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The role of global and detailed kinetics in the first-stage ignition delay in NTC-affected phenomena

Peng Zhao, Chung K. Law *

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

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ABSTRACT

Using *n*-heptane as a representative fuel exhibiting NTC (negative temperature coefficient) chemistry, a comprehensive computational and mechanism study was conducted on the role and controlling chemistry of the first-stage ignition delay in the superficially dissimilar systems of the auto-ignition of homogeneous mixtures and the nonpremixed counterflow ignition of fuel versus heated air. It is first shown that the first-stage auto-ignition delay time, τ_1, possesses a minimum value, $\tau_{1,\min}$, with increasing temperature, and that for temperatures below the range corresponding to $\tau_{1,\min}$, τ_1 is largely insensitive to the equivalence ratio (ϕ) and pressure (p) of the mixture. 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 τ_1 on ϕ and p in this temperature regime. However, when the temperature approaches that of $\tau_{1,\min}$, competition of QOOH decomposition and the β scission reactions of the alkyl radicals with the low-temperature chemistry chain reactions, as well as the equilibrium shift of the oxygen addition reactions, increases τ_1 and consequently results in $\tau_{1,\min}$. The corresponding global reaction order also increases, to about two, indicating the progressive importance of the oxygen addition reactions. Extracted values of the global activation energy are also close to those of the controlling reactions in these temperature regimes. Results from the counterflow show the same global kinetic responses by identifying the reciprocal of the counterflow strain rate as the relevant ignition delay time and the temperature of the heated air stream as the homogeneous mixture temperature. It is further found that in the temperature range corresponding to $\tau_{1,\min}$, the diminished heat release causes the counterflow to lose its characteristic, non-monotonic *S*-curve response and consequently distinct, abrupt ignition–extinction transition events.

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 is practically relevant to the intrinsically low-temperature ignition processes governing engine knock [1], accidental explosions, and the recent development of the homogeneous charge compression ignition (HCCI) engines [2]. Furthermore, while fundamental studies of this phenomenon have mostly involved homogeneous systems such as the shock tube [3], flow reactor [4] and rapid compression machine [5,6], the investigation has recently been extended to the inhomogeneous, diffusive-convective system of nonpremixed counterflow [7], which is aerodynamically quantified by its strain rate k and hence the characteristic flow time, $1/k$. In particular, it is shown that when the characteristic flow time is in the range of the characteristic chemical time, which is promoted for weakly-strained flows and/or high-pressure environments, a secondary ignition–extinction *S*-curve controlled by the NTC chemistry emerges on the lower, weakly-reactive branch of the primary *S*-curve. This indicates the presence of a complete ignition–extinction chemical response system in the low-temperature regime, and as such significantly expands the richness of related combustion phenomena.

The goal of the present study is to further extract the key chemical–physical processes and factors related to the NTC chemistry that control the ignition response of mixtures in homogeneous systems as well as inhomogeneous, strained flows. In particular, while most of previous studies with homogeneous mixtures are concerned with the response of the (total) ignition delay time, τ, it is also recognized that ignition in the NTC regime actually consists of two stages, with τ being the sum of the first and second stage ignition delays, τ_1 and τ_2, respectively. Since τ_2 is coupled to τ_1 through the heat release at the end of the first-stage, much of the essential information needed to quantify the ignition kinetics is actually embedded in τ_1. As such, we shall focus our investigation on the processes occurring during the first-stage ignition, and shall show in due course that a rational interpretation can

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* Corresponding author.
E-mail address: cklaw@princeton.edu (C.K. Law).

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be made on the controlling chemistry of τ_1, and that a unified description is achieved for the first-stage ignition of homogeneous mixtures and the low-temperature *S*-curve ignition of inhomogeneous strained flows.

The present study is computational. The fuel used is *n*-heptane and the reaction mechanism adopted is a validated skeletal one [8] consisting of 88 species and 387 reactions comprehensively reduced from the detailed LLNL mechanism [9], which has 561 species and 2539 elementary reactions. It is noted that although the pressure dependence of the rate constants of the oxygen addition reactions, alkylperoxy radical (RO_2) dissociation and isomerization reactions, is not considered, it has been recently demonstrated in [10,11] that the high-pressure limits for those reactions are sufficient to describe the low temperature chemistry in this study. We shall first investigate the global and detailed kinetics governing the first-stage ignition in homogeneous mixtures, including the identification and the associated properties of a minimum ignition delay, $\tau_{1,\min}$, as the mixture temperature increases. We shall then extend the investigation to the ignition in the transport-affected nonpremixed counterflow, and demonstrate the correspondence of the controlling chemistry governing these two superficially disparate systems.

2. Global reaction characteristics

Figure 1 shows the calculated total ignition delay time τ and the first-stage ignition delay time τ_1 as functions of the initial temperature for *n*-heptane/air mixtures with various equivalence ratios ϕ at 1 atm pressure, based on the skeletal mechanism mentioned above. Three observations can be readily made. First, τ_1 is very insensitive to ϕ as can be seen from the overlap of the unfilled symbols, which holds even in a linear plot of the Fig. This is consistent with the shock tube [12,13] and RCM measurements [14], as well as theoretical analysis [15]. Second, contrary to the insensivity of τ_1 to ϕ, the total ignition delay τ is sensitive to ϕ. Since τ is largely the sum of τ_1 and τ_2, the sensitivity of τ then implies the corresponding sensitivity of τ_2 to ϕ. Third, there is a minimum τ_1, $\tau_{1,\min}$, occurring around 760 K (at 1 atm). In other words, the first stage delay itself also shows NTC behavior. This feature does not appear to have been reported in previous experimental studies, possibly because of the short, sub-*ms* delay time that cannot be readily detected in RCM or flow reactor experimentations.

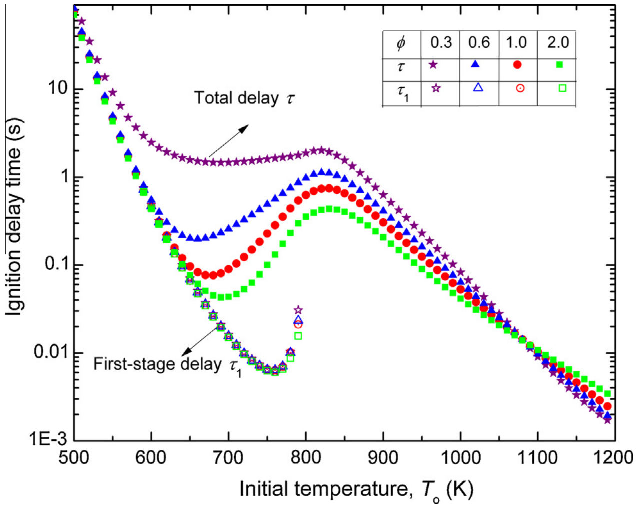

Fig. 1. Total ignition delay time τ and the first-stage ignition delay time τ_1 as a function of initial temperature T_o for *n*-heptane/air mixture with various equivalence ratio ϕ under 1 atm.

In addition to the insensitivity of τ_1 to ϕ, we have found that τ_1 is also largely insensitive to the system pressure *p*, for initial temperature T_o below that for $\tau_{1,\min}$. This weak dependence is shown in Fig. 2, for T_o of 550 K, 600 K, 650 K, from 1 to 10 atm. Since $p \sim \rho$, where ρ is the density, these results show that $\tau_1 \sim \rho^{-0.1}$. Further recognizing from the species conservation equation for a homogeneous, adiabatic reacting system that τ_1 scales with a reaction time which varies with ρ/ω, in which ω is a global reaction rate, we have $\omega \sim \rho/\tau_1 \sim \rho^{1.1}$. This then implies that the global reaction order of the low-temperature chemistry should be about unity. The insight gained is that, since the most important intermediate steps of the low-temperature chemistry are second order except for the first-order isomerization reaction of RO_2 and $QOOHO_2$, these reactions are therefore the rate-limiting steps. To further substantiate this concept, we have determined in Fig. 3 the overall activation energy E_a of the first-stage delay τ_1 in the temperature range of 550–700 K, and found that this value, 28.61 kcal/mole, deviates by only 1.76 kcal/mol from that of the RO_2 isomerization reaction $RO_2 \Leftrightarrow QOOH$, 26.85 kcal/mol. The correspondence in the global reaction order and activation energy therefore supports the notion that the isomerization reaction of RO_2 dominates the first ignition stage when the temperature is lower than 700 K, and that it further explains the insensitivity of τ_1 on *p* and ϕ in this temperature range.

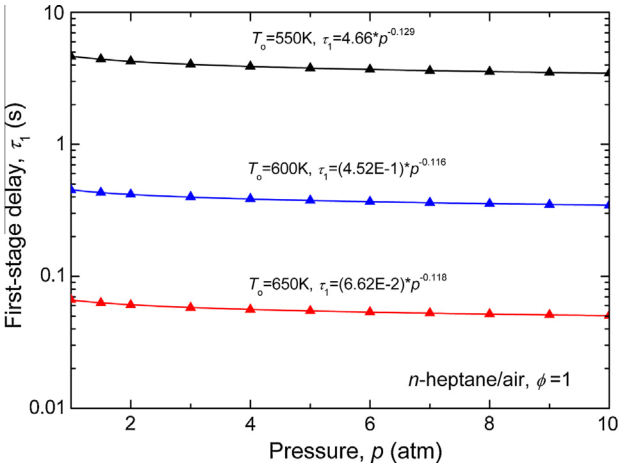

Fig. 2. The first-stage delay time τ_1 as an insensitive function of pressure with initial temperature T_o 550 K, 600 K, 650 K for *n*-heptane/air mixture.

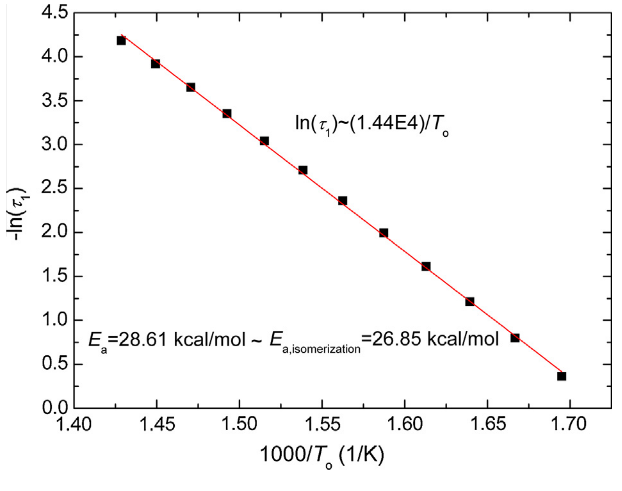

Fig. 3. Activation energy E_a for τ_1 when initial temperature T_o is less than 700 K.