Chemical Kinetic Study of Extinction and Autoignition of Nonpremixed Toluene Flames

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Abstract

Kinetic modeling and experimental studies are performed to elucidate the structure and mechanism of extinction and autoignition of toluene flames in a counterflow configuration under nonpremixed conditions. Computations are performed using detailed chemistry to determine the flame structure and to obtain values for critical conditions of extinction and autoignition. Three different mechanisms are applied and the results compared with experimental data to select the appropriate mechanism for further study. Sensitivity analysis of rate constant, reaction pathway analysis and spatial reaction rate profiles are used for that mechanism to identify the reactions that control the critical conditions of autoignition and extinction.

Experiments are conducted in a flame stabilized between two opposing streams. The fuel stream is a mixture of vaporized toluene and nitrogen, and the oxidizer stream is air. Concentration profiles of stable species are measured by removing samples from the reacting mixing layer using a quartz microprobe. The samples are analyzed using a gas chromatograph. Measured profiles include those of C$_7$H$_8$, O$_2$, N$_2$, CO$_2$, CO, H$_2$O, and H$_2$. Temperature profiles are measured using a Pt-Pt 13 % Rh thermocouple. Critical conditions of extinction are measured. Data giving the fuel mole fraction at extinction as a function of the strain rate are obtained. Also, oxidizer temperature at ignition is measured for fixed fuel mole fraction and different strain rates. The data collected in these experiments is compared with the computations to perform the above analysis.
Introduction

Alkylated benzenes are an important class of hydrocarbons because they comprise a significant portion of gasoline and diesel fuels. Knowledge of the oxidation chemistry of alkylated benzenes is needed in developing predictive models that can treat autoignition, and premixed and nonpremixed burning of transportation fuels in internal combustion engines. Toluene \((\text{C}_6\text{H}_5\text{CH}_3)\) has one of the simplest molecular structures of the alkylated benzenes and is a reasonable starting point for the development of detailed chemical-kinetic reaction mechanisms for alkylated benzenes. Much previous work has been done on the oxidation of toluene. Several research groups have developed detailed chemical-kinetic reaction mechanisms for toluene. Most recently, Klotz et al. [1] supplemented the toluene mechanism of Emdee et al. [2] to improve the predictions for the intermediates 1,3 butadiene, acetylene and benzaldehyde. Zhong and Bozzelli [3–5] developed a more accurate description of radical additions to cyclopentadiene and associations with cyclopentadienyl radical; they included these reactions in a detailed chemical-kinetic mechanism for toluene that they developed. Lindstedt and Maurice [6] developed a very comprehensive toluene mechanism whose predictions they compared to experimental results from counterflow diffusion flames, plug flow reactors, shock tubes and premixed flames. Emdee et al. [2] developed a detailed chemical-kinetic mechanism for toluene that was benchmark for many years.

There are quite a few experimental studies of toluene oxidation whose data are very useful for mechanism validation. Several experimental studies of toluene oxidation in a flow reactor were performed at Princeton University by Glassman et al. [1, 2, 7, 8]. Ignition of toluene in a rapid compression machine was performed by Griffiths et al. [9] and by Roubaud et al. [10]. Their rapid compression machine results show that toluene oxidation chemistry lacks the two stage ignition observed in paraffinic fuels. Experimental data for the critical conditions of autoignition of toluene in the counterflow configuration are given in [11]. Using this experimental data, overall chemical-kinetic rate parameters that characterize the rate of one-step overall reaction between fuel and oxygen were obtained [11].

In the present study, critical conditions of extinction and autoignition are measured for combustion of toluene under nonpremixed conditions. The flame structure is measured. The measurements are compared with predictions obtained using a detailed chemical-kinetic model developed elsewhere.

1 Description of Experimental and Computational Studies

Steady, axisymmetric, laminar flow of two counterflowing streams toward a stagnation plane is considered. Figure 1 shows a schematic illustration of the counterflow configuration. In this configuration a fuel stream made up of prevaporized toluene and nitrogen is injected from
the fuel-duct, and an oxidizer stream of air is injected from the oxidizer-duct. These jets flow into the mixing layer between the two ducts. The exit of the fuel-duct is called the fuel boundary and the exit of the oxidizer-duct the oxidizer boundary. The mass fraction of fuel, the temperature, and the component of the flow velocity normal to the stagnation plane at the fuel boundary are represented by $Y_{F,1}$, $T_1$, and $V_1$, respectively. The mass fraction of oxygen, the temperature, and the component of the flow velocity normal to the stagnation plane at the oxidizer boundary are represented by $Y_{O_2,2}$, $T_2$, and $V_2$, respectively. The tangential components of the flow velocities at the boundaries are presumed to be equal to zero. The distance between the fuel boundary and the oxidizer boundary is represented by $L$.

In the experiments the momenta of the counterflowing reactant streams $\rho_i V_i^2$, $i = 1, 2$ at the boundaries are kept equal to each other. Here $\rho_1$ and $\rho_2$ represent the density of the mixture at the fuel boundary and at the oxidizer boundary, respectively. This condition ensures that the stagnation plane formed by the two streams is approximately in the middle of the region between the two boundaries. The value of the strain rate, defined as the normal gradient of the normal component of the flow velocity, changes from the fuel boundary to the oxidizer boundary [13]. The characteristic strain rate on the oxidizer side of the stagnation
plane $a_2$ is presumed to be given by [13]

$$a_2 = \frac{2|V_2|}{L} \left(1 + \frac{|V_1|\sqrt{\rho_1}}{|V_2|\sqrt{\rho_2}}\right). \tag{1}$$

Equation 1 is obtained from an asymptotic theory where the Reynolds numbers of the laminar flow at the boundaries are presumed to be large [13].

1.1 Experimental Procedure

A detailed description of the burner is given elsewhere [11, 14]. The flow rates of gases were measured by computer-regulated mass flow controllers. The velocities of the reactants at the boundaries were presumed to be equal to the ratio of their volumetric flowrates to the cross-section area of the ducts. The temperature of the fuel stream and the temperature of the oxidizer stream at the boundaries were measured using thermocouples. A brief description of the experimental procedure is given here.

1.1.1 Critical Conditions of Extinction and Autoignition

The extinction experiments are conducted with the fuel stream temperature, $T_1 = 375\,\text{K}$, and the temperature of the oxidizer stream, $T_2 = 299\,\text{K}$. The distance between the fuel boundary and the oxidizer boundary was $L = 10\,\text{mm}$. At some selected value of the strain rate the flame was established. The strain rate was increased by increasing $V_1$ and $V_2$ until extinction was observed. Experimental results are shown later. Previous autoignition experiments were conducted with the mole fraction of prevaporized fuel maintained at 0.15 [11]. The temperature at the fuel boundary, $T_1 = 378\,\text{K}$. The distance between the fuel boundary and the oxidizer boundary was $L = 12\,\text{mm}$. At some selected value of the strain rate the flame was established. The strain rate was increased by increasing $V_1$ and $V_2$ until extinction was observed. The strain rate at extinction is denoted by $a_{2,e}$. The value of $a_{2,e}$ is recorded as a function of the mole fraction of fuel, $X_1$ in the fuel stream.

Critical conditions of autoignition are measured with $T_1 = 375\,\text{K}$, and mole fraction of fuel in the fuel stream equal to $X_1 = 0.15$. The distance between the fuel boundary and the oxidizer boundary was $L = 12\,\text{mm}$. At a given strain rate and oxidizer temperature $T_2 < T_{2,I}$ the flow field was established. The temperature at the oxidizer boundary was gradually increased until autoignition took place. The value of $T_{2,I}$ was recorded as a function of $a_2$.

1.1.2 Flame Structure

Concentrations of stable species are measured by removing gas samples from the reaction zone using a quartz microprobe and analyzing them in a gas chromatograph. The microprobe has a tip with an outer diameter of 225 microns and an inner diameter of 126 microns. The tip is placed at a location of 5 mm off the center-line of the ducts to avoid disturbance of the flow
field and influencing the reactive diffusive balance in the vicinity of the probe. The samples drawn from the flame are quantified using a SRI 8610C gas chromatograph. The instrument is equipped with a 4.5ft mole-sieve (80/100 mesh) - for separating H₂, O₂ and Ar, N₂, CH₄, and CO - and a 12ft Porapak Q column for separating all other species. Temperature programming and valve switching is employed to optimize the separation performance of both columns. The species eluding from the column are quantified using a thermal-conductivity-detector (TCD) and a flame-ionization-detector (FID). The chromatograms are analyzed using self written software, and by comparing with runs of known samples, the absolute mole fractions are determined. The expected accuracy for the maximum concentrations of most species is expected to be better than ±10%.

Temperature profiles are measured using Pt-Pt 13%Rh thermocouples. The measurements are corrected for radiative heat losses from the bead. The absolute accuracy of the temperature measurement is expected to be better than ±80 K. The location of the sampling probe and the thermocouple in the flow-field is determined using a digital photo camera. The size of one pixel corresponds to a distance in the flow field of approximately 17 microns.

1.2 Description of Computational Studies

Calculations are performed using detailed chemistry, applying the same boundary conditions as in the experiments. The computer program CHEMKIN [28], was used in the computations. The detailed chemical kinetic mechanisms employed here are described in Metcalfe et al. [29], Andrae et al. [30, 31], and Ranzi et al. [32].

2 Results

The following figures compare the predictions with experimental data. In these figures the symbols represent experimental data and the lines are predictions.

2.1 Non-premixed Ignition

Figure 2 shows the plot of oxidizer temperature \( T_{2,I} \) at ignition against the oxidizer strain rate \( a_{2,I} \). It is seen that the computations capture the trend of increase in oxidizer temperature with strain rate, but somewhat overpredict \( T_{2,I} \) for any given strain rate.

Figure 3 shows the ignition delay times of Toluene, oxygen and argon mixture as a function of temperature for a given fuel concentration, based on shock tube experiments by Vasudevan et al. [33]. It is seen that of that the numerical models well capture the trend of decrease in ignition delay time with increase in temperature.

Autoignition parameters are determined by the balance between heat generation in the reaction zone and the heat losses on the fuel and oxidizer sides [34]. In addition, they depend
Figure 2: The temperature of air at autoignition, $T_{2,I}$, as a function of the strain rate, $\alpha_2$ at fixed values of $X_{F,1} = 0.15$. The temperatures of the fuel stream is $375K$. The symbols represent experimental data and the lines are predictions.

Figure 3: Predicted and measured ignition delay times of toluene/O$_2$/Ar mixtures under shock tube conditions [33].
on concentrations of significant radicals present in reaction zone. In particular, the analysis of correlation between OH radical concentration and autoignition temperature shows importance of OH concentration for autoignition limits [34]. From Figure 4, it is seen that the maximum OH production increases with increasing oxidizer temperature and strain rate of reactants.

![Figure 4: Maximum OH concentration as functions of strain rate and oxidizer temperature for non-premixed ignition at $X_F = 0.15$.](image)

### 2.2 Sensitivity analysis of Counter Flow Configuration

Sensitivity analysis of OH radical concentration is performed for reactive flow solution very near autoignition to understand the governing kinetics for non-premixed ignition. Positive sensitivities indicate an increase in rate constant increases the OH concentration and negative sensitivities indicate an increase in rate constant decreases the OH concentration.

From Figure 5 it is seen that the chain branching reaction $H + O_2 = O + OH$ gives a very high positive sensitivity. The reaction $CO + OH = CO_2 + H$ also gives a high positive sensitivity, possibly due to H radical generation. Other reaction enhancing OH radical concentration are cresol radical decomposition: $OC_6H_4CH_3 = C_6H_6 + CO + H$ and the reaction of toluene with OH radical giving an active methyl-phenyl radical: $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$ However, the reaction: $C_6H_5CH_3 + OH = C_6H_5CH_2 + H_2O$ has negative sensitivity as it removes more active OH radical and generates less active benzyl radical. Reaction $H + O_2 = HO_2$ forming hydroperoxyl radical also gives negative sensitivity as it removes the active H radical.

We also performed rate of production and consumption pathway analysis for OH and Toluene as shown in Figure 6. The reaction $H + O_2 = O + OH$ gives maximum contribution to OH production. Other major OH producing reactions are: $HCCO + O_2 = OH + 2 CO$ and $HO_2 + O = O_2 + OH$. Major OH consumption pathways are reaction of fuel or fuel fragment with OH and the heat producing reactions forming $CO_2$ and $H_2O$. Major fuel consumption
Figure 5: Sensitivity of the OH radical concentration to changes in individual rate constants under nonpremixed conditions near autoignition (strain rate = 200 s⁻¹, oxidizer temperature $T_2 = 1233 K$).

Figure 6: OH and $C_6H_5CH_3$ production and consumption pathways for toluene diffusion flames at $X_F = 0.15$, strain rate $a_2 = 200$ s⁻¹, oxidizer temperature $T_{2,I} = 1233K$. 
pathways are its reaction with hydroxyl radical, H and O atoms.

2.3 Sensitivity analysis for shock tube

Sensitivity analysis of OH concentration under shock tube condition is shown in Figure 7. Analysis is performed when fuel is 50 % and 90 % consumed. H + O\(_2\) chain braching reaction gives high sensitivity for OH concentration. Similarly, the reaction of benzyl radical with atomic oxygen and decomposition of benzaldehyde gives positive sensitivity as they create H radical. Toluene decomposition also produces H radical and therefore gives positive sensitivity. Reaction of toluene with OH gives positive sensitivity as it produces methylphenyl (C\(_6\)H\(_4\)CH\(_3\)) which reacts with O\(_2\) and produces two radicals cresol and atomic oxygen. On the other hand, the reaction of toluene with active radicals H and OH generating less active radical benzyl gives negative sensitivity for OH concentration.

2.4 Non-Premixed Extinction

Figure 8 shows that the predicted values of critical conditions of extinction capture the trend of increase in strain rate with increasing fuel mole fraction. Computed strain rate of extinction are lower than measured values. Thus in both extinction and ignition experiments, the numerical model predicts lower overall reactivity of toluene with air than observed in the experiments.

2.5 Flame Structure

In order to study the flame structure, the temperature profile is plotted against the distance from fuel boundary as shown in Figure 9. It is seen that the predicted peak of the temperature
Figure 8: The strain rate at extinction, $a_{2,e}$, as a function of the mole fraction of fuel, $X_{F,1}$ in the fuel stream. The temperatures of the fuel stream and the oxidizer stream are 375K and 299K, respectively. The symbols represent experimental data and the line represents predictions.

Figure 9: The temperature profile as a function of the distance from the fuel boundary. The symbols represent measurements and the lines are predictions. The mole fraction of fuel and temperature of the fuel stream at the fuel boundary are $X_{F,1} = 0.15$, and $T_1 = 375K$ respectively. The temperature of the oxidizer stream is 299K. The strain rate is $a_2 = 100 \text{s}^{-1}$. 
is shifted left toward the fuel boundary in comparison to the measured peak.

Figure 10 compares the predicted and measured profiles of species mole fraction as a function of the mixture fraction, $Z$. The mixture fraction is defined as the ratio of the local mass fraction of carbon to the mass fraction of carbon in the fuel stream. The predicted profiles of $C_6H_5CH_3$, $O_2$, $CO_2$, $H_2O$, $CO$ and $H_2$ agree well with measured values. Computed profile of $C_6H_6$ (benzene) is in reasonable agreement with the measured data. Measured and computed profiles of $C_3H_6$ (propene/propylene), $CH_4$ (methane), and $C_2H_6$ (ethane) are also in reasonable agreement. The computations significantly underpredict the mole fractions of $C_3H_8$ (propane) and $C_4H_8$ (butene/butylene). However, in both cases measured and computed structure of profile is similar. Mole fraction of $C_2H_4$ (ethene/ethylene) is also somewhat underpredicted.
Figure 10: Profiles of mole fractions of the major species as a function of the distance from the fuel boundary. The symbols represent measurements and the lines are predictions. The mole fraction of fuel and the temperature of the fuel stream at the fuel boundary are $X_{F,1} = 0.15$, and $T_1 = 375K$ respectively. The temperature of the oxidizer stream is $299K$. The strain rate is $a_2 = 100 \, s^{-1}$. 
References


