Shock tube ignition measurements of *iso*-octane/air and toluene/air at high pressures

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Abstract

Ignition delay times were measured in a shock tube for *iso*-octane/air and toluene/air at conditions similar to those found in homogeneous charge compression ignition (HCCI) engines. Initial reflected shock conditions spanned the following ranges: temperature 855–1269 K, pressure 14–59 atm, and equivalence ratios ϕ of 0.5 and 1 in synthetic air. Ignition delay times were measured using sidewall pressure via piezo-electric transducers and confirmed with OH* and CH* emission measurements. The *iso*-octane ignition delay times are in excellent agreement with existing measurements by Fieweger et al. [Proc. Combust. Inst. 25 (1994) 1579; Combust. Flame 109 (1997) 599] and modeling by Ogink and Golovitchev [SAE Technical Paper Series, 2001, Paper No. 2001-01-3614]. No comparable high-pressure data exist for toluene/air, and modeling by Pitz et al. [U.S. Sections of the Combustion Institute 2nd Joint Spring Meeting, 2001, Paper 253] and Dagaut et al. [Fuel 81 (2002) 173] significantly over-predicts the toluene/air ignition delay times at $\phi = 1$. The large pressure range of the current measurements permits determination of the pressure dependence of ignition delay time at the temperatures and pressures of direct interest in HCCI engine simulations. Detailed examination of the pressure–time profiles shows evidence of significant pre-ignition energy release in both the *iso*-octane/air and toluene/air systems. Using current detailed mechanisms, the rate of this energy release is not correctly predicted either in *iso*-octane/air or toluene/air at temperatures above 850 K.
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1. Introduction

Kinetic modeling of gasoline homogeneous charge compression ignition (HCCI) relies heavily on the use of surrogate fuel mixtures for gasoline. In particular, simple ternary surrogate mixtures for gasoline can be formed from branched-chain alkanes, straight-chain alkanes, and aromatics, e.g., from *iso*-octane, *n*-heptane, and toluene [1].

However, even for the simplest gasoline surrogate, a single component such as *iso*-octane, the high pressure, lower temperature chemistry found in the HCCI engine cycle is complicated by the need to include peroxy reaction kinetics to properly simulate the time scales of the ignition process [2,3]. Rate coefficients of key peroxy reactions and heats of formations of key peroxy species are not well established and few experimental data are available to test the role of this chemistry in high-pressure ignition. Similarly, little is known about the ignition behavior and the important chemistry of toluene in the same temperature

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and pressure regime. Good kinetic validation targets are thus needed to refine the chemical mechanisms of both of these fuels.

Shock tube ignition delay time measurements can provide excellent validation targets for refinement of kinetic mechanisms in the temperature (700–1300 K) and pressure (10–60 atm) regimes of interest to HCCI modeling. Fieweger et al. [4,5] have previously measured ignition delay times in this regime for *iso*-octane/air and those data provide a first view into the complicated behavior of *iso*-octane/air ignition at high pressure and lower temperatures. On the other hand, to the best of our knowledge, there are no previous high-pressure toluene/air ignition experiments.

However, more kinetic targets than just ignition delay times are needed to refine mechanisms. Individual species concentration profiles are very important, but are difficult to acquire. This is particularly the case for the larger transient RO_2 and QOOH (and larger) species where the uncertainty of spectral data at high pressures, the large number of isomers, and the short chemical lifetimes strongly limit the use of optical absorption methods.

One set of kinetic targets that has not been fully exploited is pressure–time measurements in shock tube ignition delay time experiments. Pressure measurements have been used to determine ignition delay times at HCCI conditions [5–7] and have also been used to identify combustion process details such as cool flame, deflagration, and detonation regions as well as modeling targets for rapid compression machine (RCM) ignition studies [8]. However, pre-ignition energy release behavior derived from these pressure profiles has not been previously used in shock tube studies as a kinetic target to validate HCCI ignition processes. In shock tube experiments, pre-ignition pressure increases can be directly related to pre-ignition energy release because of the near-constant-volume behavior of the test gas before ignition [9]. The ability to correctly predict energy release rates in these shock tube experiments thus places new and very strong constraints on the reaction mechanisms of HCCI ignition models.

Current high-pressure, HCCI-relevant mechanisms for *iso*-octane/air ignition predict rapid exponential growth of pressure just before ignition at all temperatures, and smaller pre-ignition increases in pressure (and the commensurate energy release) only at the lowest temperatures (near 850 K). Measurements in *iso*-octane of the time scales of pre-ignition energy release at higher temperatures would thus place a strong constraint on the internal structure of kinetic models. Current mechanisms for toluene/air ignition do not predict any pre-ignition rise in pressure. Evidence of a distinct pre-ignition energy release in toluene/air ignition would suggest that another oxidation pathway for toluene might exist.

In this paper, we present ignition delay time and pressure profile data for *iso*-octane/air and toluene/air at high pressure and lower temperatures for a range of conditions, and compare these data with earlier studies and current models. The *iso*-octane ignition delay times are compared with the models of Ogink and Golovitchev (Chalmers University) [10,11] (520 reactions and 101 species) and of Pitsch et al. [3] (134 reactions and 47 species). The toluene experiments are compared with predictions from Pitz et al. [12] (1621 reactions and 379 species) and from Dagaut et al. [13] (921 reactions and 120 species). All kinetic modeling performed in this study used a constant volume constraint.

2. Experimental method

Ignition delay times were measured for *iso*-octane and toluene at pressures of 14–59 atm, temperatures of 855–1269 K, and equivalence ratios of 0.5 and 1.0 in synthetic air. All ignition delay time experiments were performed in a high-purity, unheated, 5 cm diameter, helium-driven, turbo-molecular-pumped, high-pressure shock tube (HPST) facility at Stanford University. The incident shock speeds were determined using six piezo-electric pressure transducers (PZT) spaced over the last 2 m of the shock tube. Typical attenuation rates for the experiments ranged from 1% to 3%/m. The overall uncertainty in the reflected shock temperature was estimated to be ±1.8%. Reflected shock conditions were determined using the one-dimensional normal shock equations and the Sandia thermodynamic database by Kee et al. [14], including additional species information as recommended by Burcat [15]. Other details about the HPST facility are given in Petersen and Hanson [16].

Ignition pressure was monitored using a PZT (Kistler Model 603B) 10 mm from the endwall. Also located at 10 mm from the endwall were observation windows for monitoring the emission from CH* (using a narrow line filter 10 nm FWHM centered at 431 nm) and OH* (using a Schott Glass UG-5 filter with >95% transmission at 306 nm).

Mixtures were prepared in a 12.8-liter, magnetically stirred, stainless steel mixing tank. To achieve higher fuel concentrations, the entire tank was insulated and heated to approximately 60 °C. Research grade *iso*-octane and toluene (Sigma–Aldrich) were measured and added volumetrically to the test gas mixtures using glass burettes. Research grade gases (Praxair N_2, O_2) were added slowly in accordance with a procedure outlined by Horning et al. [17] to inhibit condensation of fuel that could lead to inaccuracies in reported fuel composition. Each mixture was allowed to mix for a minimum of 3 h before use.

The ignition delay time is defined in this study as the time interval between the arrival of the reflected shockwave and the onset of ignition at the sidewall observation location. The arrival of the reflected shockwave was determined by the step rise in pressure, and the onset of ignition was determined by monitoring either the pressure history or the emitted light corresponding to an intermediate species. The onset of ignition from the pressure history as well as both CH* and OH* emission were defined by locating the time of steepest rise and linearly extrapolating back in time to the pre-ignition baseline. The three definitions generally agreed to within ±5%, though all the results presented here employ the pressure-based definition. The overall uncertainty in the ignition delay time measurement was ±15%, which was primarily dominated by the uncertainties in temperature. Example pressure and OH* emission data traces for *iso*-octane/air and toluene/air are shown in Figs. 1 and 2. Evidence of
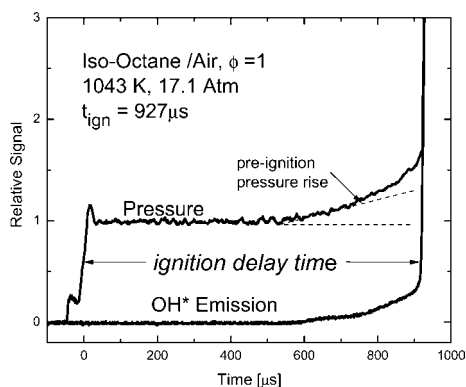

Fig. 1. Example *iso*-octane/air ignition data showing ignition delay time definition. A rise in pre-ignition pressure (energy release) and OH* emission is evident from approximately 550 μs.
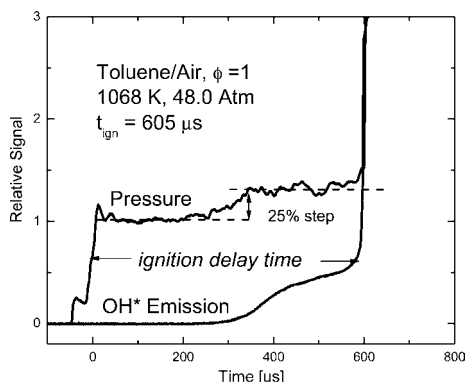

Fig. 2. Example toluene/air ignition data showing ignition delay time definition. A rise in pre-ignition pressure (energy release) and OH* emission is evident from approximately 300 μs.

pre-ignition pressure rise (and energy release) and pre-ignition OH* emission can be seen in both Figs. 1 and 2.

3. Ignition delay time measurements

The results of the ignition delay time experiments for *iso*-octane and toluene are presented in Table 1 and summarized in Figs. 3 and 4. The data are characterized by small scatter and show distinct variations with stoichiometric ratio ϕ, pressure, and temperature. The correlated *iso*-octane/air data were found to scale with pressure as $\sim P^{-0.77}$ for both $\phi = 1.0$ and $\phi = 0.5$. The correlated toluene/air data were found to scale with pressure as $P^{-0.93}$ for $\phi = 1.0$, but as $P^{-0.5}$ for $\phi = 0.5$. The activation energy for both *iso*-octane/air and toluene/air varies strongly with ϕ, and this indicates, particularly in the case of toluene/air where the pressure dependence of the ignition delay time is significantly different for the two different stoichiometries, that the dominant chemistry in the $\phi = 1.0$ systems is different than that occurring in the lean $\phi = 0.5$ case. The high-pressure ($\sim$50 atm) *iso*-octane/air data show evidence of significant negative temperature coefficient (NTC) behavior. The least-squares fits to the correlated ignition delay times have the following forms:

iso-Octane/air

$$\phi = 1.0: \quad t_{\text{ign}} = 3.7 \times 10^{-6} P^{-0.79} \exp(10,450/T),$$

$$\phi = 0.5: \quad t_{\text{ign}} = 2.7 \times 10^{-9} P^{-0.75} \exp(16,070/T),$$

Toluene/air

$$\phi = 1.0: \quad t_{\text{ign}} = 2.9 \times 10^{-6} P^{-0.93} \exp(9410/T),$$

$$\phi = 0.5: \quad t_{\text{ign}} = 5.4 \times 10^{-9} P^{-0.50} \exp(15,455/T),$$

where ignition delay time is in (s), pressure P is in (atm), and temperature T is in (K).

The *iso*-octane/air data can be compared with the data of Fieweger et al. [4,5] in Fig. 5. The current study shows little difference from the slightly lower pressure data ($\sim$40 atm) of Fieweger et al., except for a cluster of points from [5] between 800 and 900 K that are approximately twice the value of the current data. At 17 atm (not shown here but included in the table), the ignition delay times are also nearly identical to those reported by Fieweger et al. We may confidently assume, therefore, that there is strong consensus for the experimental *iso*-octane ignition delay times in this temperature and pressure regime.

Figure 5 also shows the comparison between the data and the models of Pitsch et al. [3] and of Ogink and Golovitchev [11]. The reduced Pitsch et al. mechanism strongly over-predicts the ignition delay time at temperatures above 900 K, though it

Table 1
High-pressure shock tube ignition delay time data for
iso-octane/air and toluene/air

$T5$ (K)	$P5$ (atm)	t_{ign} (μs)
iso-Octane/air $\phi = 1.0$		
984	18.1	1511
995	16.3	1535
1043	17.1	927
1077	18.4	604
1109	15.9	516
1159	14.9	214
855	56.4	1719
867	59.3	1755
894	58.5	1193
927	55.7	1067
975	51.2	871
1006	51.1	625
1015	47.8	505
1098	47.5	222
iso-Octane/air $\phi = 0.5$		
1043	15.0	1747
1071	14.9	1222
1095	14.4	916
1171	13.5	329
1009	51.1	1075
1057	51.0	598
1099	48.6	348
1147	47.8	178
Toluene/air $\phi = 1.0$		
971	17.2	1314
995	16.5	1100
1053	17.1	1288
1067	16.1	1646
1076	16.5	1174
1097	16.6	1223
1138	22.2	716
1173	14.9	767
977	54.3	1173
990	50.5	952
1005	50.4	870
1068	48.0	605
1111	46.7	397
1166	44.6	276
1179	41.5	273
1183	46.2	191
1242	42.4	121
Toluene/air $\phi = 0.5$		
1112	15.3	1250
1125	13.1	1454
1206	14.1	598
1269	14.4	279
1091	50.5	1186
1135	46.5	669
1149	44.4	579
1211	44.4	250

Fig. 3. *iso*-Octane/air shock tube ignition delay time data for $\phi = 0.5$ and 1.0. All data have been normalized to 50 atm using P^{-N} from the correlation given in the text. The linear correlation (solid line) for $\phi = 1.0$ in the text does not include the one highest and three lowest temperature points (indicated by half-filled squares). The dashed line is a quadratic fit to all the $\phi = 1.0$ data.

Fig. 4. Toluene/air shock tube ignition delay time data for $\phi = 0.5$ and 1.0. All data have been normalized to 50 atm using P^{-N} from the correlation given in the text.

Fig. 5. Ignition delay times for *iso*-octane/air, $\phi = 1.0$, high-pressure cases (~50 atm).

does recover the limiting activation energy at higher temperatures and agrees reasonably well with the data below 900 K. The Ogink and Golovitchev model replicates the consensus *iso*-octane ignition delay time data well near 50 atm in the temperature
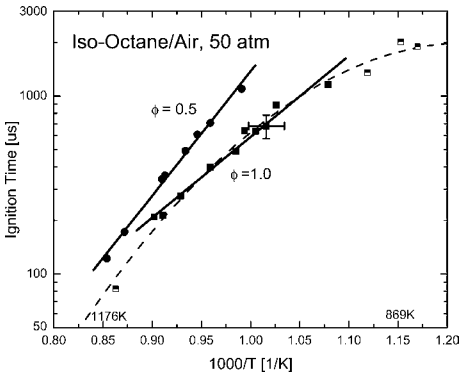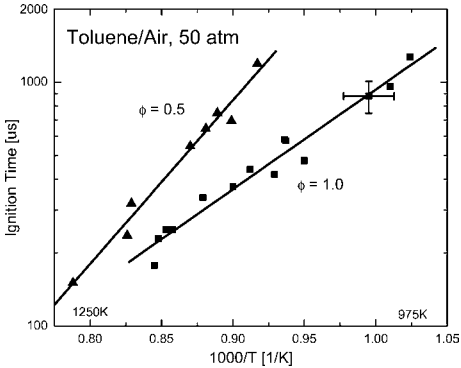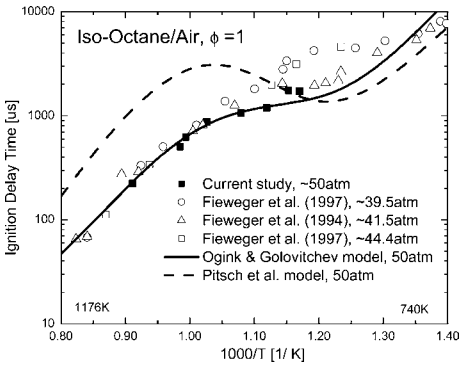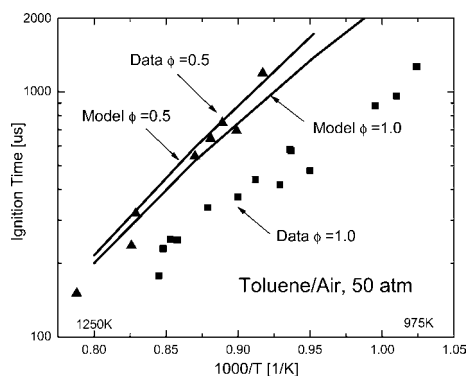
Fig. 6. Ignition delay times for toluene/air, $\phi = 0.5$ and 1.0. Solid lines, current study; dashed and dotted lines, Pitz et al. model. Data normalized to 50 atm.

Fig. 7. Modeled iso-octane/air ignition: six major species. Initial conditions: 850 K, 50 atm, $\phi = 1.0$. Pitsch et al. model.

range of the current study and the extended temperature range of Fieweger et al. At 17 atm (not shown here but included in Table 1), the data appear to show stronger NTC behavior and significantly shorter ignition delay times than the Ogink and Golovitchev model.

In Fig. 6, the toluene ignition delay time data and the predictions of the Pitz et al. model are compared. Ignition delay times predicted using the Dagaut et al. model are approximately 10× longer than the experimental values and are not shown. For $\phi = 1.0$, the Pitz et al. model predicts ignition delay times that are approximately twice those of the data, but for $\phi = 0.5$, the model recovers the ignition delay times quite well. However, the model does not capture the significant difference in the experimental activation energy and delay times between the $\phi = 1.0$ and 0.5 data. At lower pressures, the predictions of the model degrade even further. At 17 atm and 1050 K, for example, the measured ignition delay times for $\phi = 1.0$ and 0.5 are approximately 900 and 1700 μs, while the Pitz et al. model predicts delay times of 4700 and 4950 μs. Refinement of the toluene model is clearly needed to match experimental data.

4. Pressure profile measurements

4.1. iso-Octane

Test gas conditions behind reflected shocks approximate those of a constant volume reactor during shock wave experiments with weak to moderate energy release. Thus, measurements of small to moderate pressure rise in shock tubes can be directly related to small to moderate energy releases and rapid changes in chemistry. A detailed view of these pre-ignition pressure changes, and the simultaneous changes in OH* emission
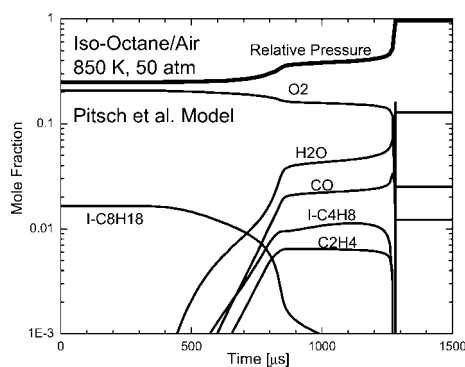
that are evidence of rapid changes in the radical pool chemistry, is shown in Figs. 1 and 2.

These pressure rises are seen in current iso-octane models under certain circumstances (but not in toluene models). For example, in the extremely low temperature case of iso-octane/air at 850 K, 50 atm, $\phi = 1.0$ using the Pitsch et al. model, see Fig. 7, the pre-ignition pressure changes and energy releases are coincident with the formation of H_2O, CO, iso-C_4H_8, and C_2H_4 and rapid removal of iso-octane. These pressure rises are not evident in the models at higher temperatures. Similar results are seen using the Ogink and Golovitchev model. Pre-ignition pressure rises are also seen in RCM ignition data [8] for iso-octane at similar conditions, and at the lower temperatures of these studies are successfully modeled.

In the following discussion, we note the significant differences between the measured and modeled pressure profiles in both iso-octane/air and toluene/air ignition that we believe are evidence of a serious disagreement between existing models and high-pressure ignition experiments at temperatures above 850 K.

Figure 8 presents modeled pressure–time histories using Ogink and Golovitchev model for iso-octane/air ignition near 17 atm. The modeled pressure–time histories show nearly flat pressure traces until the appearance of a rapid exponential rise to ignition. The relative pressure increases slowly to 1.3 and then there is an extremely rapid exponential rise to final relative pressures of near 3.

The experimental data in Fig. 9 show markedly different pressure rises. The slow exponential rise to ignition of the pressure–time histories begins at similar time scales to those of the model. However, they continue to rise to much higher relative pressures from 1.47 (at 1077 K) to 2.14 (at 984 K) before rapidly increasing to the final pressures. Note also that the ignition delay time scales are different for the modeling and the measurements.
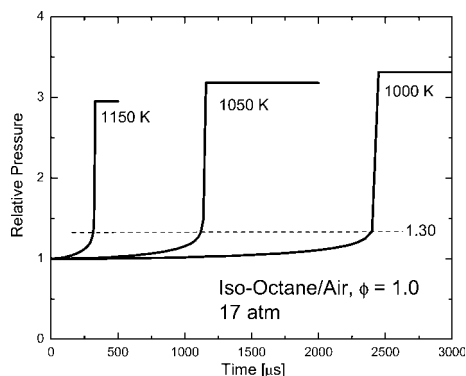
Fig. 8. Modeled pressure–time histories for *iso*-octane/air ignition at 17 atm, $\phi = 1.0$. Ogink and Golovitchev model.
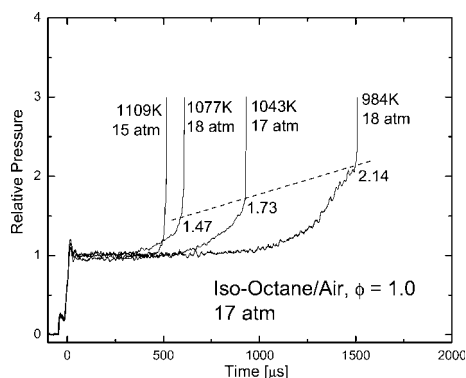

Fig. 9. Measured pressure–time histories for *iso*-octane/air ignition at 17 atm, $\phi = 1.0$.

Similar differences are seen in the *iso*-octane 50 atm pressure–time history data as well. These differences in energy release rates between the model and the data at all pressures are not easily resolved by adjusting the kinetic model. We are constrained in modifying the current Ogink and Golovitchev model because it has already successfully captured the ignition delay time behavior of *iso*-octane/air in the NTC region; but significant changes are still needed if the mechanism is to capture the pressure–energy release time-history of the current data at 17 and 50 atm.

Some direction needed to effect model changes is suggested in the following discussion. Contribution analysis indicates that the major contributor to early time formation of H_2O at 950 K, 50 atm, and hence intermediate pressure increases, is the reaction of $C_8H_{18} + OH = C_8H_{17} + H_2O$. Thus, properly describing the formation rate of OH should be of key importance in determining the rate of pressure increase or energy release. (Some information about OH formation may also be derived from the OH* emission measurements that

appear to mimic the pressure variations.) Interestingly, however, the reactions with the largest contribution to net heat change at early time in the Ogink and Golovitchev model are $neoC_5H_{11}O_2 = neoC_5H_{11} + O_2$ and $DC_8H_{17} = C_3H_6 + neoC_5H_{11}$. Accurate values for the heats of formations and rate coefficients of the various peroxy species are thus clearly important. The importance of the peroxy species is also supported by a brute force sensitivity analysis for H_2O formation (see Fig. 10). Large variations of three reactions involving the species $C_8H_{16}OOHOO$, $C_8H_{17}OH$, and $A-C_8H_{17}$ have some effect on ignition delay time, but the largest effect on the ignition delay times is created by variation of the heats of formations of selected complex peroxy species and their isomers. Variations of only 1 kcal/mol in some of these values can change the ignition delay time by 70%. Further work is needed in this area to isolate the cause of the pre-ignition pressure rise–energy release seen in the *iso*-octane/air ignition experiments and to provide improved values for key rate coefficients and thermochemical properties.

4.2. Toluene

Figure 11 presents modeled pressure–time histories for toluene/air ignition using the Pitz et al. mechanism. The character of the modeled early-time pressure remains similar for temperatures between 1150 and 950 K at 50 atm. There is a slow, almost imperceptible, rise in pressure at early times to a relative pressure of approximately 1.3, and then a late exponential rise to the final pressure.

By contrast, the measured pressure–time histories exhibit an entirely different pressure–time behavior, in addition to yielding substantially shorter ignition delays than the modeled values;
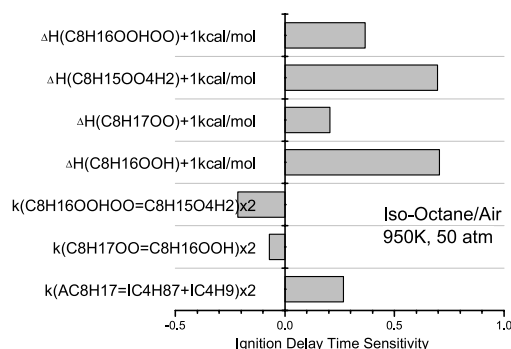

Fig. 10. Brute force sensitivity analysis of ignition delay time. Ignition delay time sensitivity $S = [t_i - t_{norm}]/t_{norm}$, where t_i is the ignition delay time with the change indicated in the chart applied to the Ogink and Golovitchev mechanism, and t_{norm} is the value from the unperturbed mechanism. Initial conditions: 950 K, 50 atm, *iso*-octane/air, $\phi = 1.0$.
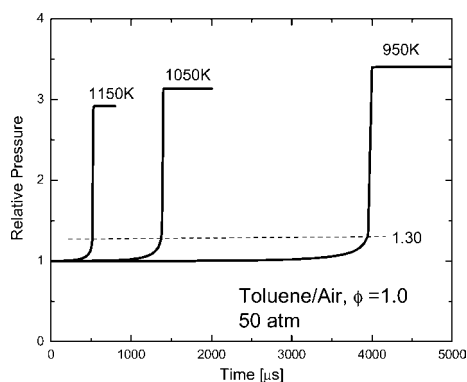
Fig. 11. Modeled pressure–time histories for toluene/air ignition at 50 atm, $\phi = 1.0$. Pitz et al. model.

see Fig. 12. The measured pressure profiles show an induction time, then a smooth rise to an intermediate plateau (with a relative pressure value of ~1.33), and then finally, a second rise at the point of ignition. This plateau is most obvious in the 1111 and 1068 K data, though it is still evident in the 1183 and 1005 K data. At the lowest temperatures, 1005 and 977 K, the final rise to ignition is at first slow and nearly linear.

The rise to the intermediate relative pressure plateau value of 1.33 (to an actual pressure plateau of ~66 atm) represents 15% of the final pressure increase (to ~150 atm under a constant volume constraint). This pressure step is indicative of an intermediate energy release of ~15% of the total energy release of the ignition event, and this large pre-ignition energy release is not predicted by current models.

At lower pressures (~17 atm), the toluene/air pressure data demonstrate an induction time and then a gradual, nearly linear pre-ignition pressure rise to the maximum pressure, usually without a large final pressure jump. Only in the highest temperature data (1138 and 1173 K) is there a subsequent final rapid jump. Again, the current model
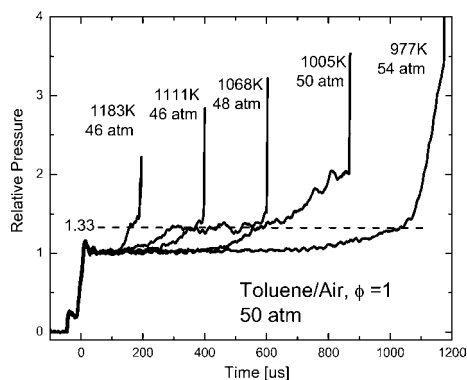
does not predict this gradual linear rise in pressure.

This pre-ignition rise in pressure has been seen before. Similar pre-ignition pressure rises were found in RCM data for some alkylbenzenes (o-xylene, 2-ethyltoluene) by Roubaud et al. [7]. They did not, however, find this effect in toluene at 907 K, which is consistent with our observation at 977 K.

By analogy to the iso-octane/air model, the intermediate pressure rise may be related to the early formation of H_2O and this may point to an important role for OH during toluene oxidation. Modification of the current Pitz et al. mechanism to generate the pre-ignition energy release process seen in the 50 atm data and the gradual linear increase in pressure seen in the 17 atm data may require the addition of new toluene oxidation sub-chemistry to the mechanism. However, knowledge about rates and heats of formations of the intermediate species that occur in this mechanism is still in its infancy, and both more theory and experiment, particularly species concentration time-history measurements of important small radicals such as OH and CH_3 and benzyl, are needed.

5. Conclusions

iso-Octane/air and toluene/air ignition delay time measurements were performed at conditions similar to those found in HCCI engines. The current iso-octane/air ignition delay data are in excellent agreement with the shock tube study of Fieweger et al. and with the predictions of the reaction model of Ogink and Golovitchev at 50 atm. The current toluene/air shock tube ignition delay time measurements at high pressures, to our knowledge, are the first of this type. These ignition delay time data provide useful kinetic targets for the validation of iso-octane and toluene oxidation reaction mechanisms at these conditions.

Although ignition delay times are critical targets for validation and refinement of reaction mechanisms, a detailed examination of the pressure profiles can also provide unique information about the time scale and magnitude of energy release during the early time before ignition. In the case of iso-octane, current models fail to predict the pre-ignition pressure rise or energy release that is seen in the experimental data. In the case of toluene, a distinct pre-ignition step in pressure is evident in the data that are not predicted in the models. Because of the current scarcity of radical species concentration time-history targets for HCCI ignition models, these pressure–time/energy-release profiles provide important new tests for high-pressure reaction mechanisms.

The next step in the shock tube study of these fuels is the measurement of species concentration

Fig. 12. Measured pressure–time histories for toluene/air ignition at 50 atm, $\phi = 1.0$.

time histories, particularly for important radicals such as OH, CH_3, and benzyl, that can be used to validate assumptions made about the internal structure and sub-mechanisms of these large reaction mechanisms. Additional studies of real gasoline and ternary gasoline surrogate blends, as well as studies of the effects of exhaust gas recirculation (EGR) on the mixture ignition, are needed and in progress.

Acknowledgments

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Comments

Volker Sick, The University of Michigan, USA. The difference in ignition delay time and decomposition rates for *iso*-octane and toluene suggest that toluene would not be a good tracer to mark *iso*-octane disappearance in PLIF experiments.

Reply. Though there has not been extensive modeling of the relative rates of initial fuel component decomposition for *iso*-octane/toluene/air mixtures, toluene is more stable against decomposition and oxidation than *iso*-octane. Preliminary analysis using the kinetic models described in this paper supports the view that toluene will be substantially longer-lived (factors of two or more) in the reaction mixture than *iso*-octane under both high temperature and cool flame conditions, and as such, will be a less than optimal indicator of *iso*-octane concentration in experiments with these fuel mixtures.

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John Kiefer, UIC, USA. After ignition, the explosion can drive compression waves forward and might account for your pre-ignition pressure changes. Have you looked at this?

Reply. An analysis of the shock tube x-t diagram for the toluene ignition experiments indicates that explosions or spiral detonations upstream of the shock tube end section would generate substantially different pressure profiles than those observed in this study. The large pressure spikes and pressure ringing expected from these detonations are not observed until after final ignition under any conditions in the current experiments. Pressure changes similar to those seen in the current higher-temperature toluene ignition experiments have been observed in shock-tube cool-flame *iso*-octane ignition studies, and are considered to be fundamental evidence for the existence of cool flame chemistry in shock tubes.