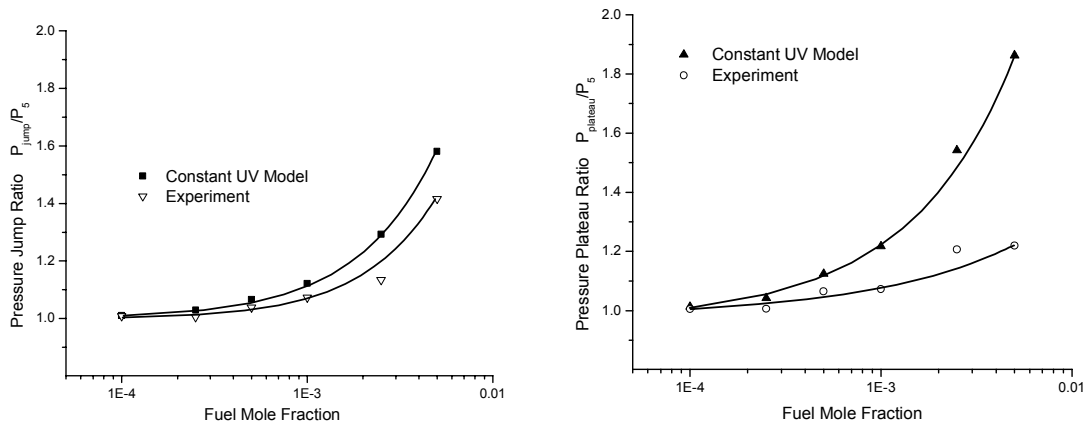

Fig. 6. A comparison of the measured and modeled pressure jump ratio and plateau pressure ratio during ignition events in iso-octane/O_2/Ar, ~1500K, 1.4-5.0 atm, ϕ=1.0.

Because this initial pressure jump occurs exponentially, its influence is limited to a small fraction of the time prior to ignition. Hence, the measured pressure profile of the ignition process can be approximated by the calculated pressure profile using a constant volume constraint up to the time of ignition. After that time, for ignition events with large energy release, the shock tube does not behave like a constant volume reactor. Figure 6 shows that only for stoichiometric iso-octane ignition experiments with mixtures of ~500 ppm or less of fuel can we assume that the entire ignition process, including the plateau region after the ignition, can be accurately modeled using a constant volume constraint.

One application of this pressure jump analysis is determining which shock tube ignition experiments can be quantitatively modeled throughout the entire ignition process. Thus in the case of 0.05% iso-octane, we may confidently use the constant volume constraint to model quantitative species concentration measurements made after the point of ignition. An example of OH data from such a shock tube experiment, Davidson et al. (2002) [9], is shown in Fig. 7. These OH data are based on cw ring-dye laser absorption measurements of the OH A-X (0,0) band $R_1(7)$ line; concentration uncertainties are of the order of ±5%.

In this experiment the difference between the final plateau values of the model and data can be attributed to discrepancies in the model. Either inaccuracies in the reaction rate coefficients or thermo-chemical data could be responsible. Recent work by Herbon et al. (2003) [15] has indicated that some of this variation in combustion product partial equilibrium values can be attributed to errors in the value used for the OH heat of formation.
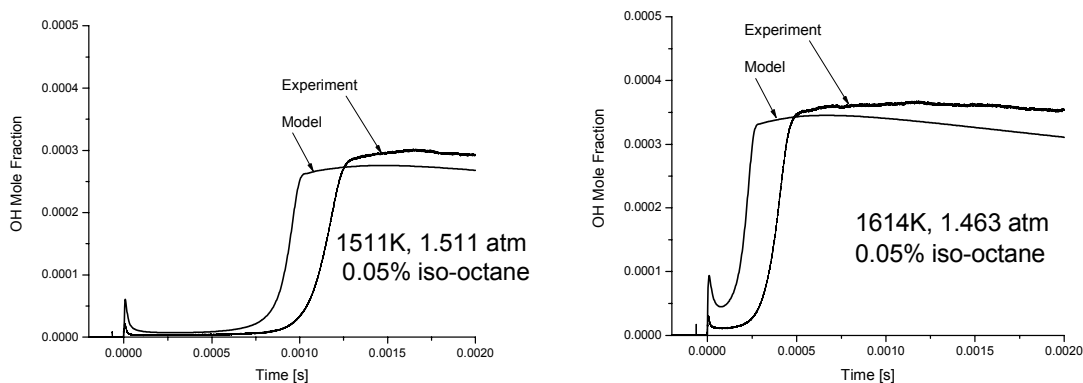

Fig. 7. Side wall OH absorption measurements and modeling during ignition events in iso-octane/O_2/Ar, Davidson et al. (2002) [9].

Boundary Layer Effects on Shock Tube Temperatures

The following discussion is based on corrections to shock tube ignition times given by the boundary layer model of Petersen and Hanson (2002) [5].

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In the ideal description of a shock wave experiment, the incident shock front passes along the length of the shock tube, leaving behind a region of shocked gas with uniform P_2, T_2, and V_2, the gas velocity in laboratory coordinates. This is followed by a reflection of the shock wave from the end wall of the shock tube and formation of a uniform reflected shock region with uniform P_5, T_5 and $V_5=0$.

The actual behavior of these shock waves is modified by formation of boundary layers behind the incident and reflected shocks. The result of the boundary layer behind the incident shock is to generate a gradul increase in temperature and pressure in the core of the flow. When the reflected shock passes through this non-uniform pressure and temperature distribution, it also experiences an increase in temperature and pressure, and this increase appears to be linear with test time.

The effects of boundary layers on shock tube performance are unavoidable, though it is possible to reduce these effects to a negligible level in some cases. The primary ways to reduce the influence of boundary layers are to employ a large shock tube diameter, raise the test gas pressure or decrease the portion of the test time that is used in the measurement. One simple way to quantify this boundary layer effect is by considering the value dT^*/dt which equals the relative change of $T^* = \Delta T_5/T_{5\ initial}$ with reflected shock test time. Typically, large diameter shock tube have dT^*/dt values less than 10 s^{-1}. This effect will also be a function of the initial fill pressure P_1. Thus a 6-inch diameter (15 cm) shock tube could have a change of temperature attributed to boundary layer effects over 1 ms of test time of less than 15 K for a 1500 K reflected shock. For a shock tube less than 4 inches diameter (10 cm) this effect can rapidly increase to values of 20 to 30 s^{-1} or more.

The increase in temperature due to the boundary layer has a dramatic effect on apparent activation energy of ignition times. Fig. 8 and Table 2 illustrate the effect that a shock tube with a small diameter (and hence a large dT^*/dt) and an experimental data set with long (1-2 ms) test times have on a hypothetical ignition time measurement where the true activation energy is 40 kcal/mol. Substantial errors in the apparent activation energy (greater than 6 kcal/mol) are possible.
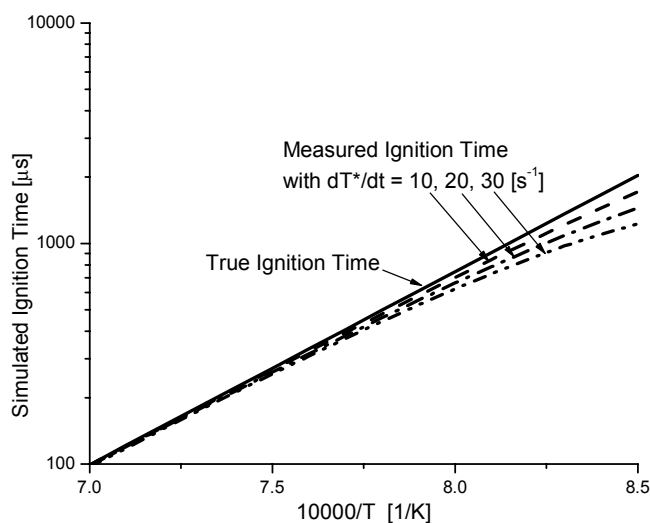
Fig. 8.   Simulated ignition times showing the effect of boundary-layer-induced test gas heating on the ignition time activation energy for a hypothetical fuel with an ignition time activation energy of 40 kcal/mol.

Without a quantification of the value of dT*/dt for a small diameter shock tube (an effect which is pressure and temperature dependent), corrections to previously published ignition time measurements are difficult.   However, an understanding of the significance of dT*/dt can be useful in explaining the apparent differences in activation energy found in shock tubes of different diameters.

Shock Tube Performance	Including ignition times up to 500 μs	Including ignition times up to 1 ms	Including ignition times up to 2 ms
dT*/dt [s^{-1}]	Measured E_A [cal/mol]	Measured E_A [cal/mol]	Measured E_A [cal/mol]
0	40000	40000	40000
10	39200	38400	37600
20	38600	37200	35800
30	37800	35600	33500

Table 2.   Example effect on ignition activation energy by boundary-layer-induced shocked gas heating. Measured E_A for true ignition activation energy of 40 kcal/mol and data over the range of 1176 to 1428K.

Effect of Bulk Carrier Gas

To improve shock tube performance, shock wave experiments are normally performed in argon, rather than nitrogen.   This eliminates the possible influence of vibrational relaxation in the carrier gas, as well as eliminating or minimizing shock wave bifurcation near the wall in the reflected shock front.   As well, for the same initial shock

pressure P_1, argon shocks can have higher reflected shock temperatures, as no energy has to go into the vibrational modes of the shock-heated gas. Argon shocks have historically been considered to have "quieter" pressure profiles and this may be related to differences in boundary layer growth.

Normal combustion occurs in air, of course, and differences in ignition time data collected in argon and air should be recognized and quantified, as should differences in modeling with these two different carrier gases. Figure 9 shows modeling of iso-octane ignition using two different reduced models for initial conditions of 1400 K, 2 atm, 2% O_2, $\phi = 1.0$ with argon and nitrogen as the carrier gas. For one model, Davis and Law, the differences are insignificant, while for the other model by Pitsch et al. the difference is significant.

A comparison between ignition times in gas mixtures with nitrogen or argon as carrier gases allows the investigator to study the effect of small temperature changes during the ignition process. During the initial fuel decomposition step, the temperature of the shock heated gas mixture drops slightly as energy is extracted to break fuel bonds. This temperature drop is larger in argon than in nitrogen. The Pitsch et al. mechanism shows much more rapid growth of the temperature in the argon carrier gas, even though the argon carrier gas minimum temperature is lower than that found with the nitrogen carrier gas. Once the temperature of the secondary reaction products begins to increase it rapidly accelerates the ignition process. In the Davis and Law mechanism this increase is not evident in the M=Ar case, indicating that the sub-mechanism controlling the secondary reaction products is not as strongly temperature sensitive. Evidence exists for some fuels that there is no experimental sensitivity to carrier gas but not for all fuels. See Petersen et al. (1999) [16] for a discussion of this effect in methane oxidation.

The effect of the heat capacity of the bulk carrier gas on shock tube test gas temperature is different than, but related to the important effect of the time scale of vibrational relaxation of a diatomic carrier gas (i.e. nitrogen and oxygen) on the shock tube test gas temperature. For very dilute mixtures (~ 0.1 % fuel) in nitrogen or air at low temperatures and pressures, vibrational relaxation times can be substantially longer than the reflected shock test time. In these cases, vibrationally-frozen thermodynamic properties should be used for determining shock temperatures and pressures. At high fuel concentrations, high pressures and/or high temperatures, vibrational relaxation times are usually short enough to use equilibrium thermodynamic properties in the shock equations for determining shock temperatures and pressures. Simple solutions for the intermediate regime have not been developed, and a standard treatment of this combination or coupling of the vibrational relaxation equations with the kinetic equations is needed.
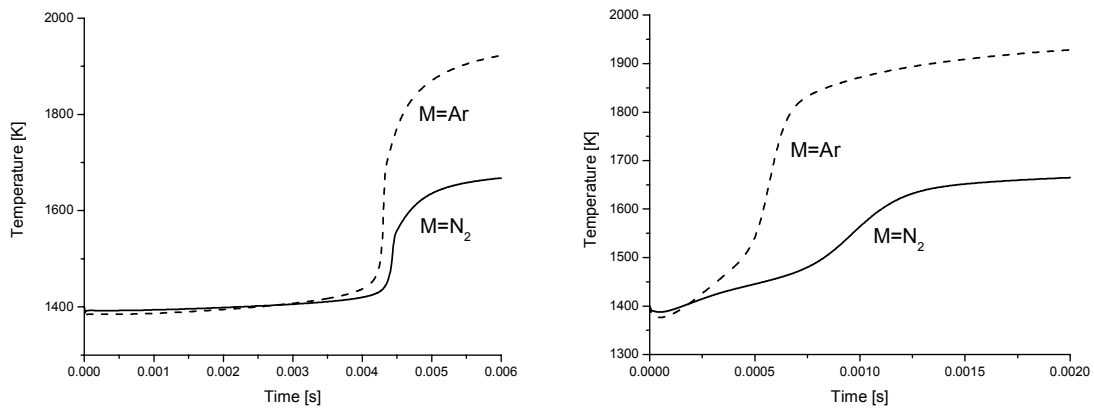
Fig. 9. A comparison of modeled iso-octane ignition using two different carrier gases. Initial conditions of 1400 K, 2 atm, 2% O_2, ϕ = 1.0. Left frame, Davis and Law mechanism [6]; right frame Pitsch et al. mechanism [11].

Effect of Impurities on Measurements

Finally, it should be mentioned that impurities in the initial mixture or shock tube itself, can in some cases have a significant effect on the ignition time. Table 3 shows predicted ignition times from model calculations for a variety of hydrocarbons under typical shock tube conditions. Impurities are simulated here by the addition of 1 ppm H atoms to the initial mixture. What is immediately evident is that the effect of impurities on various fuel species fall into two groups.

The ignition times of ethylene, acetylene and hydrogen are strongly perturbed by the addition of small amounts of H-atoms to the initial mixtures. For these fuels, the ignition time is dominated by the time it takes for the exponential growth in the radical pool. Increasing the H-atom population, shortens this time.

In the other fuels, the ignition time can be seen as a multi-step process, with the first step being the rapid decomposition of the fuel, and the second step being the slow decomposition of the intermediate products and exponential growth of the radical pool. The initially-added H-atoms are rapidly scavenged in the first step by the fuel or the major fuel decomposition products to form less reactive intermediate products, or by reaction with O_2 that forms OH, which is also rapidly scavenged by the intermediate fuel products. The overall ignition time is thus not strongly affected.

It is expected from this analysis that ignition time measurements of ethylene, acetylene and hydrogen should show large scatter unless great care is taken in maintaining high purity conditions in the shock tube. The scatter in ignition times measurements of larger hydrocarbons, on the other hand, should not be dominated by the effects of impurities.

Fuel	T5 [K]	τ_{ign} with no H added [µs]	τ_{ign} with 1ppm H added [µs]	% change	Mechanism
C_2H_4	1300	429	274	36.1	Laskin et al. (2000) [17]
C_2H_2	1150	467	333	28.7	Laskin et al. (2000)
H_2	1050	244	191	21.7	Smith et al. (1999) [18]
C_4H_6	1300	716	699	2.4	Laskin et al. (2000)
C_2H_6	1350	445	440	1.1	Smith et al. (1999)
CH_4	1800	314	313	0.3	Smith et al. (1999)
C_3H_8	1500	555	554	0.1	Smith et al. (1999)
n-C_7H_{16}	1500	269	269	0.1	Held et al. (1997) [19]
iso-C_8H_{18}	1500	684	684	0.0	Davis and Law (1998) [6]

Table 3: Effect of impurities on shock ignition times. All examples are for 5% O_2, ϕ=1, 1 atm, and constant volume calculation. Temperatures where selected so that the modeled ignition time $[d\{X_{OH}\}/dt]_{max}$ were approximately 500 µs.

Future Challenges and Needs for Shock Tube Research

In reviewing the status of ignition time measurements in shock tubes, several challenges and needs are apparent. The needs are those of the kinetics modeling community, which seeks to build ever more accurate and complete detailed models of combustion chemistry, including ignition times. The key challenges for the experimentalist are to improve the quality and extent of ignition data (e.g., through measurement of relevant species time histories over a broader range of mixtures and test conditions), and to find means to extend the useful operating envelope of shock tube experiments outside the limited regime where the ZOAM is applicable.

As a specific example, there continues to be a need to measure longer ignition times, those of order 1-2 ms and longer. For these measurements to be useful, confidence in the temperature profile of the reflected-shock-heated test gas is needed. Several approaches are possible. One method would be to measure dT(t)/dt (i.e. $T_5(t)$ for each experiment. This characterization can be done using infrared emission measurement schemes for non-reactive gas mixtures, but this method may not be suitable for ignition experiments. A more practical scheme would be to relate reflected shock temperature variation with pressure variation and take advantage of the existing capability to measure pressure time histories during shock tube experiments. This approach can be rigorously developed once accurate time-varying temperature measurement techniques are established for reactive flows. However, temperature measurements in reactive flows in shock tubes are difficult; see Schulz et al. (2002) [20] for one attempt to do this with UV CO_2 absorption.

Current modeling work of engine combustion, in particular homogeneous charge compression ignition (HCCI) studies, requires ignition times for low temperature (700-1000 K), high pressure (20-60 atm), and rich mixtures (high fuel concentration 1-2%) of practical fuels (gasoline), surrogate fuels (binary and ternary mixtures) and single fuel

components (n-alkanes, branched alkanes, cyclo-alkanes, alkenes, and aromatics). Very little data of this type exists, though early work by Ciezki and Adomeit (1993) [21] and Fieweger et al. (1997) [22] does start to address some of these needs. These measurements are difficult; in particular, measurements near 700 K, and 20 atm are expected to have very ignition times, so that methods to confirm the temperature-time profile are also needed. Tailored driver gas mixtures can also be used to extend shock tube test time, but again temperature-time profiles for the potentially very long test times must be verified.

The use of shock tubes for acquiring species concentration time-history data during energetic ignition experiments is limited at present in two ways. Either the full ignition time-history can be studied as a constant volume process if the energy release is low (as in the iso-octane example described previously), or only the early time regime (before the final large energy release) can be studied if the constant volume constraint is compromised during ignition. Improved modeling of the flow fields in shock tubes during energetic shocks, the development of one-dimensional temperature, pressure and velocity profiles behind reflected shocks for example, would permit extension of the range of conditions that concentration time-history data could be usually acquired and analyzed. Efforts are currently being made to develop these fluid codes with complete chemistry to permit a more rigorous validation of kinetic mechanisms using species concentration time-history targets over a wider regime.

And finally, critical review of existing and future ignition time measurements are needed. For the reasons described earlier, not all published data sets will necessarily be found to be consistent with one another. Before ignition time measurements should be used in validating or refining kinetic mechanisms, some estimate of the accuracy or reliability of the data set should be made. Reliance on multiple data sets from several different laboratories for tuning reaction mechanisms will enable modelers to place a great deal of scientific confidence in what continues to be an important and needed experimental activity.

Acknowledgements

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