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Shock-Tube Experiments and Kinetic Modeling of Toluene Ignition

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Recent ignition delay time studies of toluene ignition (using shock tubes and rapid-compression machines) have not achieved a strong consensus at intermediate temperatures (900–1200 K) and high pressures (near 50 atm). However, the development and refinement of reaction mechanisms for toluene at engine-relevant conditions demand an accurate knowledge of these ignition delay times. To help resolve this issue, we have measured ignition delay times for toluene/air mixtures ($\phi = 1.0$) at high pressures (near 50 atm) over the temperature range of 966 to 1211 K using pressure and emission measurements behind reflected shock waves. The new ignition delay times were found to be in good agreement with the previous study of Davidson et al. [Davidson, D. F., Gauthier, B. M., and Hanson, R. K., "Shock Tube Ignition Measurements of Iso-Octane/Air and Toluene/Air at High Pressures," *Proceedings of the Combustion Institute*, Vol. 301, 2005, pp. 1175–1182.]. Although the preignition pressure–time histories varied with the shock-tube loading protocol (e.g., cleaning and passivating), the ignition delay times were not significantly affected. Ignition delay time measurements were also compared with the predictions of several current toluene reaction mechanisms, and updated reaction rate values were suggested to improve modeling performance.

I. Introduction

TOLUENE (C_7H_8) is the major aromatic component found in practical fuels and is widely used in surrogate mixtures for practical fuels [1,2]. Because of toluene's role in engine knock, soot production, and emission of carcinogens, accurate knowledge of the chemistry controlling the oxidation of toluene is needed, especially under engine-relevant conditions. Recently, many experimental and computational studies of toluene oxidation and pyrolysis have been carried out by researchers using different facilities and techniques [3–27]. However, there still appears to be a lack of consensus among the ignition delay time measurements found in these studies. In particular, variations in the recent ignition delay time measurements of toluene/air mixtures at high pressures [3–5] have renewed interest in the sensitivity of ignition delay time to various factors such as facility gas dynamic effects, mixture uniformity and purity, etc.

Figure 1 shows a comparison of results from three recent high-pressure ignition delay time studies of toluene. Activation energies near 1000 K found in the three studies (Davidson et al. [3], Mittal and Sung [4], and Shen et al. [5]) are all different ($E_A = 20.8$, 64.9, and 31.3 kcal/mole, respectively), resulting in significantly different measured and predicted ignition delay times for temperatures of 1000 K and below.

Davidson et al. [3] first reported toluene (2.28%) and air ignition delay times for two pressures (20 and 55 atm) and two equivalence ratios ($\phi = 0.5$ and 1.0). In addition, the authors noted that their pressure profiles showed preignition step and ramp behavior. These profiles, taken from [3], are shown in Fig. 2. In step behavior (seen in the 1183–1068 K data), the pressure rises to an intermediate relative pressure plateau value of about 1.33, for these fuel–oxidizer mixtures and conditions, and represents approximately 15% of the final computed pressure increase under a constant-volume constraint. The authors note that this pressure step is indicative of a potential intermediate energy release of $\sim$15% of the total energy release of the ignition event and that this large preignition energy release was not predicted by current toluene mechanisms. In ramp behavior (seen in the 1005 and 977 K data), pressure remains constant for some time and rises almost linearly to a much higher value during the final stages of induction time before ignition. In these experiments, Davidson et al. used a wall-passivating procedure in order to avoid condensation losses of toluene in the shock tube.

Mittal and Sung [4] subsequently conducted ignition delay time experiments in a rapid-compression machine (RCM) near 45 atm and equivalence ratios of 1.0, but at lower fuel concentration (0.96%) than Davidson et al. [3]. They found that their pressure profiles showed ramp behavior when the facility was not cleaned between experiments and that this behavior disappeared when the facility was cleaned after each experiment.

More recently, Shen et al. [5] conducted ignition delay time experiments in a shock tube with mixtures and conditions similar to those of Davidson et al. [3]. They also investigated the influence of cleanliness on their pressure measurements. Shen et al. [5] did not heat or passivate their shock tube, but did passivate and heat their mixing tank (to 60°C). Data from these two shock-tube studies (Shen et al. [5] and Davidson et al. [3]) agreed well for $\phi = 0.5$ at all temperatures and for $\phi = 1.0$ at high temperatures. However, for $\phi = 1.0$ the measured ignition delay times deviate from those of Davidson et al. [3] at the lowest temperatures (see, particularly, the Shen et al. [5] data at 1021 K and 1041 K in Fig. 1).

The discrepancies mentioned in the above studies are sufficient to motivate further measurements of high-pressure toluene ignition delay times. Here, we report new ignition delay time experiments in toluene/air behind reflected shock waves at 50 atm and temperatures of 965–1211 K and we have further investigated the effect of shock-tube filling protocol and contamination on ignition delay times.

II. Experimental Details

Ignition delay times in toluene mixtures in synthetic air were measured behind reflected shock waves in Stanford University's high-purity, high-pressure shock tube (HPST). Incident shock waves were produced by rupturing scribed aluminum diaphragms of 1 to 2 mm thickness with high-pressure helium. The electropolished stainless-steel driven section of the HPST, which is 5 m long with a 5 cm internal diameter, can be heated uniformly to 200°C along its length (to ±3°C). Reflected shock wave conditions were determined

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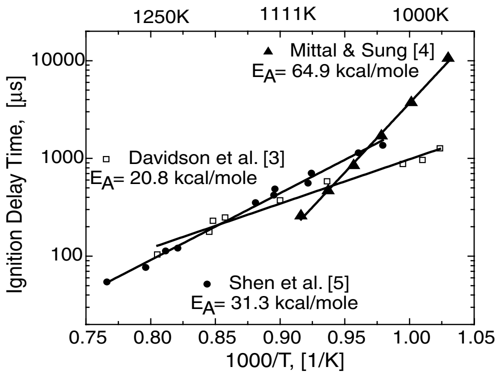

Fig. 1 High-pressure ignition delay time studies of toluene/air, 50 atm, $\phi = 1$. RCM measurements (by Mittal and Sung [4]) are at a reduced fuel concentration (0.96% compared to the shock-tube measurements with 2.28%) and have been normalized for this difference using the correlation reported by Mittal and Sung.

using chemically frozen, but vibrationally equilibrated, shock relations and incident shock speeds derived from six piezoelectric transducers (and five interval counters with ± 0.3 μs uncertainty) spaced over the last 2 m of the shock tube near the endwall [1,2,28,29]. Pressure–time-history measurements were made with two different pressure transducers (Kistler model 603B1 and PCB model 113A, each with a thin coating of GE RTV-106 silicone) located 10 mm from the endwall. Measured initial P_5 values were in good agreement with calculated values and both pressure transducers gave effectively identical pressure profiles. Ignition was also monitored using OH* emission diagnostic as detailed in [2,28]. Further details of the shock-tube facility, operation, and ignition time measurement techniques can be found in [1–3,28,29].

For chemical kinetic studies, it is important to use high-purity toluene stored in brown bottles under dark conditions (not exposed to fluorescent light overnight or sunlight) because its ignition quality can be affected [30–32]. Hence, test-gas mixtures were prepared using carefully stored (brown bottles, no exposure to light), spectrophotometry-grade (99.99% pure) toluene (OmniSolv®, EMD Chemicals, Inc.), and high-purity synthetic air (Praxair 79% N_2 and 21% O_2, greater than 99.999%) in a heated 13 liter stainless-steel mixing tank with a magnetically driven stirrer. The mixture partial pressures inside the mixing tank was monitored using three pressure transducers (one Baratron, MKS instruments and two Setra 280E solenoid pressure transducers), and the mixing tank and connecting gas lines to the shock tube were heated in a controlled manner to minimize condensation. The tank and lines were heated to 90–110C, depending on the fuel loading. In general, we kept the partial pressure of toluene below 50% of its vapor pressure in these sections to avoid condensation. Because of the low partial pressure of toluene in the shock tube, it was not heated in these experiments.

In some of the current experiments, fuel concentration inside the shock tube at our measurement location was measured using the midinfrared (3.39 μm) laser absorption technique (and absorption coefficients) of Klingbeil et al. [33,34]. The toluene concentrations derived from the midinfrared measurements agreed (within $\pm 1\%$) with the test-gas mixture concentrations determined manometrically in the mixing tank, confirming that there was no observable loss of toluene to the unheated shock-tube wall in these experiments. A sample toluene concentration measurement is shown in Fig. 3, which shows small ($\sim 1.7\%$) variation over long periods up to the maximum wait time (less than 300 s) before the arrival of the shock.

Before some shock wave experiments, both driver and driven sections of the tube were cleaned with organic solvent-drenched (acetone, methanol, or toluene) lint-free materials and dry air was blown through the tube from the driven end. Additionally, the driven end section was cleaned separately using HFC-134a.

In some experiments a passivation procedure similar to that of Davidson et al. [3] was used to fill the shock tube. The shock tube was evacuated to ~ 1 μtorr and then filled with the toluene/air mixture to ~ 3 torr. After 5 min the shock tube was evacuated again to ~ 0.12 torr and filled with the toluene/air mixture to the required preshock pressure. Midinfrared laser absorption measurements of toluene concentration in the shock tube with this passivation protocol also agreed with the manometric measurements in the mixing tank.

III. Results

A. Ignition Delay Times

Ignition delay time experiments in toluene/synthetic air mixtures with $\phi = 1.0$ near 50 atm over a temperature range of 965 to 1211 K were performed using various shock tube and mixture preparation protocols. All current ignition measurements are summarized in Table 1 and Fig. 4. Selected shock-tube pressure traces and ignition delay times are plotted in Figs. 5–7. Ignition delay time data presented in the figures have been scaled to a common pressure using $\tau_{\text{ign}} \sim 1/P$. Note that in Table 1, Atten. is the incident shock attenuation (typical shock attenuation rates, defined as the normalized slope of axial incident shock velocity extrapolated to the endwall in %/m). Other definitions are shown in Fig. 7: P_{IGN} is the pressure immediately before ignition event, τ_R is the time when pressure starts rising (in both step and ramp behaviors), τ_{PT} is the time when pressure reaches a plateau (in step behavior), and τ_{IGN} is the ignition delay time.

The measured ignition delay times are in good agreement with the previous results of Davidson et al. [3] at all temperatures. However, a small difference is seen between these two studies at temperature above 1040 K and below 1110 K, where the present data lay approximately 15% higher than the two Davidson et al. data points that exist in this temperature range. Ignition in this temperature range, as will be discussed later, falls within the weak-to-strong ignition transition regime and larger variability in the ignition delay times is expected. The current measurements are also in agreement with those of Shen et al. [5] at temperatures above 1050 K, and differ significantly only at the two lowest temperatures: 1041 and 1021 K. A quadratic best-fit line, also indicated in Fig. 4, demonstrates a consensus fit for almost all the data of the three studies. The ignition

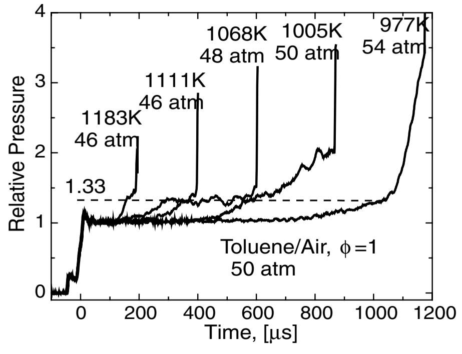

Fig. 2 Pressure–time histories from Davidson et al. [3] shock-tube study near 50 atm.

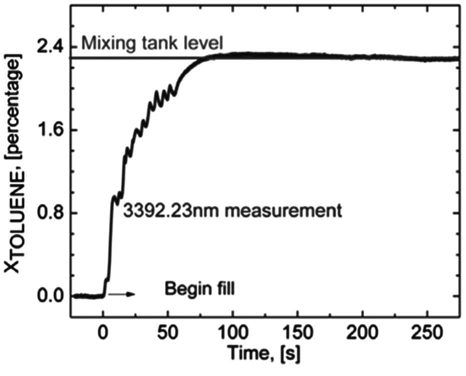

Fig. 3 Toluene concentration measurement using 3.39 μm laser diagnostic technique during filling. Measured variation from the end of fill until the arrival of shock is less than 2%.

Table 1 Ignition delay times for toluene, $\phi = 1.0$, in air

	Pressure			Time, μs		
T_5, K	Atten., %/m	P_5, atm	P_{IGN}/P_5	τ_R	τ_{PT}	τ_{IGN}[a]
Toluene/air, $\phi = 1.0$ (evidence of soot in shock tube); ramp behavior[b]						
1052	1.3	49.4	N/A	N/A	——	530
1010	1.9	44.4	N/A	N/A	——	906
1103	1.6	51.5	N/A	N/A	——	498
1010	1.9	43.5	2.78	653	——	921
1044	1.9	47.1	2.215	547	——	790
1055	1.8	47.6	2.18	516	——	750
1096	1.5	51.4	1.49	290	——	514
1101	1.8	51.3	1.28	117	——	513
Toluene/air, $\phi = 1.0$ (first shock after cleaning); step behavior[b]						
1059	1.6	48.3	1.46	346	469	686^{ac}
1043	1.7	48.8	1.39	464	631	921^{me}
1106	1.6	51.9	1.38	211	365	481to
1084	1.6	50.4	1.3	234	391	530^{ac}
Toluene/air, $\phi = 1.0$ (further shocks after cleaning); ramp behavior[b]						
1091	1.5	50.9	1.74	360	——	636
1062	1.7	48.1	1.767	398	——	780
1059	2.0	47.2	2.54	528	——	729
1057	1.8	49.1	1.87	N/A	——	742
1051	1.8	49.7	1.75	N/A	——	774
975	1.9	45.5	3.62	1086	——	1262
1006	1.7	48.8	2.98	761	——	940
966	1.8	46.2	3.35	886	——	1311
1066	1.6	48.1	1.548	292	——	807
1050	1.9	47.1	2.5	679	——	853
1082	1.5	48.8	1.95	375	——	600
1049	1.9	45.8	2.22	473	——	754
965	1.5	47.4	2.84	935	——	1192
1065	1.8	47.7	1.9	480	——	711
Toluene/air, $\phi = 1.0$ (cleaned with acetone and O_2 shocks)[b]						
1060	2.0	47.3	2.057	369	——	613
1112	1.7	52.2	1	254	387	435
1075	1.7	48.6	1.31	354	435	588
2.26% *toluene*/0.163%*heptane/air, $\phi = 1.0$; ramp behavior*[b]						
1048	1.8	53.4	1.69	526	——	705
1018	1.9	53.4	N/A	N/A	——	840
Toluene/air, $\phi = 1.0$; various passivating methods						
999	1.7	41.5	2.21	888	——	1366
1055	1.6	47.6	1.9	688	——	884
1114	1.4	49.7	1	322	——	519
1041	1.8	45.9	2.533	708	——	889
1048	1.6	46.6	2.48	764	——	917
1073	1.6	48.0	2.06	630	——	832
Toluene/air, $\phi = 1.0$, Davidson et al. [3] *passivation method*						
1056	1.7	46.1	1.6	566	734	886
1096	1.4	49.9	1.54	340	544	597
1087	1.5	49.3	1.63	202	297	585
Toluene/air, $\phi = 1.0$, Davidson et al. [3] *passivation method, shock tube at* 60°C						
1211	1.1	52.0	1.56	77	——	111
1116	0.9	54.2	1.26	100	——	349
1054	1.0	53.5	1.68	319	——	744

[a] Abbreviation ac denotes the use of acetone cleaning solvent, me denotes the use of methanol cleaning solvent, and to denotes the use of toluene cleaning solvent. Refer to Fig. 7 and Sec. III.A for definitions.

[b] Experiments without shock-tube passivation.

delay time activation energy changes significantly as the temperature changes: between 1050 and 1250 K, $E_A = \sim 27.1$ kcal/mol, and between 950 and 1050 K, $E_A = \sim 17.0$ kcal/mol.

As shown in Fig. 1, the toluene ignition delay times derived from the RCM experiments of Mittal and Sung [4] have similar magnitudes to those of the shock-tube studies but a significantly different activation energy. While the exact reason for this difference is uncertain, it should be noted that RCMs and shock tubes operate in different ways and a direct comparison of their ignition delay times may not be appropriate in all cases. Critical distinctions between the two experiments include: different temperature and pressure histories after compression, possible chemistry during RCM test-gas compression, the role of heat transfer losses to the walls of the facilities, differences in carrier gases, and varying definitions of effective temperature and pressure. The effect of these differences on measured ignition delay times has been discussed by many workers [4,5,35–42].

B. Pressure–Time Histories

While all the ignition delay times measured in the present study are in good agreement with the consensus fit, the actual pressure profiles from these experiments show widely varying structure. In particular, preignition pressure steps and ramps are seen under certain conditions. To understand why these structures existed in the pressure profiles, a preliminary study of some of the potential causes of these effects was made.

To study the influence of impurities on the pressure profiles and ignition delay times, toluene ignition experiments were conducted in the shock tube immediately after a series of fuel-rich soot-producing experiments [43], but without thorough cleaning or passivating. Visible examination of the shock-tube walls near the measurement location indicated black soot and minor submillimeter aluminum diaphragm particles. In these experiments no evidence of the step behavior was found; instead, in all cases, pressure and OH* emission profiles exhibited a ramp behavior (see Fig. 5). Pressure traces from Davidson et al. [3] at similar conditions (e.g., Fig. 2: 1068 K, 48 atm) clearly show approximately 200 μs of step plateau. Thus, it is likely that the step behavior seen in the shock-tube experiments of Davidson et al. was not due to contamination in their experiments. Ignition delay times in the current series of contaminated experiments were effectively identical to those for which thorough cleaning or passivating was performed.

It has been hypothesized that the step behavior seen by Davidson et al. [3] may be related to the presence of n-alkane impurities (which are known to show preignition step behavior at low negative temperature coefficient (NTC) temperatures [6,37–39]). In toluene/n-heptane/air experiments (toluene = 2.26%, heptane = 0.163%,

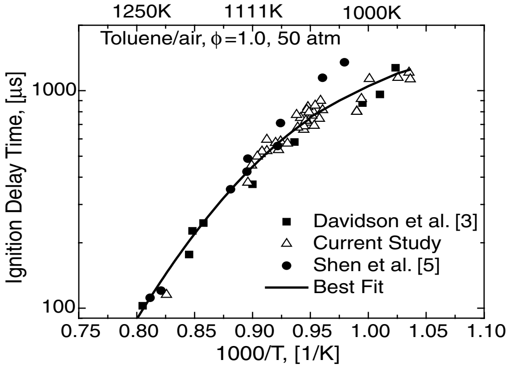

Fig. 4 High-pressure toluene/air ($\phi = 1.0$) ignition delay time data. All data normalized to 50 atm using P^{-1} scaling. The quadratic best-fit line includes all data points except the two coldest Shen et al. [5] data points.

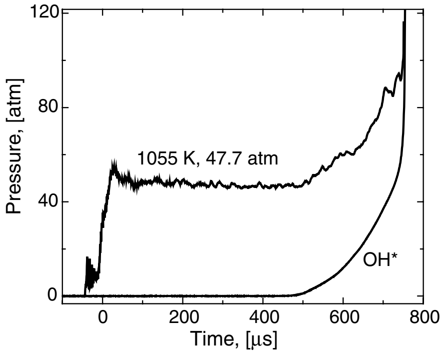

Fig. 5 Pressure and OH* emission profiles from a shock wave experiment taken after a series of soot-producing experiments and without cleaning the shock tube. Ramp behavior is evident beginning at 500 μs.

$O_2 = 20.5\%$, $N_2 = 77.08\%$) performed with a clean shock tube but without passivating, no clear step behavior was seen in the pressure or OH* emission profiles (Fig. 6). Other researchers have reported the same behavior. Herzler et al. [44] found in reflected shock wave experiments that even 35% of heptane and 65% toluene mixtures at similar temperatures did not produce step behavior. Thus, we conclude that the step behavior seen by Davidson et al. [3] was not the result of *n*-alkane impurities.

In ignition delay time experiments in which the shock tube was not passivated or heated but was thoroughly cleaned with solvents, step behavior in the pressure profile could be seen in the first shock wave experiment after the cleaning (see Fig. 7). The step behavior was observed regardless of the cleaning solvent used (methanol, acetone or toluene). As the step behavior was also seen when using toluene as a cleaning solvent, we may assume that the step behavior is not due to a chemical interaction between the toluene and the cleaning solvent.

Table 2 Toluene mechanisms used in this study

Mechanism	Year	No. of species	No. of reactions
Sivaramakrishnan et al. [16]	2005	98	538
Bounaceur et al. [22]	2004	148	1035
Sakai et al. [19]	2009	758	2884
Yahyaoui [25]	2005	234	1863
Andrae et al. [24]	2008	138	633

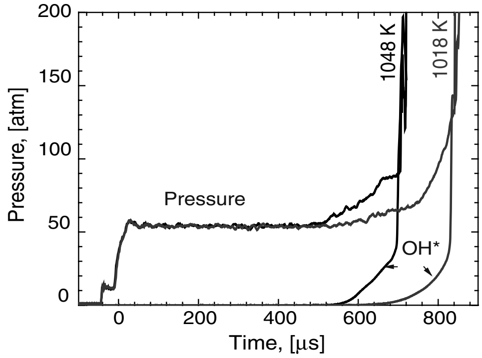

Fig. 6 Pressure and emission profiles from toluene/*n*-heptane ignition experiments taken in clean shock tube for a mixture of toluene/*n*-heptane/air, $\phi = 1.0$ (0.163% *n*-heptane, 2.26% toluene, $O_2 = 20.5\%$, and $N_2 = 77.08\%$).

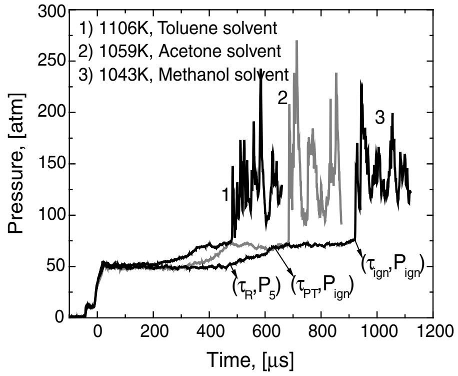

Fig. 7 Pressure profiles exhibiting step behavior in the first experiment after cleaning in toluene/air ($\phi = 1.0$) mixtures for various cleaning solvents: 1106 K, 51.8 atm, toluene solvent; 1059 K, 48.3 atm, acetone solvent; and 1043 K, 48.8 atm, methanol solvent. Time of the initial pressure rise, plateau formation, and ignition are indicated.

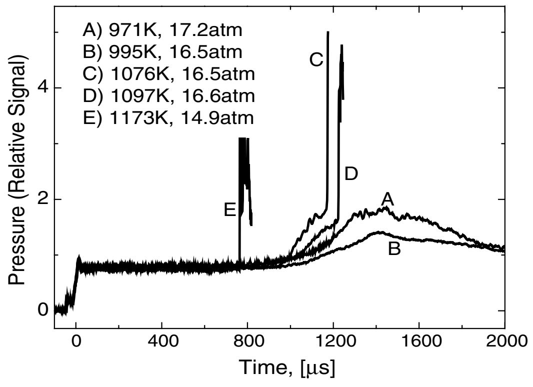

Fig. 8 Pressure–time histories for reflected shock wave ignition experiments near 20 atm from Davidson et al. [3].

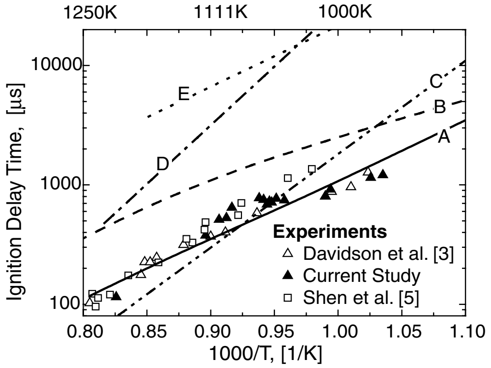

Fig. 9 High-pressure toluene/air ($\phi = 1.0$) ignition delay time data comparison with constant U, V kinetic modeling predictions. All data are normalized to 50 atm using P^{-1} scaling; Andrae et al. [24] (line A), Sivaramakrishnan et al. [16] (line B), Sakai et al. [19] (line C), Bounaceur et al. [22] (line D), and Yahyaoui [25] (line E).

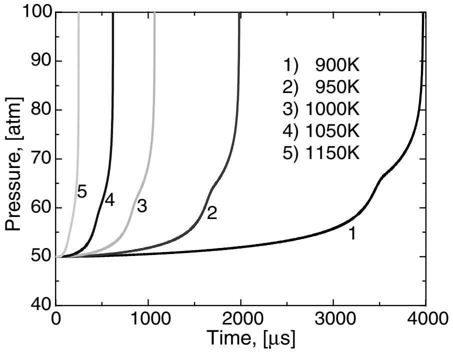

Fig. 10 Pressure–time histories according to Andrae et al. [24] mechanism using a constant U, V constraint. Initial conditions are 50 atm, toluene/air mixtures, and $\phi = 1$.

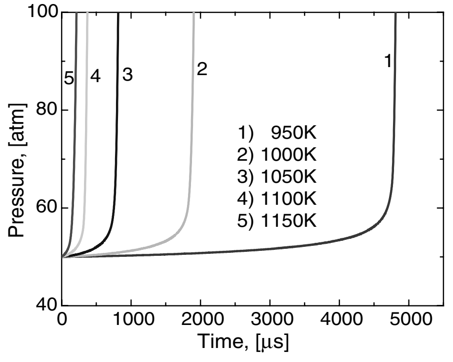

Fig. 11 Pressure–time histories according to Sakai et al. [19] mechanism using a constant U, V constraint. Initial conditions: 50 atm, toluene/air mixtures, $\phi = 1$.

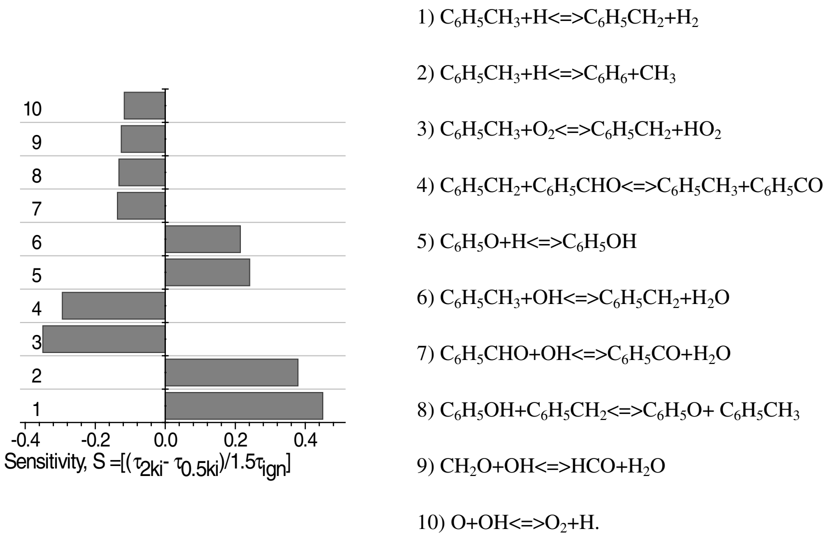

Fig. 12 Brute-force sensitivity analysis results (1050 K, 50 atm) for toluene ($C_6H_5CH_3$)/air $\phi = 1.0$ using the Sivaramakrishnan et al. [16] mechanism.

It should be noted, however, that step behavior was not seen (instead only the ramp behavior was observed) in the second and all subsequent shock wave experiments in a series after a thorough cleaning with solvents. Interestingly, in all shock wave experiments in this series, no systematic difference was seen in ignition delay times between the first shock wave experiment and all subsequent shock wave experiments in a series after thorough cleaning.

Finally, in an attempt to reproduce the different types of pressure profiles seen by Davidson et al. [3] in their shock-tube toluene ignition delay experiments, their filling protocol was used. In these experiments, step behavior was again seen with results similar to those of Davidson et al. in the range 1050 K to 1100 K near 50 atm. Thus we conclude that the Davidson et al. passivation procedure was responsible for the step behavior seen in their experiments. However, this does not explain the previous observation in the present study of the step behavior seen in the first shock wave experiments after cleaning (Fig. 7), and we do not currently have an explanation why step behavior occurs for either process. Nonetheless, regardless of the heating and passivation schemes used, the effect on ignition delay times was minimal, and all the current data are in good agreement with the Davidson et al. data and the data of Shen et al. [5] at temperatures above 1050 K.

The occurrence of ramp behavior during toluene ignition near 50 atm may be related to the ignition regimes or modes of ignition. Figure 8 provides unpublished pressure traces from the Davidson et al. [3] study at pressures near 20 atm. These pressure traces show three ignition modes (strong, mild, and mild-to-strong transition). Mild ignition occurs at low temperatures (traces A and B in Fig. 8); there are no postignition pressure oscillations, and only a smooth gradual rise in pressure is seen. Emission measurements confirmed that there is mild ignition in these cases. Strong ignition occurs at higher temperatures (trace E in Fig. 8); here, the pressure rises rapidly due to a rapid release of energy and is accompanied with a strong pressure peak and oscillations. No ramp occurs before ignition in this case. Ignition in the mild-to-strong transition regime occurs between these two limits (traces C and D in Fig. 8); in the two cases shown, mild ignition is followed by a strong ignition event.

We have quantified the features of the pressure traces in the present work (in both step and ramp behavior cases) in Table 1. Definitions of the ramp and step parameters are shown in Fig. 7. In the present study at 50 atm only strong ignition and mild-to-strong transition ignition cases were seen, with strong ignition occurring typically above 1050–1100 K. Detailed discussion on classification of ignition modes and their behavior can be found in [45–48].

IV. Kinetic Modeling of Toluene Ignition

Substantially fewer mechanisms for toluene have been developed than for alkanes [13–26]. We have chosen five recent mechanisms (these are listed in Table 2) for comparison with the toluene ignition delay time data, and the results are presented in Fig. 9. In this work, in comparing shock-tube experimental data with model predictions of available toluene mechanisms, the calculations were done assuming homogeneous adiabatic conditions behind reflected shock waves, with the common constant-internal-energy, constant-volume constraint (constant U, V) using CHEMKIN 4.1.1 [49]. Reflected shock wave experiments can produce stationary, uniform mixtures, and behave like near-ideal constant-volume reactors up to the time of ignition. Typically, for short ignition delay times (less than about 2 ms), for which the facility-dependent changes in pressure and temperature are small, the constant U, V constraint is an excellent assumption for the purpose of ignition delay time calculations (see [40,50] for further discussion on this topic).

The Sakai et al. [19] mechanism ignition delay time predictions are of the same magnitude as the data, but show a larger activation energy. The Andrae et al. [24] mechanism results are in relatively good agreement with the Davidson et al. [3] data over the entire temperature range studied, though the simulations exhibit less curvature in ignition delay time than the data at the lowest temperatures. This agreement is expected as the Davidson et al. [3] data were

Table 3 Reactions in this table represent new reactions rates (according to the latest studies in literature) for most sensitive reactions from the Sivaramakrishnan et al. [16] mechanism for $k = AT^n \exp(-Ea/RT)$[a]

Reaction	A	n	Ea	Reference
$C_6H_5CH_3 + H = C_6H_5CH_2 + H_2$ (1)	6.47E + 00	3.98	3,384	Oehlschlaeger et al. [11]
$C_6H_5CH_3 + H = C_6H_6 + CH_3$ (2)	3.90E + 08	1.25	2,371	See Sec. IV
$C_6H_5CH_3 + O_2 = C_6H_5CH_2 + HO_2$ (3)	2.18E + 07	2.5	46,045	Oehlschlaeger et al. [10]
$C_6H_5CH_2 + C_6H_5CHO = C_6H_5CH_3 + C_6H_5CO$ (4)	1.30E + 11	0.0	11,500	Bounaceur et al. [22]
$C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$ (6)	1.81E + 05	2.39	−602	Seta et al. [51]
$H + O_2 = O + OH$ (−10)	2.65E + 16	−0.6707	17,041	GRI 3.0 [52]
$C_6H_5CH_2 + H = C_6H_5CH_3$	2.59E + 14	0	0	Baulch et al. [53]

[a] Reaction numbering is taken from Fig. 12. Reaction rate $k = AT^n \exp(-Ea/RT)$. Rate constant units are mol, s, cm^3, and cal.

validation targets for the Andrae et al. [24] mechanism. Andrae et al. reported that additional reactions involving the formation and destruction of benzylperoxide radical were crucial to modeling shock-tube data. The magnitude of the Sivaramakrishnan et al. [16] mechanism predictions are higher than the current data for the entire temperature range, but show a similar activation energy variation with temperature to the Davidson et al. [3] data. Both the Bounaceur et al. [22] and the Yahyaoui [25] mechanism ignition delay time predictions are significantly longer over the entire temperature range of present data.

The toluene oxidation mechanisms can be divided into two classes based on their predictions of preignition pressure–time histories: those that predict a small intermediate rise before ignition and a near-step-like behavior at certain temperature and pressure conditions, and those that do not. Modeling predictions (for pressures of 50 atm) using the mechanism of Andrae et al. [24] are shown in Fig. 10 for different temperatures. Simulated pressure profiles show near-step-like and ramp behavior at different temperatures (with the near-step-like behavior more pronounced at lower T). Similar structure is seen with the Sivaramakrishnan et al. [16] model.

Mittal and Sung [4] noted steplike pressure traces in their RCM modeling studies using the Sivaramakrishnan et al. [16] mechanism and attributed this behavior to the increased rate of benzyl + HO_2 reaction from that used in the parent Klotz et al. [14] mechanism. For the conditions presented in Fig. 10 changing the rate of this reaction to that used in the Klotz et al. [14] mechanism did not eliminate the step behavior predicted by the Sivaramakrishnan et al. [16] mechanism for a sample case at 1050 K.

The three other toluene mechanisms studied (Bounaceur et al. [22], Sakai et al. [19], and Yahyaoui [25]) do not predict steplike behavior, but rather predict a ramplike gradual rise to pressure and then an abrupt ignition step. Representative pressure traces using the Sakai et al. [19] mechanism are shown in Fig. 11. Further work at low temperatures (below 950 K) is needed to better distinguish these different mechanism classes.

A brute-force sensitivity analysis was carried out for the Sivaramakrishnan et al. [16] mechanism that most closely approximated the activation energy variation of the toluene ignition delay time data. The results are shown in Fig. 12. Brute-force sensitivity coefficient is defined as $S = [(\tau_{2ki} - \tau_{0.5ki})/1.5\tau_{\text{ign}}]$, where τ_{ign} is the ignition delay time predicted by the unmodified mechanism and τ_{2ki} and $\tau_{0.5ki}$ are ignition delay times predicted when the rate k_i of the ith reaction alone was multiplied and divided by a factor of 2, respectively.

It is possible to improve the predictive ability of the Sivaramakrishnan et al. [16] mechanism by updating the rates of the most sensitive rate coefficients. Updated reactions and the rates (which reflect recent measurements and evaluations) used are provided in Table 3. Note that a three-parameter fit is obtained for $C_6H_5CH_3 + H = C_6H_6 + CH_3$ reaction using the program from the NIST Standard Reference Database[§] in order to obtain a best rate from the two review recommendations by Baulch et al. [53] and Ellis et al. [54]. The modified mechanism predicts ignition delay times and variation in activation energy very well over the entire temperature range, as shown in Fig. 13. This modified mechanism also gives better agreement with the Davidson et al. [3] $\phi = 0.5$ data (not shown here). We have conducted brute-force sensitivity analysis with all mechanisms, and the results are very similar and demonstrate that toluene chemistry is dominated by benzyl radical chemistry. Using a similar approach we also noted a considerable improvement in the predictions of the Yahyaoui [25] mechanism by using the Oehlschlaeger et al. [10] measured rate for the toluene + O_2 = benzyl + HO_2 reaction (not shown here).

Note that Andrae et al. [24] used the experimentally measured rate by Fenter et al. [55] (which recently was confirmed through ab initio quantum chemical calculations by [56]) for the benzylperoxy formation reaction $C_6H_5CH_2 + O_2 = C_6H_5CH_2OO$, and they used an estimated rate for the decomposition of benzylperoxy ($C_6H_5CH_2OO = C_6H_5CHO + OH$), which lies in between those estimated by Bounaceur et al. [22] and Lindstedt and Maurice [17]. In the case of the Andrae et al. [24] mechanism, the authors adjusted the rate of the most sensitive (according to their mechanism) reaction $C_6H_5CH_2OO = C_6H_5CHO + OH$ to improve agreement with the Davidson et al. [3] data.

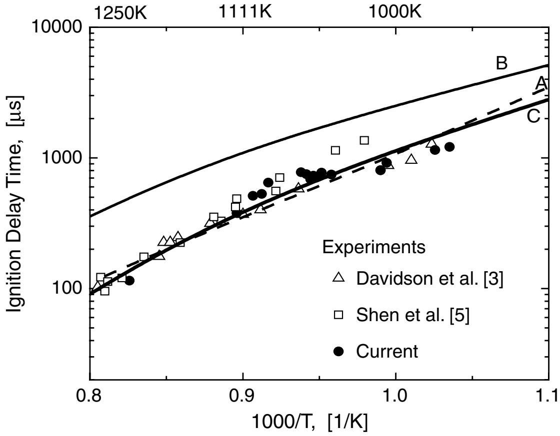

Fig. 13 Comparison of mechanism predictions and data. Toluene/air, $\phi = 1.0$, 50 atm Andrae et al. [24] (line A), Sivaramakrishnan et al. [16] (line B), and modified mechanism (line C).

Autoignition of toluene is not well understood in the NTC region, mainly due to lack of experimental data in this region [57], and further study is needed to unravel the kinetics of low-temperature toluene ignition. Both ignition delay time measurements at temperatures below 950 K (at high pressures) and species time histories are needed to test and refine the toluene oxidation mechanism in this regime. This work is currently being pursued in our laboratory.

V. Conclusions

We have measured ignition delay times for $\phi = 1$ toluene/air mixtures behind reflected shock waves at pressures near 50 atm and temperatures between 966 and 1211 K. These new measurements are in good agreement with the earlier work of Davidson et al. [3] and Shen et al. [5]. The measurements show evidence of strong ignition and mild-to-strong transition ignition regimes, and these different regimes can be distinguished by examining the structure of the pressure profiles. Significant differences are seen in the pressure–time histories of these ignition experiments, depending on the preshock cleaning and passivating protocols, but these modifications in protocol have little influence on the ignition delay time itself.

Current toluene mechanisms differ in their predictions of toluene ignition delay times and preignition pressure–time-history profiles. A sensitivity analyses show the importance of benzyl and benzyl peroxy reactions on the ignition of toluene and improvements to the mechanism predictions of Sivaramakrishnan et al. [16] are possible using recently measured rates for several of the key reactions. The trend to a lower activation energy seen in the ignition delay time measurements at the lowest temperatures of this study is supported by some mechanisms (Sivaramakrishnan et al. and the revision suggested in this study) but not others (Andrae et al. [24]) Further work is needed experimentally and theoretically to understand the behavior of the toluene reaction mechanism at high pressures and at even lower temperatures than the present study.

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