Abstract

Computation was first performed for the first-stage ignition delay, $\tau_1$, in the homogeneous autoignition of $n$-heptane/air mixtures. Results show that $\tau_1$ possesses a minimum value, $\tau_{1,\text{min}}$, in that it first decreases and then increases with increasing temperature, and that $\tau_1$ is largely insensitive to the equivalence ratio ($\phi$) and pressure ($p$) of the mixture when the temperature is sufficiently below the initial temperature corresponding to $\tau_{1,\text{min}}$. This is consistent with the experimental results from shock tubes and rapid compression machines. Furthermore, in this regime the global reaction order was found to be close to unity, hence supporting the notion that the limiting steps in this temperature regime are the RO$_2$ isomerization reactions, which in turn explains the insensitivity of $\tau_1$ on $\phi$ and $p$. However, when the temperature approaches that of $\tau_{1,\text{min}}$, competition of the $\beta$ scission reactions of the alkyl radicals with the low-temperature chemistry chain reactions as well as the equilibrium shift of the oxygen combination reactions increases the first-stage ignition delay and consequently results in $\tau_{1,\text{min}}$. The corresponding global reaction order also increases, to about two, indicating the progressive importance of the oxygen combination reactions. Additional simulation of ignition in the nonpremixed counterflow showed that the characteristic time scale given by the critical strain rate, hence the reaction order, also follows the same density (pressure) dependence as those for $\tau_1$ and $\tau_{1,\text{min}}$, indicating the preservation and thereby essential role of the NTC-chemistry in transport-affected ignition.

1. Introduction

The phenomenon of negative temperature coefficient (NTC) is an essential feature of the chemical kinetics of large hydrocarbons at low to intermediate temperatures, and as such has been extensively studied. Practically, the NTC behavior is relevant to the intrinsically low-temperature phenomenon of ignition, such as engine knock (Griffiths et al. 2002), accidental explosions and the recent interest in HCCI (homogeneous charge compression ignition) engines (Yao et al. 2009). This phenomenon has been mostly observed and studied in homogeneous systems such as the shock tube (Gauthier et al. 2004), flow reactor (Wada 2011) and rapid compression machine (RCM) (Minetti et al. 1995). The focus of these studies has been on the growth of the radical concentrations due to the chain reactions and the thermal feedback through the chemical kinetics. Among all the measurements, the ignition delay time, $\tau$, is the mostly used quantity to validate chemical kinetic models. However, implications drawn on the basis of $\tau$ are incomplete. Specifically, since ignition in the NTC regime actually consists of two stages, $\tau$ is a summation of the first and second stage ignition delays, $\tau_1$ and $\tau_2$ respectively. Since $\tau_2$ is coupled to $\tau_1$ through the heat release at the end of the first-stage, much of the essential information needed to quantify the ignition chemical kinetics is actually embedded in $\tau_1$. Furthermore, it has been found that $\tau_1$ is completely controlled by the low-temperature chemistry, and as such characteristics of the first-stage ignition delay are expected to provide significant fundamental insight towards understanding the entire ignition process.

In the next section, we shall perform a chemical kinetics study on several special features of $\tau_1$. The fuel used is $n$-heptane and the study is computational. The reaction mechanism adopted is a skeletal one consisting of 88 species and 387 reactions reduced from the detailed LLNL mechanism, which has 561 species and 2539 elementary reactions (Curran et al. 1998). The comprehensiveness of the reduced mechanism in simulating the performance of the detailed mechanism has been conclusively demonstrated (Yoo et al. 2011). The sensitivity of $\tau_1$ on the equivalence ratio ($\phi$) and pressure ($p$), and the transition of the global reaction order when the temperature increases are studied and then correlated with the characteristic time scale of NTC-chemistry in transport-affected nonpremixed counterflow ignition.
2. Global Reaction Characteristics of the Low-temperature Chemistry

In Figure 1, the total ignition delay time $\tau$ and the first-stage ignition delay time $\tau_1$ are plotted as functions of the initial temperature $T_o$ for $n$-heptane/air mixtures with various equivalence ratios at 1 atm pressure. The result shows that unlike $\tau$, $\tau_1$ is very insensitive to $\phi$ as can be seen from the overlap of the unfilled symbols. This is consistent with previous shock tube experimental investigations in (Ciezki & Adomeit 1993, Herzler et al. 2005), RCM experiments in (Guang et al. 2012), and theoretical analysis by Peters et al. (2002). However, few explanation or analysis can be found in the literature on this characteristic behavior. To quantify the sensitivity on pressure, $\tau_1$ with initial temperatures $T_o$ 550K, 600K, 650K from 1 to 10 atm are plotted in Figure 2. It is seen that in this range, $\tau_1$ depends only weakly on $p$ and thus density $\rho$, to a power of about -0.1, i.e., $\tau_1 \sim p^{-0.1}$.

![Figure 1. Total ignition delay time $\tau$ and the first-stage ignition delay time $\tau_1$ as a function of initial temperature $T_o$ for $n$-heptane/air mixture with various equivalence ratio $\phi$ under 1 atm.]

![Figure 2. The first-stage delay time $\tau_1$ as an insensitive function of pressure with initial temperature 550K, 600K, 650K for $n$-heptane/air mixture.]

![Figure 3. Activation energy $E_a$ for $\tau_1$ when $T_o$ is less than 700K.]

![Figure 4. Density $\rho$ and specific volume $1/\rho$ dependence of the minimum first-stage delay $\tau_{1,min}$ from 1 to 10 atm.]

From scaling of the species conservation equation for a homogeneous, adiabatic reacting system, $\tau_1$ should scale with a reaction time scale given by $\rho/\omega$, in which $\omega$ is the global reaction rate. Consequently, the global reaction order of the low-$T$ chemistry should be about unity, as given through $\omega \sim \rho/\tau_1 \sim \rho^{-1.1}$. The insight then is that, since the important reactions of the low-temperature chemistry are all second order except for the first-order isomerization reaction $RO_2 \leftrightarrow$QOOH, which is therefore the limiting step. To further demonstrate this concept, we have plotted in Figure 3 the
overal activation energy $E_a$ of the first-stage delay $\tau_1$ in the temperature range of 550~700K. It is then significant to note that this value deviates from that of the isomerization reaction by only 1.76 kcal/mol. The correspondence in the global reaction order and activation energy therefore indicates that the isomerization reaction dominates the first ignition stage when the temperature is lower than 700K, which further explains the insensitivity of $\tau_1$ on $p$ and $\varphi$ in this range.

If the temperature increases further, then $\tau_1$ shows a minimum point $\tau_{1,min}$, as was also indicated in the computational study of (Yoo et al. 2011). However, since the sub-ms first stage delay time is too short for either RCM or flow reactor to detect, this feature has not been reported in experimental studies. To further identify the characteristics of this minimum value, we have extrapolated the density (pressure) dependence of the global reaction order from the $\tau_{1,min}$ under different pressures, as shown in Figure 4, as was done for $\tau_1$. It is then found that $\tau_{1,min} \sim p^{-1}$. Following the same scaling argument for $\tau_1$, the global reaction order at $\tau_{1,min}$ is approximately 2. Figure 5 then shows the increasing pressure dependence, and thereby the global reaction order of $\tau_1$, when the temperature is increased in the entire temperature range of interest. It is seen that while the reaction order remains close to unity for $T_o$ less than 700 K, it increases very rapidly to 2 when $T_o$ exceeds 700K, indicating the high sensitivity in terms of the transition in the controlling chemistry around the state of the minimum ignition delay.

![Figure 5. Global reaction order $n$ of the first-stage delay $\tau_1$.](image)

Figures 3 to 5 then demonstrate the transition in the controlling chemistry from first order to second order reaction, hence supporting the notion that $R+O_2 \leftrightarrow RO_2$ reaction progressively approaches equilibrium and becomes the limiting step at higher temperatures, as previously noted in (Benson 1981, Curran et al. 1998, Griffiths et al. 2002). At even higher temperatures, the backward reaction of RO$_2$ dissociation takes over, thus the low-temperature chemistry chain reaction shuts down and the first-stage becomes hardly discernible.

3. Implications of Detailed Kinetics

In Figure 6, the first-stage ignition delay time $\tau_1$ is shown for different reaction mechanisms. We first note that simulation results based on the 88 species skeletal model and the 561 species LLNL detailed model agree well, both qualitatively and quantitatively, hence demonstrating the validity of the skeletal mechanism. In order to understand the reaction pathways causing the minimum $\tau_{1,min}$, we first consider a major step model A, consisting of the following 9 elementary reactions as:

$$nC_7H_{16}+O_2 \rightarrow R+HO_2 \quad (k_1)$$

$$nC_7H_{16}+OH \rightarrow R+H_2O \quad (k_2)$$

$$R+O_2 \leftrightarrow RO_2 \quad (k_{3f} \& k_{3b})$$

$$RO_2 \rightarrow QOOH \quad (k_4)$$

$$QOOH+O_2 \leftrightarrow QOOHO_2 \quad (k_{5f} \& k_{5b})$$

$$QOOHO_2 \rightarrow nC_7KET+OH \quad (k_6)$$

3
\( nC_7\text{KET} \rightarrow \text{Products} + \text{OH} \quad (k_7) \)

The choice of these reactions was based on the understanding of the low-temperature chain reactions (Curran et al. 1998, Kazakov et al. 2006), and all the kinetic parameters were taken from the LLNL detailed mechanism, based on which the first-stage delay time was calculated using the major step model A. Also, analytical solution based on model A for the first-stage delay time was derived with the QSS assumption of OH, R, QOOH, and QOOHO\(_2\) radicals. The form of the analytical solution is basically the same as that previously obtained in (Peters et al. 2002) using a 4-step lumped mechanism. Figure 6 shows that while the simulation result as well as the analytical solution based on model A agrees well with that using the detailed/skeletal mechanism when \( T_o \) is less than 700K, both solutions diverge and fail to show a minimum. Model A therefore fails to capture the complete behavior of \( \tau_1 \).

To further understand \( \tau_{1,\text{min}} \), the computational diagnostic method of CEMA (Lu et al. 2010) was performed at each initial temperatures, in which chemical reactions are grouped into independent modes through eigendecomposition of the Jacobian matrix of the chemical source term. A positive eigenvalue of the chemical Jacobian indicates a chemical explosive mode with the corresponding mode growing exponentially in time. In addition, explosion pointer and explosion participation index are defined as the projection of the contribution of each species and reactions on the explosive mode, respectively. Both provide important information to identify the relevant species and elementary reactions at ignition. Details of CEMA can be found in (Lu et al. 2010, Liu et al. 2010).
Figure 6 shows that the reciprocal of the chemical explosive mode (CEM) $\lambda_{exp}$, which provides a characteristic time scale, captures the nonmonotonic behavior of the first-stage delay. Consequently the controlling reactions responsible for the occurrence of the minimum is contained in $\lambda_{exp}$. By comparing the explosion participation index of each reaction, the $\beta$ scission reactions of the R radical, i.e., $\text{C}_6\text{H}_{15}$-2$\rightarrow$7$\text{C}_4\text{H}_8$+2$\text{C}_2\text{H}_4$ and $\text{C}_7\text{H}_{15}$-3$\rightarrow$7$\text{C}_2\text{H}_4$-1$\rightarrow$$\text{nC}_2\text{H}_4$ are added in model A to form a new model B. Results show that when $T_a$ is higher than 700K, models A and B diverge from the detailed models quantitatively. However, model B does capture the trend of a minimum although it occurs at around 780K instead of 760K. The results then indicate that the $\beta$ scission reactions of $\text{nC}_2\text{H}_4$ contribute to the existence of the minimum first-stage delay time, and that some other pathways also need to be included to make up for the quantitative difference. The explosion radical pointer then shows that the HO$_2$ radical to be the most important one at 780K, implying the important role of HO$_2$ radical at the intermediate temperature range. Thus reactions involving HO$_2$ should be added in the loop when constructing major step models.

Recognizing the above, the reason for the occurrence of $\tau_{1,\text{min}}$ is then the following, as shown in Figure 7 for the species fluxes: the $\beta$ scission reactions break more alkyl radicals which otherwise will be involved in the RO$_2$ formation reaction and eventually participate in the low-T chain branching reactions. Thus the competition for the alkyl radicals, together with the equilibrium shift of RO$_2$ formation reaction at higher temperatures, retards the low-T chemistry chain process and increases $\tau_1$, and eventually shuts it down.

4. NTC-affected Ignition in Nonpremixed Counterflow

Previous studies on the NTC phenomenon were mostly conducted through homogeneous autoignition. However, nonuniformities invariably exist in practical flows and it is of interest to explore the role of NTC in such inhomogeneous systems, particularly those in strained flows. Indeed, the recent work of Law & Zhao (2012) on nonpremixed counterflow ignition showed that, when the flow time and chemical time become comparable, the NTC chemistry becomes coupled to the transport processes to strongly affect the system ignition behavior. In particular, it was shown that, for either sufficiently small strain rate $k_s$ or sufficiently high pressure, a secondary S-curve is grafted onto the lower branch of the primary S-curve, with distinctive ignition and extinction turning points, hence demonstrating the sensitivity of the NTC chemistry induced ignition. Furthermore, it was found that, above a critical strain rate $k_{sc}$, the folded, ignition-extinction secondary S-curve loses its non-monotonicity and becomes a stretched one (Figure 8), thereby will fail to exhibit distinct ignition-extinction events.

![Figure 8. Regime boundary of NTC-affected ignition in a nonpremixed counterflow of 10% n-heptane in N$_2$.](image)

It is then of interest to examine if the global kinetics of the homogeneous auto-ignition carries over to the present inhomogeneous systems of strained flow field with diffusive transport. For counterflow ignition, assuming potential flow, then from the scaling of the convection and reaction terms, we obtain $\rho \delta y \frac{d}{dy} \sim \omega$, which essentially yields the same time scale of $k^{-1} \sim \rho/\omega$ as for the homogeneous case; noting that the density $\rho$ here is the local density at the ignition kernel. Following Law (2006), it is more relevant to evaluate residence time in the counterflow system by the pressure-
weighted strain rate at ignition. By substituting the calculated pressure-weighted ignition strain rates into the scaling argument and fitting in terms of pressure, the reaction order is found to be about unity as shown in Figure 9. For example, the reaction order for the air boundary temperature 650K is 1.104 and 700K is 1.137, corresponding to the same unity reaction order as the homogeneous autoignition $\tau_1$ in the lower temperature conditions. In addition, the activation energy extrapolated from the ignition strain rate at various boundary temperatures from 600 to 700K (Fig. 9) is 25.04 kcal/mol, which deviates from that of the isomerization reaction in this temperature range by only 1.81 kcal/mol. However, with increasing air boundary temperature, it is then shown that the reaction order gradually increases, with the S-curve approaching a stretched one.

![Figure 9. Global reaction order and activation energy extrapolated from ignition strain rate for counterflow NTC-affected ignition.](image)

![Figure 10. Characteristic time of NTC-affected ignition in a non-premixed counterflow of 10% & 20% n-heptane in N2.](image)

In Figure 10, the critical time scales for NTC-affected ignition are calculated for both 10% and 20% n-heptane versus heated air, from 1 to 10 atm. The characteristic time scale is then plotted as a function of the local specific volume ($1/\rho$).

In order to explain why the system will lose non-monotonicity at higher temperatures, calculations of the first stage temperature increment in homogeneous autoignition are done with various equivalence ratio under 1 atm. It’s found that first-stage temperature increment increases with equivalence ratio, however, decreases linearly with initial temperature for each equivalence ratio and eventually becomes negligible. Hence it indicates that when temperature goes up, due to the decreasing amount of heat release rate of the low temperature chemistry, the arrhenius feedback becomes so weak that the system turns to respond monotonically to the independent variables. Essentially, it is the thermal feedback that causes the NTC S-curve response, facilitated by the S-curve calculation without heat release in (Law & Zhao 2012).

5. Conclusions

Computation was first performed on the first-stage ignition delay, $\tau_1$, in the homogeneous autoignition of $n$-heptane using a reduced LLNL mechanism. Results show that $\tau_1$ possesses a minimum value, $\tau_{1,\text{min}}$ and that it is largely insensitive to $\phi$ and $p$ when the temperature is sufficiently below that of $\tau_{1,\text{min}}$, consistent with the existing experimental results. Furthermore, in this regime the global reaction order was found to be close to unity and the overall activation energy is close to that of the RO2 isomerization reactions, hence demonstrating the dominant role of the RO2 isomerization reactions, which in turn explains the insensitivity of $\tau_1$ on $\phi$ and $p$. However, when the temperature approaches that of $\tau_{1,\text{min}}$, competition of the $\beta$ scission reactions of the alkyl radicals together with the equilibrium shift of RO2 formation reactions increases the first-stage ignition delay and thus results in $\tau_{1,\text{min}}$. The global reaction order also
correspondingly increases, to about two, indicating the progressive importance of the RO₂ formation reactions. Additional simulation of ignition in nonpremixed counterflow implies the importance of thermal feedback on the foldedness and stretchedness of NTC S-curve and shows that the characteristic time scale and hence the reaction order follow the same density (pressure) dependence as those for \( \tau_\text{i} \) and \( \tau_{\text{i, min}} \), showing its significance in NTC-affected ignition phenomena.

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**References**