

Experimental study and modeling of shock tube ignition delay times for hydrogen–oxygen–argon mixtures at low temperatures

G.A. Pang*, D.F. Davidson, R.K. Hanson

Department of Mechanical Engineering, Stanford University, Stanford, CA 94305-3032, USA

Abstract

Recent literature has indicated that experimental shock tube ignition delay times for hydrogen combustion at low-temperature conditions may deviate significantly from those predicted by current detailed kinetic models. The source of this difference is uncertain. In the current study, the effects of shock tube facility-dependent gasdynamics and localized pre-ignition energy release are explored by measuring and simulating hydrogen–oxygen ignition delay times. Shock tube hydrogen–oxygen ignition delay time data were taken behind reflected shock waves at temperatures between 908 to 1118 K and pressures between 3.0 and 3.7 atm for two test mixtures: 4% H₂, 2% O₂, balance Ar, and 15% H₂, 18% O₂, balance Ar. The experimental ignition delay times at temperatures below 980 K are found to be shorter than those predicted by current mechanisms when the normal idealized constant volume (V) and internal energy (E) assumptions are employed. However, if non-ideal effects associated with facility performance and energy release are included in the modeling (using CHEMSHOCK, a new model which couples the experimental pressure trace with the constant V , E assumptions), the predicted ignition times more closely follow the experimental data. Applying the new CHEMSHOCK model to current experimental data allows refinement of the reaction rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$, a key reaction in determining the hydrogen–oxygen ignition delay time in the low-temperature region.

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1. Introduction

Recent studies by Blumenthal et al. [1] and Dryer et al. [2] have highlighted the failure of current hydrogen combustion kinetic models to predict experimental shock tube ignition delay times

at low-temperature conditions. The failure cast doubts on the ability to simulate ignition delay times at these conditions in synthesis gas (syngas), a mixture of hydrogen and carbon monoxide in various compositions. Syngas is being considered as an alternative fuel for combustion applications, such as power-generation gas turbines. As reported by Petersen et al. [3], a well-developed chemical model for hydrogen at low temperatures is crucial for the proper design of such applications.

Shock tube ignition delay times of hydrogen have been studied extensively. Previously measured

* Corresponding author. Address: Mechanical Engineering Department, Stanford University, 452 Escondido Mall, Building 520, Room 520I, Stanford, CA 94305-3032, USA. Fax: +1 650 723 1748.

E-mail address: genn@stanford.edu (G.A. Pang).

shock tube ignition delay times for various hydrogen–oxygen and syngas–oxygen mixtures at temperatures below 1000 K are consistently shorter than predicted by current models for pressures from 1 to 20 atm [1,3,4]. Representative experimental reflected-shock ignition delay data taken by Blumenthal et al. [1] and Wang et al. [4] are shown in comparison with current chemical models in Fig. 1. Clearly, at temperatures below about 1050 K, for a mixture of 15% H₂ in air ($\phi = 0.42$) at 3–4 atm, the experimental ignition delay times are shorter than predicted by current models. At temperatures below about 960 K, the difference between the data and modeling exceeds an order of magnitude. The same behavior is present in syngas ignition delay data, as reported by Petersen et al. [3]. Localized ignition, particle effects, and facility irregularities have been mentioned as potentially responsible for these differences [2]. Others, including Blumenthal et al. [1], cite partially inaccurate modeling of the reaction mechanisms as a source of the problem. Notably, all these simulations are based on a thermodynamic–gasdynamic model of constant volume (V) and internal energy (E), as traditionally done for post-reflected-shock reactions.

In the current study, we first extend the database of low-temperature shock tube ignition delay times for hydrogen, and confirm the discrepancy between experimental data and current models at low temperatures. We then move away from constant V , E modeling and apply a new thermodynamic–gasdynamic model called CHEM-SHOCK [5] to the data to study the influence of facility-dependent effects and localized energy release. This CHEMSHOCK modeling reveals that these two effects are responsible for the most

of the discrepancy seen between the ignition delay time data and detailed kinetic modeling. An ignition-delay sensitivity analysis is also performed, and the results suggest a refinement to the chemical reaction mechanism for hydrogen combustion. In particular, a revised rate for the reaction $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ near 975 K is proposed.

2. Experimental set-up

All experiments were performed in the Stanford stainless-steel shock tube described by Oehlschlaeger et al. [6]. The shock tube inner diameter is 14.13 cm, and the driven section is 8.54 m in length, separated from the driver section by a polycarbonate diaphragm. Under normal shock tube operation, the driver section is 3.35 m long and helium is used for the driver gas. This set-up provides approximately 2 ms of high-quality (near-uniform temperature and pressure reaction conditions) test time before a significant pressure change occurs due to the arrival of the rarefaction fan.

The low-temperature ignition region requires longer test times and provides a challenge for shock tube experimentation. Conventional shock tube test time is limited by either the arrival of rarefaction waves from the driver section, or reflected shock-contact surface interactions near the test section. To extend the test time of our shock tube to access ignition delay time data at low temperatures, two modifications were made to the shock tube and its operation: (1) the driver section was lengthened to a total of 6.4 m to allow more time before arrival of the rarefaction fan in the test section and (2) tailored driver gas mixtures of 30–40% N₂ in He were used to minimize shock wave-contact surface interactions. These changes increase the available test time with nearly uniform reflected-shock temperature and pressure to about 20 ms, after which expansion waves arrive from the driver, substantially lowering the test gas pressure.

The driver section extension is also stainless steel, 14.13 cm in diameter and U-shaped, with a 23-cm radius of curvature on the centerline. Data were taken with both the normal shock tube operation (short driver section and helium driver) and modified shock tube operation (long driver section and tailored driver gas mixture).

Two test mixtures were used: a lower concentration test mixture of 4% H₂, 2% O₂, balance Ar, with an analytical accuracy of $\pm 2\%$ for each component, prepared by Praxair; and a higher concentration test mixture comprised of 15.0% H₂, 17.9% O₂, balance Ar, all ultra-high purity gases supplied by Praxair. The 15.0% H₂, 17.9% O₂, balance Ar mixture was prepared manometrically in a stainless steel mixing cylinder and

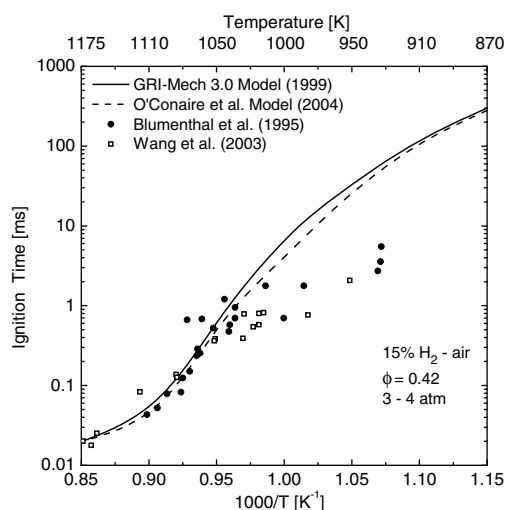


Fig. 1. Reflected-shock ignition delay time data compared to current kinetic models.

mechanically mixed with a magnetically driven stirrer. All measurements were made behind the reflected shock wave. Pressure was measured with a Kistler 603B1 piezoelectric pressure transducer coated with RTV at a sidewall location 2 cm from the endwall. Emission from OH^* chemiluminescence was also measured at this location, through a vertical slit, lens and Schott Glass UG5 filter using a modified UV-enhanced Thorlabs PDA55 photodiode detector; the temporal resolution of this entire system is typically 10 μs . The incident shock velocities were determined using four time-interval counters triggered by five pressure transducers spread over the last meter of the shock tube located near the endwall, allowing an accurate ($\pm 0.2\%$) determination of the incident shock velocity at the endwall. The reflected-shock temperature was calculated using 1D shock relations assuming vibrational equilibrium behind both the incident and reflected shock. The uncertainty in the initial temperature and pressure is approximately $\pm 0.7\%$ and $\pm 1\%$, respectively, due primarily to uncertainties in the measurement of the incident shock velocity and the initial temperature of the gas mixture.

3. Results and analysis

The experimental ignition delay time is taken as the interval between time zero, defined by the passing of the reflected shock measured by the pressure transducer, and the initial rise in the pressure and OH^* emission trace, shown in Fig. 2. The initial rise was located by linear extrapolation of the signal at the time of maximum rate of rise to the baseline. The ignition delay time measured by the pressure trace typically agreed with that found by the OH^* emission trace within $\pm 1\%$.

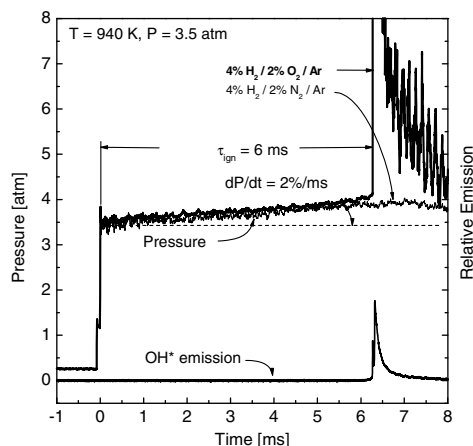


Fig. 2. Experimental data for a 4% $\text{H}_2/2\% \text{O}_2/\text{Ar}$ test gas mixture at initial post-shock conditions of 940 K and 3.5 atm for reactive and inert mixtures.

The attenuation rate of the incident shock speed ranged from 0.0–0.9% per meter. After the passing of the reflected shock, the pressure is observed to increase steadily at a rate of $\sim 2\%$ per millisecond, as seen in Fig. 2, owing principally to the facility-dependent effect of boundary layers and incident shock attenuation. This effect of a ($2.0 \pm 0.5\%$) per millisecond pressure rise is seen for all the reflected shock experiments of the current study.

The ignition time delay data are compared to the predictions of one current reaction mechanism, though the results are similar to those of other mechanisms. The current mechanism used is the GRI-Mech 3.0 model [7] with an updated rate for the reaction $\text{H} + \text{O}_2 + \text{M} \leftrightarrow \text{HO}_2 + \text{M}$ ($\text{M} = \text{Ar}, \text{H}_2\text{O}$) from Bates et al. [8] with collision efficiencies ($\text{Ar}:\text{O}_2:\text{M}$) = (1:1.5:2.6), and the new enthalpy of formation of OH from Herbon et al. [9]. Reflected-shock kinetic modeling traditionally uses constant volume (V) and internal energy (E) constraints, and this standard approach is used in preliminary comparisons with our data. The effects of the pressure perturbations in the reflected-shock region have typically been neglected in data analysis, as is reasonable for short ignition delay times. However, these effects are not negligible at the long times of interest in the low-temperature region, as we show in our analysis.

3.1. Lower concentration gas mixture

Data were taken for the lower-concentration gas mixture under normal shock tube operation at reflected shock temperatures from 987 to 1118 K and pressures from 3.3 to 3.7 atm. Using the modified shock tube with the driver extension and tailored driver gas mixture, data were taken for temperatures ranging from 924 to 1021 K in the same pressure range. Ignition delay time data taken using the modified shock tube were found to be consistent with data taken under normal shock tube operation, verifying the reliability of using the driver extension and tailored driver gas mixture.

The experimental ignition delay time data are shown in Fig. 3. Also shown are calculated ignition delay times for 3.5 atm using CHEMKIN [10] with constant V , E constraints and our modified version of GRI-Mech 3.0. Small variations in the ignition delay time due to pressure differences from 3.5 atm were scaled to a pressure of 3.5 atm using the apparent pressure dependence predicted by the model. The temperature and pressure used to plot and scale the experimental data in Fig. 3 are the temperature and pressure initially behind the reflected shock (i.e. at time zero) as calculated using 1D shock relations.

Note that the measured ignition delay times at temperatures above 980 K are consistent with the CHEMKIN model. For temperatures below

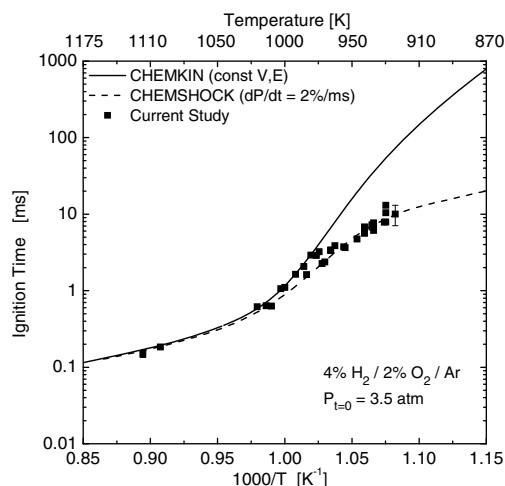


Fig. 3. Reflected-shock ignition delay times for a 4% $\text{H}_2/2\% \text{O}_2/\text{Ar}$ mixture. Experimental data and calculated values from two different modeling constraints.

980 K, however, the experimental ignition delay times roll off from the model and are shorter than predicted with the usual constant V , E constraint. At temperatures lower than the roll-off point, the disagreement between model and experiment grows up to almost an order of magnitude near 930 K. These observations are consistent with previous shock tube studies [1].

We hypothesize that non-ideal gasdynamics in the shock tube facility may contribute to the ignition delay time roll-off because at longer test times non-ideal effects can accrue and become significant. As seen in Fig. 2, a gradual pressure rise of about 2% per millisecond is present in our reflected shock data as a result of facility-dependent effects, including sidewall boundary layers and concomitant incident shock attenuation. A nearly identical pressure rise is obtained in experiments without reaction (i.e. $\text{H}_2/\text{N}_2/\text{Ar}$) as shown in Fig. 2. The pressure rise indicates that a temperature rise is also present, as the gas may be assumed to compress nearly isentropically. For test times over a few milliseconds, the change in temperature and pressure can be large enough to significantly affect the chemistry leading to ignition.

3.2. Higher concentration gas mixture

Data were taken using the higher concentration gas mixture at reflected shock temperatures from 906 to 1049 K at pressures from 3.0 to 3.5 atm. A typical pressure trace for the higher concentration test mixture is shown in Fig. 4. Ignition delay time is defined in the same manner as for the lower concentration tests. One can observe that the gradual pressure rise in the reflected-

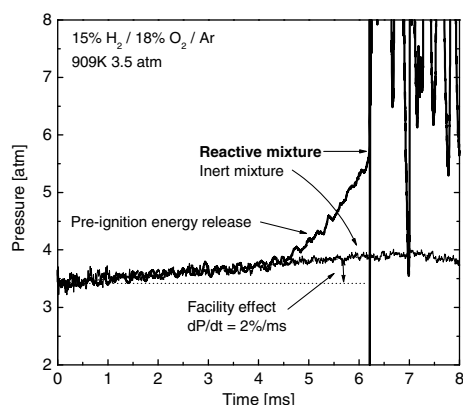


Fig. 4. Experimental data for a 15% $\text{H}_2/18\% \text{O}_2/\text{Ar}$ mixture test gas mixture at initial post-shock conditions of 909 K and 3.5 atm for reactive and inert mixtures.

shock region due to facility-dependent effects is also present in the higher concentration mixtures, and the slope of the pressure rise appears to be independent of mixture concentration. In addition to the facility-dependent effects, a pre-ignition energy release is apparent in the pressure trace for the higher concentration mixture, shown by a rise in pressure, and thus temperature, just prior to ignition.

Figure 5 shows the high concentration ignition delay time data in comparison to computed values using CHEMKIN with constant V , E constraints and our modified GRI-Mech 3.0 mechanism. For temperatures above 990 K, the experimental data are consistent with the model. However, at lower temperatures the roll-off from the model is again present. In addition to the importance of non-

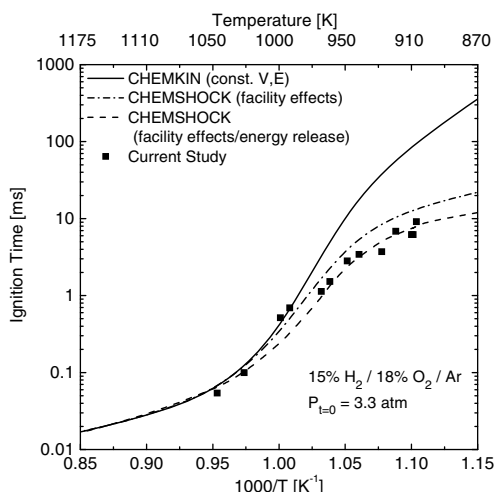


Fig. 5. Ignition delay times for a 15% $\text{H}_2/18\% \text{O}_2/\text{Ar}$ mixture. Experimental data and calculated values from various modeling constraints using our modified GRI-Mech 3.0 mechanism.

ideal gasdynamics in the shock tube facility, the energy release present in the higher concentration mixture may also be of importance in the modeling process, as discussed further in the following section. Presently, we are uncertain of the cause of the energy release phenomena, though others have suggested the appearance of random flame kernels [2]. Another hypothesis is that ignition time may be dependent on axial location, which could contribute to the appearance of the pre-ignition pressure rise at our measurement location. We plan to test these hypotheses in the near future with additional diagnostics and detailed modeling.

3.3. CHEMSHOCK Modeling

A gasdynamic model called CHEMSHOCK [5], developed by our group, was used to simulate complex chemical kinetic phenomena under specific pressure constraints. The CHEMSHOCK model assumes a two-step process over each small time step: (1) reaction by the normal constant V , E process; followed by (2) an assumed isentropic adjustment in conditions to recover the measured value of pressure at this time. Li et al. [5] has validated the CHEMSHOCK model against results from a 1D computational fluid dynamics code for a representative heptane/ O_2 /Ar mixture, using a reduced mechanism, and also against experimental results for gas temperature and water vapor concentration in an H_2/O_2 /Ar mixture at 1440 K and 1.4 atm.

The pressure measurement from the sidewall Kistler pressure transducer in our current shock tube tests showed an average pressure rise of 2% per millisecond after the reflected shock due to facility-dependent effects. Hence, using CHEMSHOCK, the simulated reaction history was constrained to a constant pressure rise of 2% per millisecond. The calculated ignition delay time was defined by the time of initial rise of the computed OH concentration defined by extrapolation of the maximum slope to the zero OH intercept. While the peak OH concentration computed will not necessarily correspond exactly to the actual amount of the species measured, the time until the species is formed should provide an accurate representation of the modeled ignition delay time. Petersen and Hanson [11] have previously explored the effect of increasing temperature and pressure in shock tube modeling, however their model assumed that the temperature and pressure increases due to reaction are negligible. CHEMSHOCK allows for temperature increase due to reaction, which can be critically important during the ignition event.

The calculated times from the CHEMSHOCK model for the conditions of the present data are shown in Figs. 3 and 5. Several important observations can be made from the CHEMSHOCK calculations. First, both the CHEMSHOCK and

constant V , E results are in close agreement for ignition delay times less than about 0.6 ms, as may be expected. For tests with short ignition times (i.e. high temperatures), the pressure and temperature rise prior to ignition are negligible. Second, and most importantly for present purposes, the ignition delay times calculated with CHEMSHOCK and the pressure constraints roll off from the constant V , E model at lower temperatures and follow the experimental data much more closely than with the constant V , E constraint. Note that the difference between constant V , E model and CHEMSHOCK exceeds a factor of 10 at the lowest temperature studied.

For the higher concentration test mixture at the lower temperatures especially, in addition to the constant 2% per millisecond pressure rise associated with the facility-dependent effects, a pre-ignition energy release pressure rise is observed at later times, as seen in Fig. 4. If the measured pressure trace is used in the calculation, rather than just the facility-dependent 2% per millisecond pressure rise, the calculated ignition delay times are somewhat shorter but similarly close to the measured values at the lowest temperatures, as shown in Fig. 5. Based on this comparison, we conclude that use of the experimental pressure trace and the CHEMSHOCK model more accurately models the reflected-shock ignition process in hydrogen than the traditional approach using CHEMKIN with a constant V , E constraint, and this new approach allows for facility-dependent effects and energy release phenomena in the reflected shock environment.

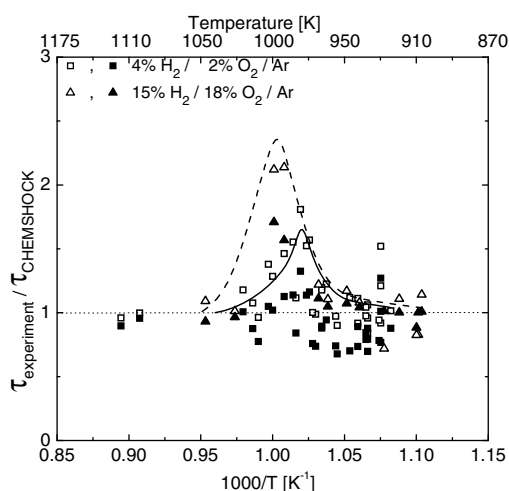


Fig. 6. Ratio of experimental ignition delay time to CHEMSHOCK modeled ignition delay time for two different rates of $H + O_2 + Ar \leftrightarrow HO_2 + Ar$ for mixture compositions of 4% H_2 /2% O_2 /Ar and 15% H_2 /18% O_2 /Ar. Open symbols are using the Bates et al. rate; filled symbols are using the best-fit rate. Lines show trend of open symbols.

Deviations from the experimental data and CHEMSHOCK model predictions are largest for temperatures from 950 to 1010 K, as seen in Fig. 6. We believe these differences result, at least in part, to inaccuracies in the reaction mechanism used. Results of a sensitivity analysis for the hydrogen reaction mechanism are explored in the next section.

3.4. Sensitivity analysis

Brute force sensitivity calculations for ignition delay time were computed for our modified GRI-Mech 3.0 mechanism at a pressure of 3.5 atm and the lower concentration mixture. Sensitivity is defined as

$$S = \frac{\Delta \tau_{\text{ign}}}{\Delta k_i} \frac{k_i}{\tau_{\text{ign}}} \tag{1}$$

where S is the ignition delay time sensitivity, τ_{ign} is the ignition time and k_i is the reaction rate of a particular elementary reaction in the mechanism. Sensitivity was computed at temperatures of 930, 975, and 1100 K. The reactions with the four highest sensitivity values are shown in Fig. 7. The ignition delay time is most sensitive to the reactions $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ and $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$. All other reactions in the reaction mechanism have a negligible effect on the ignition time at the conditions of interest. The ignition time sensitivity is highest in the intermediate temperature region, and this is where the largest discrepancy exists between the experimental data and CHEMSHOCK model, as shown in Fig. 6.

In addition to the modified GRI-Mech 3.0 reaction mechanism used, three other mechanisms

involving hydrogen–oxygen chemistry are examined here: O’Conaire et al. [12], Wang et al. [13], and Li et al. [14]. In these four mechanisms, the reaction rate for $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ differs by less than $\pm 4\%$ in the temperature range studied here while the uncertainty in this reaction rate is given as $\pm 25\%$ by Baulch et al. [15]. While large changes in the rate for $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ could also duplicate many of the adjustments discussed here, the small uncertainty in this reaction likely precludes this as a possible explanation. The reaction rate for the $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ reaction, by contrast, differs by up to 60% among the four

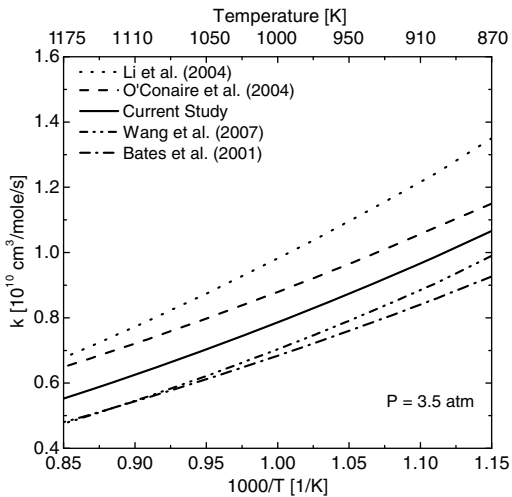


Fig. 8. Reaction rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ for different kinetic mechanisms and the rate providing a best fit to the experimental data.

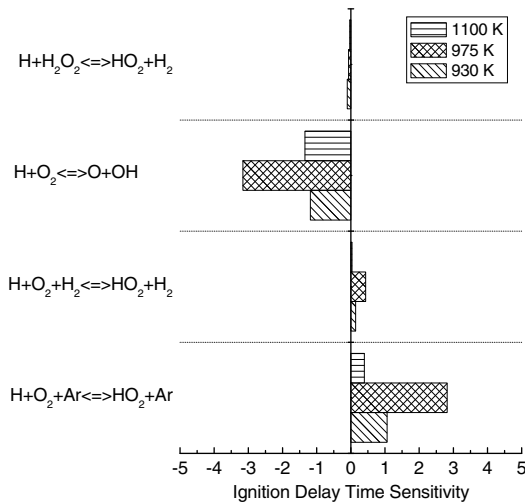


Fig. 7. Ignition delay time brute force sensitivity using our modified GRI-Mech 3.0 mechanism for a 4% H_2 /2% O_2 /Ar mixture at 3.5 atm.

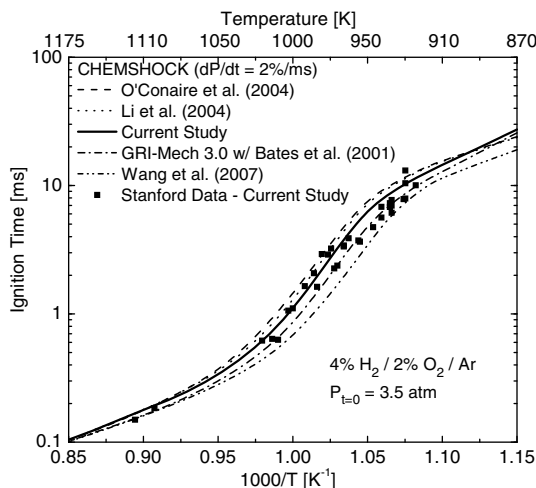


Fig. 9. Experimental ignition time data and CHEMSHOCK modeling using different chemical mechanisms for a 4% H₂/2% O₂/Ar mixture.

mechanisms. The reaction rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ at 3.5 atm is shown in Fig. 8 for each mechanism.

Figure 9 shows the experimental data for the lower concentration mixture and CHEMSHOCK model with a 2% per millisecond pressure rise constraint using each of the reaction mechanisms discussed. Both the modified GRI-Mech 3.0 and Wang et al. mechanism are seen to underpredict the ignition delay, while the O'Conaire et al. and Li et al. mechanisms slightly overpredict the ignition delay times.

The pre-exponential constant for the $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ rate was adjusted in our modified GRI-Mech 3.0 mechanism in order to obtain the lowest least-squares scatter to the experimental data. The modeling results with the best-fit rate are shown in Fig. 9. The rate constant used for this model is given by the Troe falloff form [16] using $k_\infty = 1.04 \times 10^{13} \text{ T}^{0.2} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$ and $k_0 = 6.99 \times 10^{18} \text{ T}^{-1.2} \text{ cm}^6 \text{ mole}^{-2} \text{ s}^{-1}$ and $F_{\text{cent}} = 0.7$. This rate is 15% higher than the $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ rate determined by Bates et al. [8] (and within his stated uncertainty bounds), and 11% higher than the rate used in the Wang et al. mechanism. The O'Conaire et al. mechanism uses a rate which is on average 12% higher than our best-fit rate, and the Li et al. mechanism uses a rate about 24% higher. These latter two reaction mechanisms predict the experimental data for ignition delay time best out of the four mechanisms examined. Figure 8 compares the rate providing the best fit to the experimental data, with the rates used in other kinetic mechanisms.

This best-fit rate for the $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ reaction yields considerably better agreement between the CHEMSHOCK model and the lower concentration mixture experimental

data, as displayed in Fig. 6. The experimental data agrees with this model within $\pm 30\%$. Using this new rate in the CHEMSHOCK model for the higher concentration mixture shows the same effect. The new calculated ignition delay times predict the higher concentration data within 70% whereas previously the CHEMSHOCK model with the original rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ showed discrepancies of up to more than twice the experimental value.

While a reaction rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ is proposed to show better agreement with the experimental data, it should be noted that a 10% reduction in the GRI-Mech 3.0 rate constant for the $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ reaction also produces similar agreement between the CHEMSHOCK model and experimental data.

4. Concluding remarks

Hydrogen–oxygen ignition delay time data for mixtures containing 4% or 15% fuel taken in a shock tube at Stanford University at low temperatures show large disagreement between the times predicted by CHEMKIN modeling with the commonly employed constant volume (V) and internal energy (E) constraint and four current detailed reaction mechanisms, including a modified version of the GRI-Mech 3.0 mechanism. The experimental data rolls off from the simulations at temperatures around about 980 K, and differences of over an order of magnitude are present at temperatures below 930 K. Analysis of the low-temperature data indicates that constant V , E modeling for shock tube ignition delay times is inadequate for long test times (which occur at low temperatures) because pressure and temperature perturbations caused by facility-dependent

non-ideal gasdynamics generally grow with time. Additionally, energy release can be present before ignition, especially in mixtures with high fuel concentration, causing the constant V , E modeling to be inaccurate. The facility-dependent effects and energy release are apparent through the pressure data.

The new gasdynamic model called CHEM-SHOCK can effectively account for the effects of facility-dependent non-ideal gasdynamics and energy release by using measured pressure data. The resulting modeled ignition delay times closely match the experimental data, both in the high temperature region where the constant V , E model agrees with the data, and in the low-temperature region where the constant V , E model fails. We believe that CHEM-SHOCK modeling of shock tube ignition delay times substantially resolves the discrepancy found in the detailed kinetic modeling of hydrogen ignition, which has been a source of controversy in recent literature. Moreover, CHEM-SHOCK has illustrated how non-ideal phenomena in shock tube experiments can affect the chemical reaction progress, and these effects can similarly affect the kinetics in other chemical systems.

Sensitivity analysis shows that the rate for the $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$ reaction in the hydrogen reaction mechanism is important in calculating the ignition delay time. Various reaction mechanisms use rates for this reaction that differ by up to 60%, causing large differences in modeled ignition delay times. The rate for this reaction was adjusted, and the results indicate that a rate 15% higher than that proposed by Bates et al. [8] minimizes the least-squares scatter with the experimental data.

Future research will include further examination of the $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ reaction rate at low temperatures, as well as new experiments targeted at refining the rate for $\text{H} + \text{O}_2 + \text{Ar} \leftrightarrow \text{HO}_2 + \text{Ar}$. Planned experiments include ignition delay times and species concentration measurements (OH , HO_2 , and others) in hydrogen–oxygen–argon mixtures. Another step in our research will be to further refine the CHEM-SHOCK model, particularly including the addition of accurate measurements of temperature history in the reflected-shock region. Combined measurement of temperature and pressure will allow direct inference of the density history and removal of the isentropic assumption for pressure and temperature adjustment. The observations made in this study also motivate efforts to reduce the facility-dependent non-ideal gasdynamic

effects and the associated variations in pressure and temperature in the reflected shock region.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2008.06.014.

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