Understanding low-temperature first-stage ignition delay: Propane

Shamel S. Merchant[†], C. Franklin Goldsmith^{‡,⊥}, Aäron G. Vandeputte[†], Michael P. Burke^{‡,§}, Stephen J. Klippenstein[‡] and William H. Green^{†,*}

[†]*Department of Chemical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA*

[‡]*Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA*

[⊥]*School of Engineering, Brown University, Providence, RI 02912, USA*

[§]*Department of Mechanical Engineering, Department of Chemical Engineering and Data Sciences Institute, Columbia University, New York, NY 10027*

Abstract

The low-temperature auto-ignition of fuels is a complex process, occurring in multiple stages with distinct chemical processes governing each stage. The conversion from alkyl radical to chain branching products, which occurs through successive O_2 additions followed by thermal decomposition of the products, is at the core of the auto-ignition process. Our detailed

understanding of this central process continues to evolve, with recent theoretical kinetics studies providing a particularly comprehensive description of the radical oxidation process for propane. In this study, we employ this improved description in a detailed numerical and analytical exploration of the first-stage ignition delay for low-temperature auto-ignition of propane, which may be considered as a prototype for larger alkane fuels. The traditional first-stage of ignition can be divided into two stages (stage-1A and stage-1B). During stage-1A, the concentration of radicals grows exponentially, and both OH and HO₂ are important in the consumption of the fuel and generation of alkyl radicals. Stage-1A ends when the concentration of HO₂ is sufficiently high that the chain-terminating bimolecular reaction HO₂ + HO₂ becomes competitive with other HO₂ reactions including HO₂ + fuel, thus slowing the HO₂ concentration rise such that is no longer key contributor to fuel consumption. During stage-1B, increasing temperature and growing side reactions with secondary chemistry reduce the positive feedback and the concentrations of ketohydroperoxide species stop growing exponentially. The end of this stage is associated with the maximum in ketohydroperoxide, after which it is depleted. We present simple analytical approximations for the time it takes to complete these two sub-stages. These expressions clarify which rate constants control first-stage ignition, and they quantify how the ignition is influenced by mixture composition, temperature and pressure. The analysis is also extended to longer alkane fuels and is shown to provide fairly reliable predictions of the first-stage ignition delay.

KEYWORDS: propane, low temperature combustion, peroxy chemistry, first-stage ignition delay.

1. Introduction

Low temperature (600-800 K) ignition delay is among the most important chemical properties of ground transportation fuels; it is the basis of the octane rating system for gasoline and the cetane rating system for diesel [1-3], and it is critical in new engine concepts like homogenous charge compression ignition (HCCI), premixed charge compression ignition (PCCI), and reactivity controlled compression ignition (RCCI) [4, 5]. Low-temperature auto-ignition is also a highly complex phenomenon; it exhibits non-Arrhenius (sometimes even non-monotonic) temperature behavior, and it has strong sensitivities to modest changes in fuel structure and pressure. Models aimed at a complete description of the ignition process, typically involve hundreds of species and thousands of reactions, thereby complicating the analysis and obscuring the essential chemistry. Here we present a different perspective which allows a simple analysis of what is important during the first stage of ignition.

To facilitate understanding, several prior authors have also attempted to identify the rate-controlling processes to focus attention on what controls pre-ignition chemistry. These analyses have proven helpful in clarifying which reactions are most important; we note in particular significant papers in this vein by Gibson et al. [6], Keck and Hu [7], Griffiths [8], Westbrook [9], Peters et al. [10], Kazakov et al. [11], Zhao and Law [12], and Beeckman et al. [13]. Many of the recent studies like [11] base their analysis on the Curran et al. n-heptane model, first published in 1998 [14]. Other recent studies [10-12] base their analysis on skeletal models for n-heptane [10, 15].

However, as demonstrated by Kazakov et al. [11], different conclusions regarding the controlling chemistry can be drawn using different models that employ different rate coefficients

and thermochemistry, especially when they involve simplifications in generating the skeletal scheme. Therefore, it would appear valuable to use a detailed model that is as fundamentally sound as possible in order to draw reliable conclusions regarding the controlling chemistry for low-temperature oxidation.

Since the time of development of the models employed in previous studies, our fundamental understanding of low-temperature oxidation processes has significantly improved. For example, due to limited understanding at the time of their study, several critical reactions were not included in the detailed model of Curran et al.[14], and subsequent model studies have each retained some of these shortcomings. Three important examples include (i) the very important concerted reactions of the type $\text{RO}_2 \rightleftharpoons \text{HO}_2 + \text{alkene}$, where RO_2 is an alkylperoxy radical [16-19], (ii) molecular elimination of carboxylic acids and aldehydes from ketohydroperoxides [20-25], and (iii) the interception of vibrationally excited free radicals by O_2 [26, 27]. The thermochemistry and elementary rate coefficients for many peroxy radicals have also been significantly revised during the last few years [28-37]. Also, there have been tremendous methodological advances for computing the pressure-dependence of rate-coefficients [38-41], but few large mechanisms consider pressure-dependence in a consistent way. Only a small fraction of the many reactions in these mechanisms have been measured experimentally or computed theoretically, so most rate coefficients are approximated from rough estimates; this crude approach is particularly true for peroxide chemistry, where the multiplicity of possible isomers and pathways is commonly replaced with a single lumped irreversible pathway and an empirically adjusted rate coefficient [14, 42, 43]. Detailed mechanisms for large fuel systems such as heptane and gasoline surrogate mechanisms still lack the fidelity to accurately capture

the time for first stage ignition delay and pressure rise rate as shown recently by Sarathy et al. [44] and Campbell et al. [45].

For propane, the number of intermediates is small enough to permit detailed exploration (*e.g.* five distinct isomers on the $C_3H_7O_2$ potential energy surface (PES), and five distinct isomers on the $C_3H_7O_4$ PES), and mechanisms for propane oxidation have been developed in which all of the reactions are represented by reversible elementary rate coefficients, *e.g.* by Healy et al. [46]. A recent study of Hughes et al. [47] presented a global uncertainty analysis for low temperature autoignition of propane, which highlighted a number of the key reactions and species. Goldsmith et al. [30] performed high-level quantum calculations on most of the species and reactions involved in the low-temperature ignition of propane, and made predictions of the pressure-dependent rate coefficients. A follow-up study explored the global uncertainty in the predicted rate coefficients for the *n*-propyl + O_2 reaction [48]. Here we use a comprehensive detailed propane mechanism drawn from the prior studies, which provide a secure basis for analysis.

As has been discussed in the literature [9, 10], ignition chemistry depends dramatically on both the temperature and the pressure of the initial state, with remarkably different species and reactions being important at 650, 800, and 1100 K. The chemistry of low-temperature ignition goes through several distinct stages, which are driven largely by the temperature changes during the process. It is often possible to experimentally discern two distinct stages in the ignition process [49]. The end of the first-stage is marked by a small increase in temperature (*e.g.* ΔT of 10-100 K), followed by a second induction period before the more violent “hot” or “explosive” ignition. When the ignition is initiated at low temperature, the first-stage is typically much longer

in duration than the second stage, see for example the experimental data in Figure 1. Consequently, accurate prediction of the final ignition delay time for those conditions requires accurate prediction of the first-stage ignition delay.

Although detailed kinetic models have been developed for the low-temperature oxidation of a many fuels, our understanding of low-temperature ignition chemistry is far from complete. Simple changes to the fuel structure can have significant impact on ignition delay, and these effects are not reproduced in all models. Our goal in the present work is to elucidate the chemistry occurring during the first-stage of ignition. Rather than merely catalogue all the reactions, however, we aim to simplify the process first by identifying the most important reactions and second by quantifying the effects of these reactions on the first-stage ignition delay in a manner that is both illuminating and practical for combustion chemists and engineers alike. To that end, we present simple algebraic formulae for estimating the duration of the first-stage ignition in propane, and we demonstrate how these formulae can be extended to cover larger, more complex fuels.

Figure 1: Experimental measured overall (filled symbols) and first-stage (open symbols) ignition delays in a rapid compression machine (RCM) for methylcyclohexane (MCH) [50] and dimethylether (DME) [51] at $P_0 = 15$ bar, $\phi(\text{MCH}) = 1$ and $\phi(\text{DME}) = 0.75$. For low temperatures the measured first-stage ignition delay is almost equal to the overall measured ignition delay. For higher temperatures the later stages of ignition contribute more to the overall ignition delay.

2. Propane as an archetype for low temperature peroxy ignition pathways

Low temperature ignition of alkanes is governed by a complex set of reactions that involve alkylperoxy radicals. Zádor et al. [52] recently presented a thorough review of this topic, and only a brief summary is provided here. Figure 2 shows a schematic mechanism for low temperature alkane oxidation and auto-ignition chemistry, adapted from [52]. The alkyl radical, R , reacts with molecular oxygen to form an energetically excited adduct, $RO_2^\ddagger$, which can undergo collisional stabilization, isomerization, or decomposition into bimolecular products.

At low temperatures and normal or high pressures, the $R + O_2$ reaction leads primarily to RO_2 . The RO_2 radical under these conditions will mainly undergo isomerization to form hydroperoxyalkyl radical, $QOOH$. However as the temperature is increased the branching ratio to $QOOH$ decreases with a significant fraction of RO_2 radicals instead converted to $HO_2 + \text{alkene}$,

which is often effectively terminating because HO_2 is largely non-reactive at low to moderate temperatures. Higher temperatures also cause the $\text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2$ equilibrium to shift towards the reactants. Consequently, the production of RO_2 and QOOH effectively ceases and the energetically excited adduct, $\text{RO}_2^\ddagger$, either returns back to $\text{R} + \text{O}_2$ or decomposes to alkene + HO_2 . The cumulative effect is the negative temperature coefficient (NTC) regime, where the ignition delay actually increases with increasing temperature.

All of the above reactions are at best chain propagating. For a radical driven auto-ignition to occur, however, the total number of radicals must increase. Two pathways can lead to chain branching. In the first pathway, RO_2 abstracts an H atom from the parent fuel molecule (RH), leading to formation of alkylhydroperoxide, ROOH , which decomposes to an alkoxy radical (RO) and OH . This pathway is thought to be the main source of radicals at very low temperatures and high densities – *e.g.* in oxidation of liquid hydrocarbons [53].

The second chain-branching pathway involves QOOH . In the gas-phase the unimolecular isomerization reaction $\text{RO}_2 \rightleftharpoons \text{QOOH}$ is often faster than the bimolecular reaction $\text{RO}_2 + \text{RH} \rightarrow \text{ROOH} + \text{R}$. The QOOH radical can then undergo addition with a second O_2 molecule to form a hydroperoxyalkylperoxy radical, O_2QOOH , which rapidly decomposes to a ketohydroperoxide (OQ'OOH) and OH at most conditions. As in the alkylhydroperoxide, the $\text{O}-\text{O}$ bond in the ketohydroperoxide is quite weak (typically ~ 40 kcal/mol), and this species often decomposes to form ketoalkoxy radical (OQ'O) + OH . Consequently, the reaction sequence $\text{R} + 2\text{O}_2 \rightarrow \text{RO}_2 + \text{O}_2 \rightarrow \text{QOOH} + \text{O}_2 \rightarrow \text{O}_2\text{QOOH} \rightarrow \text{OQ'OOH} + \text{OH} \rightarrow \text{OQ'O} + 2\text{OH}$ is chain branching, since three radicals are formed ($\text{OQ'O} + 2\text{OH}$) for every one radical consumed (R).

For chain branching to be fast, the concentration of QOOH needs to be sufficiently high. However, at low temperatures, the $\text{RO}_2 \rightleftharpoons \text{QOOH}$ equilibrium favors RO_2 , while at high temperatures the $\text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2$ equilibrium favors $\text{R} + \text{O}_2$, so there is a limited temperature regime in which QOOH concentrations will be sufficiently high. QOOH is formed by intramolecular H transfer reaction from a peroxy radical. Although there may be several possible intramolecular H transfer reactions for a given RO_2 , the energetically most favorable reactions involve either a six- or seven-membered ring, so the most relevant QOOH radicals are those with the HOO- group in the gamma or delta position, relative to the radical site. *n*-Propyl is the smallest alkyl radical that has the key six-member ring transition state (e.g. to form the γ -QOOH, 3-hydroperoxypropyl from *n*-propylperoxy). As a result the *n*-propyl radical exhibits all the key features of ignition of larger alkyl radicals, such as second O_2 addition, and propane is considered as a combustion archetype [30, 37, 54].

Figure 2: Schematic mechanism for the low temperature alkane oxidation and autoignition chemistry adapted from the work of Zádor et al. [52], including the Korcek reaction [24]. The pathways shown by a blue arrow lead to additional OH radicals (chain branching) while the pathways indicated by a red arrow lead to chain termination. Some of the intermediates may not live long enough to thermalize, they may not even be stationary points on the PES [30].

3. Propane kinetic model

The chemical kinetic mechanism that is used in this study is a combination of several previously published mechanisms. The core of the mechanism is based upon the high-level ab initio calculations for $\text{C}_3\text{H}_7 + \text{O}_2$, $\text{C}_3\text{H}_7\text{O}_2 + \text{O}_2$, and $\text{C}_3\text{H}_6\text{O}_3$ decomposition kinetics of Goldsmith et al [30]. The hydrogen/oxygen sub-mechanism was taken from Li et al. [55]. The rest of the mechanism was taken from Dooley et al [56], which itself was the union of four previous mechanisms: the $\text{CH}_2\text{O}/\text{CH}_3\text{OH}$ mechanism of Li et al. [57]; the CH_3OCH_3 mechanism of Zhao et al. [58]; the $\text{C}_1\text{-C}_4$ mechanism of Healy et al.[59]; and the methyl-ester mechanism of Fisher et al. [60]. The Korcek reaction was included in the full model with the rate coefficient adopted from calculations by Jalan et al. [24], however in line with the conclusion from Goldsmith et al.[25] $\text{OH} + \text{OQ}'\text{O}$ is the only significant product channel from $\text{OQ}'\text{OOH}$ decomposition above 600 K. The fraction of $\text{nR} + \text{O}_2 + \text{O}_2$ that directly proceeds to $\text{OH} + \text{OQ}'\text{OOH}$ via a non-Boltzmann kinetic sequence was calculated by Burke et al. [27] to be less than 1% at similar conditions to those investigated here (10 atm and $T < 800$ K). Thus, those sequences were not included in the full model.

The full propane model employed here as a basis of our simple analysis is provided in supporting information. All model simulations presented in this work are performed using Chemkin Pro [61].

4. Low temperature oxidation of propane

A detailed schematic for the initial stage of the oxidation of propane is presented in Figure 3. The oxidation is initiated by hydrogen abstractions by O_2 . The resulting nR (nC_3H_7) and iR (iC_3H_7) radicals will react with the oxygen leading to their respective peroxy radicals (nRO_2 and

iRO₂). The nRO₂ can undergo a facile isomerization via a six-membered ring transition state to a QOOH radical which will go on to react with a second oxygen molecule to form an O₂QOOH radical. This radical will decompose to give one OH radical and ketohydroperoxide, OQ'OOH, which itself decomposes to a second OH and OQ'O radical. The OQ'O radical decomposes to CH₂O and vinoxy, CH₂CHO, which reacts with a third O₂ molecule to form CO, CH₂O and a third OH radical. This overall sequence starting with nRO₂ thus releases three reactive OH radicals. By contrast, iRO₂ cannot undergo a six-membered isomerization and instead mostly decomposes to give C₃H₆ + HO₂.

The main chain-branching mechanism is the cyclic pathway, shown in black. Reactions that produce OH are shown in blue, and pathways that consume OH are shown in red. Pathways that divert flux away from the central chain-branching mechanism, such as the formation of iC₃H₇ from C₃H₈, the formation of C₃H₆ + HO₂ from nRO₂, reactions of OH and nRO₂ with XH (e.g. CH₂O and HO₂), and the Korcek pathway from OQ'OOH, are each shown with a dotted line. Whether or not the system is explosive (supercritical) depends on whether the OH production is larger than the OH consumption, i.e. is there net positive feedback, such that an initially small concentration of radicals is exponentially amplified. Note that to a good approximation both of these rates are linear in OH concentrations during the early stages of ignition. For propane, over the temperature range from 500 K to 700 K two of the steps in the positive feedback in Figure 3 are particularly lossy, they are labeled as α and β . We define these two important ratios as follows:

$$\alpha = \frac{\text{net rate of } \text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{nR} + \text{H}_2\text{O}}{\text{total consumption rate of OH}} \quad (1)$$

$$\beta = \frac{\text{net rate of } \text{nRO}_2 \rightarrow \text{QOOH}}{\text{total consumption of } \text{nRO}_2} \quad (2)$$

The values of the branching ratios α and β depend on the temperature, pressure and the composition of the reactive system. If there are no losses, 3 OH radicals are later generated for each OH entering the cycle. Considering the losses of OH characterized by α and β , the gain (f_{OH}) in OH is defined as:

$$f_{\text{OH}} = 3\alpha\beta \quad (3)$$

There is positive feedback and the OH concentration grows rapidly if $f_{\text{OH}} > 1$, while values lower than 1 indicate that the OH concentration will diminish with time.

Figure 3: Schematic of major reaction pathways during the first-stage of propane ignition. Reactions shown in blue lead to formation of OH radicals while those in red consume OH radicals. The reactions shown by dotted lines divert radicals away from the main chain branching pathway and delay the first-stage ignition. During stage-1A, HO_2 radicals reacts with

the fuel accelerating the chemistry, but later much of it recombines reducing the concentration of radicals. Note: For clarity some well-skipping pathways and reactions of HO_2 are omitted from the figure.

Figure 4: OH and HO_2 mole fraction profile (on semi-log scale) and temperature profile for isochoric (constant-volume) adiabatic simulation for a stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650\text{K}$. τ_{overall} is the overall ignition delay of the fuel. $\tau_{\text{stage-1}}$ is the first-stage ignition delay of the fuel, the time when the temperature (or pressure) of the system makes a small jump prior to the main ignition event. The first-stage ignition delay can be further divided into two stages A and B that are characterized by different time constants for the exponential rise of the OH concentration. $\tau_{\text{stage-1A}}$ is the time when the early exponential rise in OH concentration ends.

Figure 4 shows the simulated temperature evolution and OH and HO_2 concentration for an isochoric (constant-volume), adiabatic system containing a stoichiometric mixture of propane and air (at a representative low-temperature condition of $\phi = 1$, $P_0 = 10$ bar, and $T_0 = 650$ K). As seen in Figure 4, the temperature increases in two stages, with a small rise at 0.56 s and a much larger rise at 0.78 s. Though not readily apparent from the temperature profile, the OH and HO_2 profiles demonstrate that the first-stage itself can be divided into two stages, denoted stage-1A and stage-1B.

The first noticeable time scale $\tau_{\text{stage-1A}}$ (see Figure 4) corresponds to a distinct change in the slope of the OH rise ($d\ln[\text{OH}]/dt$). $\tau_{\text{stage-1A}}$ marks the end of stage-1A and the beginning of stage-1B. This time scale is usually not observed experimentally, since there is little or no change in the temperature and the OH concentrations are still too low to be detected. Both in stage-1A and 1B an exponential build-up of radicals is observed. The different exponential rise rate observed between stage-1A and 1B is mainly due to reactions involving HO_2 radicals. At early times (on the order of 10's and 100's of milliseconds), essentially every OH and HO_2 formed reacts with the fuel. Since OH and HO_2 are formed in comparable amounts, they each contribute comparably to fuel consumption during Stage-1A. In this period, the HO_2 concentration is about 5 orders of magnitudes higher than OH (see Figure 4). Consequently, even though the rate coefficients for fuel + OH are about five orders of magnitude larger than the rate coefficients for fuel + HO_2 at these conditions, HO_2 nonetheless is responsible for a significant percentage of the total fuel consumption in stage-1A, as illustrated by the red bars in Figure 5.

The concentration of HO_2 radicals continues to build until the rate of the recombination reaction, $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$, becomes one of the dominant HO_2 consumption channels (see Figure 6). This happens at around ~ 0.2 s for the conditions presented in Figure 4 and just precedes the observed kink in the OH concentration profile which indicates the start of stage-1B. At this point the exponential growth rate of HO_2 concentration decreases significantly and the fuel + HO_2 reactions become relatively unimportant (see Figure 5). Similar behavior will be observed for all fuels that produce significant amounts of HO_2 (e.g. propane, *iso*-butane, alcohols).

Figure 5: Fraction of propane consumed by each reaction during stage-1A (0.1s) and stage-1B (0.39s). HO_2 reaction with the fuel is significant during stage-1A, but negligible during stage-1B.

Figure 6: Magnitudes of the rates of important reactions producing or consuming HO_2 , for stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650K$. The transition from stage-1A to stage-1B occurs when HO_2 recombination becomes comparable to other reactions.

Stage-1B ends at time $\tau_{stage-1}$, which is called the first-stage ignition delay of the fuel. The first-stage ignition delay may be experimentally observed if there is a detectable change in the temperature (or pressure) of the system followed by a second induction time prior to the main ignition event. $\tau_{stage-1}$ is generally defined as the time when there is the first point of inflection in $T(t)$. The last important time scale (Figure 4) is the overall ignition delay of the fuel, $\tau_{overall}$. $\tau_{overall}$ is observed experimentally when there is a sudden, dramatic change in the thermodynamic state of the system. Although the ignition event is relatively unambiguous, several different diagnostic techniques are used to measure $\tau_{overall}$ in practice, and these methods do not always agree precisely [62, 63]. Here we have defined the overall ignition delay as the time required for the first derivative of the temperature to reach its global maximum.

Figure 7: Evolution of key species during isochoric adiabatic reaction of stoichiometric mixture of propane:air at $P_o=10$ bar and $T_o= 650$ K. It should be noted that OQ'OOH peaks shortly before $\tau_{stage-1}$. The full scale values of H₂O₂, CH₂O and OQ'OOH were chosen to be of twice the maximum value reached in the simulation.

Figure 7 summarizes the evolution of four key closed-shell species at the conditions of Figure 4. The oxidation process begins with an exponential rise in the concentration of ketohydroperoxide (OQ'OOH). As the temperature gradually increases, the concentration of OQ'OOH reaches a maximum ($\tau_{\text{OQ'OOHpeak}}$). It can be seen from Figure 7 that this maximum occurs shortly before the first-stage ignition delay $\tau_{\text{stage-1}}$. Both the first-stage ignition delay and overall ignition delay can also be identified from the concentration profiles of the intermediates. For example, the H_2O_2 concentration profile shows a clear kink around $\tau_{\text{stage-1}}$ while its concentration drops toward zero at τ_{overall} .

The peak in the OQ'OOH concentration (Figure 7) can be attributed to decrease in both α and β components of the gain. First, the reaction cycle illustrated in Figure 3 is net exothermic and this leads to a rise in the temperature of the system. As the temperature increases, the rate coefficient for $n\text{RO}_2 \rightarrow \text{alkene} + \text{HO}_2$ increases and the equilibrium constants for $n\text{R} + \text{O}_2 \rightleftharpoons n\text{RO}_2$ and $\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}$ shift back towards the reactants, thereby decreasing the ratio β (given by (2)). So every time an OQ'OOH decomposes a smaller fraction of the OH radicals created will return back to the cycle to form new OQ'OOH. The second contributing factor to the peak in OQ'OOH is the loss of $n\text{RO}_2$ and OH radicals to the growing secondary products. Prior to $\tau_{\text{stage-1A}}$ (stage-1A), the concentration of products is sufficiently low that secondary reactions such as $\text{OH} + \text{products}$ and $n\text{RO}_2 + \text{products}$ are negligible. Under these conditions there are more OH radicals being produced than consumed (i.e. OH gain factor $f_{\text{OH}} > 1$), thereby propagating the chain branching cycle, e.g. the sequence of black and blue lines in Figure 3. However eventually, the product concentrations are no longer negligible, and any reaction of OH or $n\text{RO}_2$ with these products diverts the active radicals away from the chain branching pathway,

thereby reducing the gain of the feedback system. The most important products in this context are CH_2O and H_2O_2 for diverting OH and CH_2O and HO_2 for diverting nRO_2 , these pathways are illustrated by the dotted lines in Figure 3.

By $\tau_{\text{OQ'OOHpeak}}$ the gain f_{OH} has decreased close to unity, hence additional losses will result in the cycle no longer being able to sustain itself. Beyond $t > \tau_{\text{OQ'OOHpeak}}$ the OQ'OOH concentration that has built-up during the initial stages of the oxidation decreases, primarily decomposing via pathways that create two OH radicals (see Figure 3). The release of these radicals in the system causes a sudden jump in the temperature (and pressure), signaling the first-stage ignition, $\tau_{\text{stage-1}}$. At the same time the CH_2O concentration, which is a side product of the OQ'OOH decomposition, is also seen to spike (see Figure 7). For this sequence, $\tau_{\text{OQ'OOHpeak}}$ is a fairly reliable approximation for $\tau_{\text{stage-1}}$. This correlation is illustrated in Figure 8, where the solid line is the overall ignition delay, the dashed line is the first-stage ignition delay (as determined by the inflection point in the temperature), and the dashed-dotted line is the time of the peak OQ'OOH. Note that the peak in OQ'OOH is an excellent predictor of the first-stage ignition delay, even well into the NTC regime, at which point the first-stage ignition delay is no longer a reliable predictor for the overall ignition delay anyway.

Figure 8: Arrhenius plot for adiabatic isochoric stoichiometric mixture of propane in air initially at $P_0 = 10$ bar comparing $\tau_{OQ'OOHpeak}$ to $\tau_{stage-1}$ (determined by inflection in temperature). The $\tau_{OQ'OOHpeak}$ is a good estimate of $\tau_{stage-1}$.

Before we can derive analytical expressions that describe the low temperature combustion of propane, it is important to know whether or not quasi-steady state assumptions can be made for the system presented in Figure 7. Therefore, the net rate of reaction for the main oxidation reactions of nR (nC_3H_7) are shown in Figure 9. The net rate of reaction is defined as the flux for the forward reaction minus the reverse flux. Figure 9 illustrates that most rates of production quickly converge to the corresponding rates of destruction. First, at $t \approx 5 \times 10^{-5}$ s, the net rates for $nRO_2 \rightarrow QOOH$ (dashed blue) and $O_2 + QOOH \rightarrow O_2QOOH$ (solid blue) converge. This indicates that the net accumulation of $QOOH$ is very small compared to its throughput and $QOOH$ is in quasi-steady state beyond this time. Next, at $t \approx 5 \times 10^{-3}$ s, the net rates for $O_2 + QOOH \rightarrow O_2QOOH$ (solid blue) converges with that for $O_2QOOH \rightarrow OQ'OOH + OH$ (dashed green) signaling O_2QOOH comes in quasi steady state. The net rate for $OQ'OOH \rightarrow OQ'O + OH$ and $OQ'O \rightarrow CH_2CHO + CH_2O$ converge $t \approx 2 \times 10^{-3}$ s, this reaction is not shown in the plot.

Other reactions not shown in the plot are the net rate of formation ($\text{RH} + \text{O}_2/\text{OH}/\text{HO}_2 \rightarrow \text{nR} + \text{HO}_2/\text{H}_2\text{O}/\text{H}_2\text{O}_2$) and consumption of nR which converge within microseconds, indicating nR to be the first species to reach quasi-steady state. . Figure 9 shows that nRO_2 is close to quasi steady state while $\text{OQ}'\text{OOH}$ is not in quasi steady state during first-stage of ignition.

Figure 9: a) Net rate of production for reactions involved in *n*-propyl (nR) peroxy cycle, for adiabatic isochoric simulations ($P_0 = 10$ bar, $T = 650$ K) of stoichiometric mixture of propane and air using the full propane model. The arrows indicate the time when the species come into quasi-steady state, most species are in quasi-steady state after $t \sim 5$ ms. b) Inset of plot 5a) - the rate of $\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH}$ and $\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$ are significantly different indicating $\text{OQ}'\text{OOH}$ is not in quasi-steady state. For reference $\tau_{\text{stage-1A}}$, $\tau_{\text{OQ}'\text{OOH}}$ and $\tau_{\text{stage-1}}$ are ~ 0.2 , ~ 0.44 and ~ 0.56 s respectively.

5. Reduced model formulation for low temperature ignition

The objective of this paper is not to provide a new propane mechanism; rather, it is to elucidate analytically what reactions in the larger mechanism are responsible for the low-temperature, first-stage ignition delay. Based upon the preceding analysis, we begin with a simple reduced model that consists of only the most important reactions prior to first-stage

ignition (the predicted ignition delay for the reduced and full model are within a factor of 2, see supplemental material for the comparison). This reduced model includes reactions for: fuel + O₂ initiation, fuel + radical, O₂ + R, O₂ + QOOH, OQ'OOH decomposition, and other important sources and sinks of OH from secondary chemistry of key species, including hydrogen abstraction from HO₂, H₂O₂ and CH₂O. The H₂O₂ generation loop and the secondary chain branching loop (involving the alkyloxy radical), which were found to be important in previous studies [64, 65], also are included. During the prelude to ignition some reactions will rapidly equilibrate, and the corresponding reverse rate coefficients are included. For other reactions, the reverse reaction is negligible, and only the forward rate coefficient is required. The complete list of reactions in the reduced model is provided in Table 1.

Table 1: Simplified reaction mechanism for low-temperature propane ignition

Label	Reaction	Rate coefficient	Reference
R1	$\text{RH} + \text{O}_2 \rightarrow \text{nR} + \text{HO}_2$	k_1	[46]
R2	$\text{RH} + \text{O}_2 \rightarrow \text{iR} + \text{HO}_2$	k_2	[46]
R3	$\text{RH} + \text{OH} \rightarrow \text{nR} + \text{H}_2\text{O}$	k_3	[46]
R4	$\text{RH} + \text{OH} \rightarrow \text{iR} + \text{H}_2\text{O}$	k_4	[46]
R5	$\text{RH} + \text{HO}_2 \rightarrow \text{nR} + \text{H}_2\text{O}_2$	k_5	[66]
R6	$\text{RH} + \text{HO}_2 \rightarrow \text{iR} + \text{H}_2\text{O}_2$	k_6	[66]
R7	$\text{nR} + \text{O}_2 \rightleftharpoons \text{nRO}_2$	k_7, k_{-7}	[30]
R8	$\text{iR} + \text{O}_2 \rightleftharpoons \text{iRO}_2$	k_8, k_{-8}	[30]
R9	$\text{nR} + \text{O}_2 \rightleftharpoons \text{QOOH}$	k_9, k_{-9}	[30]
R10	$\text{nR} + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{10}	[30]
R11	$\text{iR} + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{11}	[30]

R12	$n\text{RO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{12}	[30]
R13	$i\text{RO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{13}	[30]
R14	$n\text{RO}_2 \rightleftharpoons \text{QOOH}$	k_{14}, k_{-14}	[30]
R15	$\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}$	k_{15}, k_{-15}	[30]
R16	$\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH}$	k_{16}	[30]
R17	$\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$	k_{17}	[30]
R18	$\text{OQ}'\text{O} \rightarrow \text{CH}_2\text{CHO} + \text{CH}_2\text{O}$	k_{18}	[30]
R19	$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{CO} + \text{OH}$	k_{19}	[67]
R20	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	k_{20}	[68]
R21	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2$	k_{21}	[69]
R22	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	k_{22}	[70]
R23	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	k_{23}	[71]
R24	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	k_{24}	[71]
R25	$\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}$	k_{25}	[71]
R26	$n\text{RO}_2 + \text{CH}_2\text{O} \rightarrow n\text{ROOH} + \text{HCO}$	k_{26}	[46]
R27	$n\text{RO}_2 + \text{HO}_2 \rightarrow n\text{ROOH} + \text{O}_2$	k_{27}	[46]

The mechanism listed in Table 1 represents a system of non-linear ordinary differential equations that consists of 20 species and 27 reactions (plus equations for the thermodynamic state variables). The original full model and reduced model are provided in the Supplemental Materials.

5.1. Analytic solution for stage-1A

The extent to which the growth in radical concentration is exponential depends upon the comparative rates of production for radicals versus their loss to other channels. If OQ'OOH decomposition to produce OH radicals exceeds OH losses (*e.g.* R4, R20 and R23), then there will be explosive growth.

During stage-1A the concentration of products is negligible, and the fuel and O₂ concentration remain essentially constant. These two assumptions effectively linearize the system of equations. For a system of linear ordinary differential equations, the solution is a sum of exponentials, and after an initial incubation period the eigenmode with the largest positive exponent (λ) will dominate all the other modes. This incubation period is expected to be on the order of the larger of the two quantities: 1) the induction period where the initiation reactions contribute non-negligibly to the production of radicals and 2) $\sim 1/(\lambda - \lambda_1)$ where λ_1 is the second largest eigenvalue. We expect that to a good approximation, after the incubation period, all species (except for fuel, O₂, N₂) will grow approximately exponentially with a single growth rate defined by the positive eigenvalue, *e.g.*

$$[\text{OH}] \approx C_{\text{OH}} \exp(\lambda t)$$

$$[\text{OQ'OOH}] \approx C_{\text{OQ'OOH}} \exp(\lambda t)$$

$$[\text{HO}_2] \approx C_{\text{HO}_2} \exp(\lambda t)$$

The ratios of the pre-exponential factors, C_X , and the exponent λ can be evaluated numerically by diagonalizing the rate coefficient matrix (for details see Supplemental Materials). These parameters depend upon the initial concentrations, $[\text{RH}]_0$ and $[\text{O}_2]_0$, and upon the rate coefficients evaluated at the initial conditions, T_0 and P_0 . To simplify the analysis, we note that

after the initial induction period, several of the species will be in a quasi-steady state, including nR, iR, QOOH, and O₂QOOH, OQ'O, OH, and CH₂CHO. It is also assumed that the vast majority of QOOH is formed via isomerization from nRO₂, while the chemically activated production of QOOH from nR + O₂ is negligible [30]. This leads to the following equations (see Supplemental Material for how these equations were obtained):

$$[\text{nR}] = \frac{(k_1[\text{O}_2] + k_3[\text{OH}] + k_5[\text{HO}_2])[\text{RH}] + k_{-7}[\text{nRO}_2] + k_{-9}[\text{QOOH}]}{(k_7 + k_9 + k_{10})[\text{O}_2]} \quad (4)$$

$$[\text{iR}] = \frac{(k_2[\text{O}_2] + k_4[\text{OH}] + k_6[\text{HO}_2])[\text{RH}] + k_{-8}[\text{iRO}_2]}{(k_8 + k_{11})[\text{O}_2]} \quad (5)$$

$$[\text{QOOH}] = \frac{k_9[\text{nR}][\text{O}_2] + k_{14}[\text{nRO}_2] + k_{-15}[\text{O}_2\text{QOOH}]}{k_{-9} + k_{-14} + k_{15}[\text{O}_2]} \quad (6)$$

$$[\text{O}_2\text{QOOH}] = \frac{k_{15}}{k_{-15} + k_{16}}[\text{O}_2][\text{QOOH}] \quad (7)$$

$$[\text{OQ'O}] = \frac{k_{17}[\text{OQ'OOH}]}{k_{18}} \quad (8)$$

$$[\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ'OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] + 2k_{25}[\text{H}_2\text{O}_2]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{23}[\text{H}_2\text{O}_2]} \quad (9)$$

$$[\text{CH}_2\text{CHO}] = \frac{k_{18}[\text{OQ'O}]}{k_{19}[\text{O}_2]} \quad (10)$$

Three dimensionless parameters are introduced that will prove helpful in evaluating the differential equations:

$$\alpha = \frac{k_3}{k_3 + k_4} \quad (11)$$

$$\beta = \frac{\theta k_{14}}{\theta k_{14} + k_{12}} \quad (12)$$

$$\theta = \frac{k_{16}[\text{O}_2\text{QOOH}]}{k_{14}[\text{nRO}_2]} = \frac{\frac{k_{15}k_{16}}{k_{-15} + k_{16}}[\text{O}_2]}{k_{-14} + \frac{k_{15}k_{16}}{k_{-15} + k_{16}}[\text{O}_2]} \quad (13)$$

In equation (11) above, α is defined as the fraction of OH radicals consumed that form nR (nC_3H_7) under the assumption that during stage-1A the OH radicals will predominantly react by abstracting hydrogen from the parent fuel. However, α can be more generally interpreted as the fraction of OH radicals that reacts to form radicals that have the potential for chain branching. β is the fraction of nRO_2 radicals that react to form OQ'OOH via the sequence R14, R15 and R16 relative to the loss of nRO_2 due to concerted HO_2 elimination. θ in equation (13) is defined as the fraction of QOOH formed which goes on to form OQ'OOH (ratio of flux through $\text{O}_2\text{QOOH} \rightarrow \text{OQ'OOH} + \text{OH}$ over the flux for $\text{nRO}_2 \rightarrow \text{QOOH}$). θ can be interpreted as a correction factor for cases where $\text{nRO}_2 \rightarrow \text{QOOH}$ is not the rate limiting step. It is constrained to be between 0 and 1 and it decreases with increasing temperature and decreasing pressure as illustrated in Figure 10. At low temperatures and high oxygen partial pressures, θ is close to 1 indicating that the reaction $\text{nRO}_2 \rightarrow \text{QOOH}$ is the rate limiting step. As the temperature increases, θ starts to decrease primarily because of strong temperature dependence of k_{-15} ($\text{O}_2\text{QOOH} \rightarrow \text{QOOH} + \text{O}_2$) which begins to significantly compete with $\text{O}_2\text{QOOH} \rightarrow \text{OQ'OOH} + \text{OH}$. This shift in the $\text{O}_2\text{QOOH} \rightleftharpoons \text{QOOH} + \text{O}_2$ equilibrium can also be achieved by lowering the pressure at fixed stoichiometry: at 600 K in air θ drops from 1 at 100 bar to 0.3 at 1 bar.

Figure 10: Effect of temperature on θ (equation (13)) at three different pressures for oxygen mole fraction of 0.2. As the temperature increases, the fraction of nRO_2 that participates in the chain branching sequence approaches zero. The fraction of nRO_2 that participates in the chain branching sequence is higher at higher pressures.

Using equations (4)-(13), it is possible to decouple the differential equations for nRO_2 , iRO_2 , $OQ'OOH$, and HO_2 from the remaining species. This leads to the following set of equations:

$$\begin{bmatrix} \frac{d[nRO_2]}{dt} \\ \frac{d[iRO_2]}{dt} \\ \frac{d[HO_2]}{dt} \\ \frac{d[OQ'OOH]}{dt} \end{bmatrix} = \begin{bmatrix} -\left((1-\alpha) + \frac{(1-\beta)}{\beta}\right)\theta k_{14} & 0 & k_5[RH]_0 & 2\alpha k_{17} \\ (1-\alpha)\theta k_{14} & -k_{13} & k_6[RH]_0 & 2(1-\alpha)k_{17} \\ \frac{(1-\beta)\theta k_{14}}{\beta} & k_{13} & -(k_5 + k_6)[RH]_0 & 0 \\ \theta k_{14} & 0 & 0 & -k_{17} \end{bmatrix} \begin{bmatrix} [nRO_2] \\ [iRO_2] \\ [HO_2] \\ [OQ'OOH] \end{bmatrix} + \begin{bmatrix} k_1[RH]_0[O_2]_0 \\ k_2[RH]_0[O_2]_0 \\ (k_1 + k_2)[RH]_0[O_2]_0 \\ 0 \end{bmatrix} \quad (14)$$

This system of equations can be written as

$$\frac{d\underline{C}}{dt} = \underline{M}\underline{C} + \underline{R} \quad (15)$$

which has an exact solution given by (see Supplemental Material for complete details)

$$\underline{C} = \underline{V} \exp(\underline{\Lambda} t) \underline{V}^{-1} \underline{C}_0 + \underline{V} (\exp(\underline{\Lambda} t) - \underline{I}) \underline{\Lambda}^{-1} \underline{V}^{-1} \underline{R} \quad (16)$$

where $\underline{\underline{V}}$ and $\underline{\underline{\Lambda}}$ are the eigenvector and eigenvalue matrices of $\underline{\underline{M}}$ (i.e. $\underline{\underline{M}} = \underline{\underline{V}} \underline{\underline{\Lambda}} \underline{\underline{V}}^{-1}$). From this set of four linear ordinary differential equations, we obtain four eigenvalues. For $P_0 = 10$ bar and $T_0 = 650$ K, the two real eigenvalues are $\lambda_{1A} = 55.4 \text{ s}^{-1}$ and $\lambda_{2A} = -39.4 \text{ s}^{-1}$; the remaining eigenvalues λ_{3A} and λ_{4A} are complex with a negative real component $(-542 \pm 42j) \text{ s}^{-1}$ (Note that, while the values above are obtained through a numerical solution of equations (14) - (16), an analytical solution is possible under an additional simplifying approximation as shown in the Supplemental Material, but this introduces significant error). The positive real eigenvalue can be interpreted as the rise rate (inverse of the time constant) during stage-1A. It is perhaps worth noting that the smallest time constant of decay for the other eigenmodes is $\sim 1 / 94.8 \text{ s}^{-1}$ or 0.011 s; and the induction time during which initiation reactions contribute non-negligibly to production of radicals is on the order of ~ 0.01 s. Thus, after a brief incubation time much shorter than the relevant ignition time scales, the concentration of the various species in this stage can hence be written as:

$$[X] \approx C_{X,A} \exp(\lambda_{1A} t) \quad (17)$$

This exponential growth should continue until one of the following events occurs and introduces nonlinearities to the system:

1. One of the species builds up to such a high concentration that its second-order reactions between itself and other minor species (i.e. not C_3H_8 and O_2) become significant.
2. Concentrations of the fuel or O_2 are no longer sufficiently close to their initial concentrations.
3. The net heat release alters the temperature (and pressure) enough to affect the kinetics through rate constants and/or equilibrium constants. Effects due to temperature are

expected to be dominant over effects due to pressure rise. Note that while the linear approximation holds, we expect the temperature to follow $T = T_0 + C_T \exp(\lambda_{1A}t)$.

For all the cases studied, stage-1A ends when the concentration of HO_2 increases to the point where the self-recombination reaction, $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ dominates the HO_2 disappearance. This time can be estimated by the following approximation:

$$\frac{d[\text{HO}_2]}{dt} \approx \lambda_{1A}[\text{HO}_2] - 2k_{24}[\text{HO}_2]^2 = 0 \quad (18)$$

Substituting for HO_2

$$\frac{d[\text{HO}_2]}{dt} \approx \lambda_{1A} C_{\text{HO}_2, A} \exp(\lambda_{1A} \tau_{\text{stage-1A}}) - 2k_{24} \left(C_{\text{HO}_2, A} \exp(\lambda_{1A} \tau_{\text{stage-1A}}) \right)^2 = 0 \quad (19)$$

Solving equation (19) for $\tau_{\text{stage-1A}}$ yields

$$\tau_{\text{stage-1A}} \approx \frac{1}{\lambda_{1A}} \ln \left(\frac{\lambda_{1A}}{2k_{24} C_{\text{HO}_2, A}} \right) \quad (20)$$

The pre-exponential factor for HO_2 ($C_{\text{HO}_2, A}$), can be determined using the eigenvector, eigenvalues, vector R and the initial conditions of the system, the exact equation is provided in the Supplemental Materials (S 53).

5.2. Analytic solution for stage-1B

The transition from stage-1A to stage-1B occurs when the self-reaction $\text{HO}_2 + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$ becomes the major HO_2 consumption channel and slows the growth rate of HO_2 . In this stage, hydrogen abstractions by HO_2 from the parent fuel are much less important than those by OH and it can be assumed that HO_2 no longer contributes significantly to the production of propyl radicals. This observation implies that the differential equation for HO_2 can be decoupled

from those for nRO_2 and OQ'OOH , and yields the following set of differential equations for stage-1B:

$$\begin{aligned} \begin{bmatrix} \frac{d[\text{nRO}_2]}{dt} \\ \frac{d[\text{OQ'OOH}]}{dt} \end{bmatrix} &= \begin{bmatrix} -\left((1-\alpha) + \frac{(1-\beta)}{\beta}\right)\theta k_{14} & 2\alpha k_{17} \\ \theta k_{14} & -k_{17} \end{bmatrix} \begin{bmatrix} [\text{nRO}_2] \\ [\text{OQ'OOH}] \end{bmatrix} \\ \begin{bmatrix} [\text{nRO}_2] \\ [\text{OQ'OOH}] \end{bmatrix}_{t=\tau_{\text{stage-1A}}} &= \begin{bmatrix} [\text{nRO}_2]_{\text{stage-1A}} \\ [\text{OQ'OOH}]_{\text{stage-1A}} \end{bmatrix} \end{aligned} \quad (21)$$

The eigenvalues for this system are:

$$\lambda_{1B} = \frac{k_{17}}{2} \left(-\left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}}\right) + \sqrt{4 \frac{(3\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}}\right)^2} \right) \quad (22)$$

$$\lambda_{2B} = \frac{k_{17}}{2} \left(-\left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}}\right) - \sqrt{4 \frac{(3\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}}\right)^2} \right) \quad (23)$$

The second eigenvalue is negative under all conditions (with a value of -505.2 s^{-1} for $P_0 = 10 \text{ bar}$ and $T_0 = 650 \text{ K}$) such that its time constant for decay is small compared to the relevant ignition time scales. For $P_0 = 10 \text{ bar}$ and $T_0 = 650 \text{ K}$, the positive eigenvalue is $\lambda_{1B} = 25.3 \text{ s}^{-1}$.

Using this linearized model the OH concentration during stage-1B ($t > \tau_{\text{stage-1A}}$) is given by:

$$[\text{OH}] = C_{\text{OH,B}} \exp(\lambda_{1B} t) \quad (24)$$

Where the pre-exponential factor is given as

$$C_{\text{OH,B}} = C_{\text{OH,A}} \exp((\lambda_{1A} - \lambda_{1B}) \tau_{\text{stage-1A}}) \quad (25)$$

Using the above equations we can plot the predicted rise of OH radicals for stage-1B in propane ignition. Figure 11 provides a comparison between the predicted and simulated OH mole fraction during stage-1A and stage-1B for an adiabatic, isochoric system at $P_0 = 10 \text{ bar}$ and $T_0 = 650 \text{ K}$

using the full propane oxidation model. It can be seen that both the rise rate in stage-1A and the initial rise rate of stage-1B are reproduced well. At later times in stage-1B the rise rate decreases due to loss of OH and $n\text{RO}_2$ radicals to secondary reactions. End of stage-1B will occur when the rise rate has decreased to zero therefore the initial rise rate in stage-1B (λ_{1B}) represents an upper bound and the expressions based on this rise rate give a lower bound on the predicted first-stage ignition delay.

Figure 11: Comparison of the predicted and the simulated OH mole fraction profiles, for adiabatic isochoric simulations at $P = 10$ bar, $T = 650$ K and stoichiometric mixture of propane: air using the full model. The red line corresponds to the stage-1A prediction while the black line corresponds to the stage-1B prediction. The predictions are made using the equation $[\text{OH}] = C_{\text{OH},X} \exp(\lambda_{1X}t)$ where $\lambda_{1A} = 55.4 \text{ s}^{-1}$ and $\lambda_{1B} = 25.3 \text{ s}^{-1}$.

5.2.1. Predicting first-stage ignition

Similar to stage-1A, stage-1B will end when secondary reactions become important and interfere with the chain mechanism presented in Figure 3 or when the temperature rises enough to significantly alter the kinetics. The end of this stage may be experimentally observed if there is a large enough change in temperature (or pressure) of the system. The kink in the temperature profile is correlated with the depletion of QOOH , which had built-up in the initial stages of the

ignition. For straight-chain alkanes as shown in Figure 8 (for propane) and also by Musculus et al. [72] (for heptane), there is only a small delay between the peak in OQ'OOH and the point of inflection in $T(t)$. A reasonable approximation is, hence to equate the first-stage ignition delay with the peak in OQ'OOH .

The OQ'OOH concentration will peak when the rise rate has decreased to zero:

$$\lambda_{1B}(\underline{C}, T) = 0 \quad (26)$$

where λ_{1B} here is both a function of the temperature and the composition of the system, the former due to rate coefficients and equilibrium constants and latter due to secondary reactions.

The rise rate λ_{1B} (equation (22)) will be zero when the following condition is satisfied:

$$f_{\text{OH}} = 3\alpha\beta = 1 \quad (27)$$

In other words, OQ'OOH peaks when the three OH radicals that are generated by the decomposition of O_2QOOH , are insufficient to overcome losses in order to maintain the radical chain mechanism. Both α and β depend on the temperature, i.e. through the rate coefficients, and also on the composition of the mixture. As the concentrations of the secondary products grow, additional loss channels (primarily due to hydrogen abstractions from CH_2O and H_2O_2) will influence the OH balance of the chain mechanism. In that case α and β can be represented as:

$$\alpha = \frac{k_3}{k_3 + k_4 + k_{20} \frac{[\text{CH}_2\text{O}]}{[\text{RH}]} + k_{23} \frac{[\text{H}_2\text{O}_2]}{[\text{RH}]}} \quad (28)$$

$$\beta = \frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26} [\text{CH}_2\text{O}] + k_{27} [\text{HO}_2]} \quad (29)$$

The evolution of α and β during the various stages of the ignition for the adiabatic case at 650 K and 10 bar using the full model is shown in Figure 12. It can be seen that α starts from a

value of around 0.5 and hardly decreases while the value of β drops from an initial value of 0.85 to 0.66 at the end of stage-1B. As the relative decrease in β is much larger than that in α , the variation in β will have a larger influence on the OH balance of the chain mechanism. The OH loss due to hydrogen abstraction from the secondary products is partially compensated by the additional production of OH radicals from the decomposition of hydroperoxides ($\text{ROO} + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \rightarrow \text{RO} + \text{OH} + \text{O}_2$). The inclusion of this cycle makes the system very complex and for sake of simplicity here we assume that $\alpha \approx 0.5$ throughout the simulation under all conditions, yielding equation (30) for the condition of peak OQ'OOH . In the following sections it is demonstrated how equation (30) can be used to predict first-stage ignition delay under adiabatic conditions.

$$\frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26}[\text{CH}_2\text{O}] + k_{27}[\text{HO}_2]} = \frac{2}{3} \quad (30)$$

Figure 12: Simulated OH loss terms α and β as function of time for stoichiometric mixture of propane at $T_0 = 650$ K and $P_0 = 10$ bar under adiabatic conditions. The dashed grey line indicates the time when OQ'OOH peaks in the simulation.

5.2.2. First-stage ignition delay under adiabatic conditions

Under adiabatic conditions, the time at which OQ'OOH peaks is determined by both the temperature increase of the system and the loss of $n\text{RO}_2$ (active RO_2) radicals to the growing secondary chemistry. At higher temperatures $n\text{RO}_2$ radicals are more likely to react by the higher barrier HO_2 elimination channel which yields HO_2 and propene reducing β and thereby reducing the gain term f_{OH} .

The temperature rise can be modeled by assuming overall reactions for the chain mechanism presented in Figure 3. As OH is the main fuel abstractor in stage-1B, this can be achieved by introducing two global reactions:

R1 corresponds to the sum of the hydrogen abstraction from the secondary carbon atom in propane and the decomposition of $n\text{RO}_2$ into C_3H_6 and HO_2 . R2 is the overall reaction for the chain mechanism presented in Figure 3 and starts with the hydrogen abstraction by OH from the primary carbon atom. Reaction enthalpies (at 298 K) for R1 and R2 amount to $-153.5 \text{ kJ mol}^{-1}$ and -399 kJ mol^{-1} , respectively [73]. As the rate coefficients for hydrogen abstractions by OH from the primary and secondary site in propane are almost identical, the effective heat released per mole of propane consumed amounts to approximately $\sim 275 \text{ kJ mol}^{-1}$ (Most of the heat is released later in stage-1 since this is an exponential process).

In stage-1B, the fuel conversion X and temperature are correlated:

$$dT = -\frac{\Delta H_{\text{eff}}}{c_V C_{\text{tot}}} d[\text{RH}] = \frac{\Delta H_{\text{eff}} X_{0,\text{RH}}}{c_V} dX \quad (31)$$

with ΔH_{eff} the effective reaction enthalpy, c_v the average molar specific heat capacity of the system and $x_{0,\text{RH}}$ the initial fuel mole fraction. Integrating the above equation will give

$$T - T_0 = \frac{\Delta H_{\text{eff}} x_{0,\text{RH}}}{c_v} X \quad (32)$$

where T_0 is the initial temperature of the system. Assuming that formaldehyde and OQ'OOH have the stage-1B exponential behavior and HO_2 is in quasi-steady state (see Supplemental Material), yields:

$$[\text{CH}_2\text{O}] = C_{\text{CH}_2\text{O},\text{B}} \exp(\lambda_{1\text{B}} t) = \frac{C_{\text{CH}_2\text{O},\text{B}} [\text{OQ'OOH}]}{C_{\text{OQ'OOH},\text{B}}} \quad (33)$$

$$[\text{HO}_2] = \sqrt{\frac{k_{17}}{k_{24}}} [\text{OQ'OOH}] \quad (34)$$

Since both the ketohydroperoxide and the fuel conversion are assumed to be exponentially increasing at the same rate, equation (33) and (34) can also be expressed in terms of fuel conversion

$$[\text{CH}_2\text{O}] = C_{\text{CH}_2\text{O},\text{B}} \exp(\lambda_{1\text{B}} t) = \frac{C_{\text{CH}_2\text{O},\text{B}} X}{X_{0,\text{B}}} \quad (35)$$

$$[\text{HO}_2] = \sqrt{\frac{k_{17}}{k_{24}}} \frac{C_{\text{OQ'OOH},\text{B}}}{X_{0,\text{B}}} X \quad (36)$$

where the fuel conversion is given by $X = X_{0,\text{B}} \exp(\lambda_{1\text{B}} t)$. The pre-exponential factor $X_{0,\text{B}}$ is given by

$$X_{0,\text{B}} = X_{0,\text{A}} \exp((\lambda_{1\text{A}} - \lambda_{1\text{B}}) \tau_{\text{stage-1A}}) \quad (37)$$

Where $X_{0,A}$ is obtained from full model simulations, for $T_0 = 650$ K and $P_0 = 10$ bar $X_{0,A}$ was $\sim 3E-7$. The value of $X_{0,A}$ will vary by an order of magnitude, depending on conditions. Sensitivity analysis shows that the exact value has little impact on the predictions; hence we keep it fixed for all the conditions studied. The pre-exponential factor for CH_2O and $OQ'OOH$, $C_{X,B}$ is given by

$$C_{X,B} = C_{X,A} \exp((\lambda_{1A} - \lambda_{1B}) \tau_{stage-1A}) \quad (38)$$

As stated in the previous section the criterion to determine the end of stage-1 is given by (30). Substituting for $[CH_2O]$ and $[HO_2]$ using equation (35) and (36) in (30), we reduce it to a function of conversion and temperature.

$$\frac{\theta k_{14}}{\theta k_{14} + k_{12} + k_{26} \frac{C_{CH_2O,B} X}{X_{0,B}} + k_{27} \sqrt{\frac{k_{17}}{k_{24}} \frac{C_{OQ'OOH,B}}{X_{0,B}} X}} = \frac{2}{3} \quad (39)$$

If we substitute for conversion with (32), we reduce the above equation to be only a function of temperature, that can be solved for $T_{stage-1}$, which is also the cross over temperature described by Peters et al. [10] (or alternatively fuel conversion at end of stage-1 $X_{stage-1}$).

5.2.2.1. Critical temperature for the autocatalytic $QOOH$ cycle

It is interesting to note that if the secondary chemistry is ignored (set $k_{26}[CH_2O]$ and $k_{27}[HO_2] = 0$), equation (30) simplifies to an equation giving a specific temperature $T_{stage-1,max}$, at which the system becomes subcritical:

$$\frac{\theta(T_{stage-1,max}, P_0, [O_2]_0) k_{14}(T_{stage-1,max}, P_0)}{\theta(T_{stage-1,max}, P_0, [O_2]_0) k_{14}(T_{stage-1,max}, P_0) + k_{12}(T_{stage-1,max}, P_0)} = \frac{2}{3} \quad (40)$$

In that case, $T_{stage-1,max}$ is independent of the initial temperature T_0 of the system. At this temperature, the loss of radicals from the autocatalytic cycle due to concerted HO_2 elimination

alone becomes large enough to decrease the value of β to 0.66. $T_{\text{stage-1,max}}$ also represents the maximum possible temperature to which the system can rise before OQ'OOH peaks. For propane in air at $P = 10$ bar, $T_{\text{stage-1,max}} = 690$ K. Above the critical temperature the autocatalytic cycle does not operate; positive feedback leading to ignition must come from other cycles (e.g. H_2O_2). Using equations (32) and (37) the time required for the temperature to reach $T_{\text{stage-1,max}}$ will be given by

$$\tau_{\text{OQ'OOHpeak}} \approx \frac{1}{\lambda_{1B}(T_0)} \ln \left(\frac{T_{\text{stage-1,max}} - T_0}{\frac{\Delta H_{\text{eff}} X_{0,\text{RH}}}{c_V} X_A} \right) + \tau_{\text{stage-1A}} \quad (41)$$

where λ_{1B} is the rise rate at the start of stage-1B as given by (22).

Figure 13 provides a comparison of the $\tau_{\text{OQ'OOHpeak}}$ obtained from the full model simulations and predicted using (41) for adiabatic isochoric conditions. The time delay for peak OQ'OOH as predicted by (41) is longer than that computed by the full model simulations; however they are within 30% over the temperature range investigated. Equation (41) provides a practical way to estimate first-stage ignition delays for $T_0 < T_{\text{stage-1,max}}$ (≈ 690 K for mixtures of propane: air at $P_0 = 10$ bar) and to understand how they depend on initial temperature, stoichiometry and mixture heat capacity. The dependence on rate coefficients and thermochemistry is manifested in $\tau_{\text{stage-1A}}$, λ_{1B} , ΔH_{eff} and $T_{\text{stage-1,max}}$. The first-stage ignition delay as estimated by equation (41) is an analytical expression depending on 10 rate coefficients, while the full model is a stiff system of differential equations involving 630 rate coefficients.

Figure 13: Comparison of the first-stage ignition delays ($\tau_{OQ'OOH_{peak}}$) obtained from 1) the time of the inflection point in the temperature profile from full model simulation, 2) the time of the OQ'OOH peak in the full model simulation 3) the time for $f_{OH} = 1$ predicted from the solution to equations (31)-(36) and 4) the time for $f_{OH} = 1$ predicted by equation (41) for adiabatic, isochoric simulations of stoichiometric mixtures of propane and air, $P_0 = 10$ bar.

It is important to note that the above discussion is only valid for fuel/air mixtures (or mixtures close to fuel/air mixtures) and would not yield satisfactory results under very dilute or rich conditions. For sufficiently dilute mixtures the temperature rise would never drive the system to end of stage-1 and the system remains close to isothermal. Under these conditions the secondary reactions play a dominant role in the end of stage-1. We provide only a brief analysis of these cases in the Supplementary Materials; future work will address these cases in greater detail.

6. Predicting first-stage ignition delay for longer chain alkane fuels

The framework developed for interpreting propane ignition can be extended to larger n-alkane fuels. For longer straight chain fuels (e.g. butane, pentane etc.), all sites on the carbon chain can participate in the peroxy chemistry cycle ($R + 2O_2 \rightarrow$ intermediates $\rightarrow OQ'OOH$) to

[illegible]

delay the first stage ignition of the fuel.

For long chain fuels the OH radicals can abstract hydrogen from the fuel and also secondary products with carbonyl groups (that tend not to contribute to chain branching, these secondary products are labeled as “aldehyde” in the equations below). In this case, since all hydrogen abstractions by OH from the fuel lead into potential chain branching sequences for all alkyl radical sites, the generalized fraction of OH consumption reactions that can lead to chain branching, α can be represented as:

$$\alpha = \frac{\text{fuel} + \text{OH} \rightarrow \sum_i \text{R}_i + \text{H}_2\text{O}}{\text{total consumption rate of OH}} = \frac{\sum_i k_{\text{RH}+\text{OH} \rightarrow \text{R}_i + \text{H}_2\text{O}} [\text{RH}]}{\sum_i k_{\text{RH}+\text{OH} \rightarrow \text{R}_i + \text{H}_2\text{O}} [\text{RH}] + \sum_i k_{\text{aldehyde}+\text{OH} \rightarrow \text{P}_i} [\text{aldehyde}] + k_{\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}} [\text{H}_2\text{O}_2]} \quad (42)$$

In long straight chain alkanes all n sites are assumed equivalent, which reduces α to:

$$\alpha = \frac{k_{\text{RH}+\text{OH} \rightarrow \text{R} + \text{H}_2\text{O}} [\text{RH}]}{k_{\text{RH}+\text{OH} \rightarrow \text{R} + \text{H}_2\text{O}} [\text{RH}] + \sum_i \frac{k_{\text{aldehyde}+\text{OH} \rightarrow \text{P}_i}}{n} [\text{aldehyde}] + \frac{k_{\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}}}{n} [\text{H}_2\text{O}_2]} \quad (43)$$

β for long chain alkanes is given by:

$$\beta = \frac{\text{net rate of } \text{RO}_2 \rightarrow \text{QOOH}}{\text{total consumption of } \text{RO}_2} = \frac{\sum_i \theta_i k_{\text{RO}_{2i} \rightarrow \text{QOOH}_i}}{\sum_i \theta_i k_{\text{RO}_{2i} \rightarrow \text{QOOH}_i} + k_{\text{RO}_2 \rightarrow \text{Alkene} + \text{HO}_2} + \sum_i k_{\text{RO}_{2i} + \text{aldehyde}} [\text{aldehyde}] + \sum_i k_{\text{RO}_{2i} + \text{HO}_2} [\text{HO}_2]} \quad (44)$$

We simplify the above expression by assuming all n sites to be equivalent to the secondary RO_2 radical going to secondary γ -QOOH radical, which reduces β to:

$$\beta = \frac{\theta k_{\text{RO}_2 \rightarrow \text{QOOH}}}{\theta k_{\text{RO}_2 \rightarrow \text{QOOH}} + k_{\text{RO}_2 \rightarrow \text{alkene} + \text{HO}_2} + \sum_i \frac{k_{\text{RO}_{2i} + \text{aldehyde}}}{n} [\text{aldehyde}] + \sum_i \frac{k_{\text{RO}_{2i} + \text{HO}_2}}{n} [\text{HO}_2]} \quad (45)$$

where the expression for θ is given by equation (46).

$$\theta = \frac{\frac{k_{\text{QOOH}+\text{O}_2 \rightarrow \text{O}_2\text{QOOH}} k_{\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH}+\text{OH}}}{k_{-\text{QOOH}+\text{O}_2 \rightarrow \text{O}_2\text{QOOH}} + k_{\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH}+\text{OH}}} [\text{O}_2]}{k_{-\text{RO}_2 \rightarrow \text{QOOH}} + \frac{k_{\text{QOOH}+\text{O}_2 \rightarrow \text{O}_2\text{QOOH}} k_{\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH}+\text{OH}}}{k_{-\text{QOOH}+\text{O}_2 \rightarrow \text{O}_2\text{QOOH}} + k_{\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH}+\text{OH}}} [\text{O}_2]} \quad (46)$$

For long straight chain alkanes the carbonyl radical formed by decomposition of OQ'O radical can either react with an additional O₂ to give OH radical or decompose to give radical + stable product. However, we found that current detailed mechanisms have no systematic treatment for this species. To account for this we define an additional ratio

$$\gamma = \frac{\text{rate of Carbonyl} + \text{O}_2 \rightarrow \text{OH} + \text{Side Product}}{\text{total consumption rate of Carbonyl}} \quad (47)$$

The value of γ is uncertain and ranges from 0 to 1. The gain in OH for the cycle shown in Figure 14 can be defined as follows

$$f_{\text{OH}} = (2 + \gamma) \alpha \beta \quad (48)$$

The concentration of HO₂ to OH for long straight chain alkanes is often so low that HO₂ does not contribute significantly to fuel consumption. The two sub-stages are therefore not observed distinctly ($\lambda_{IA} \approx \lambda_{IB}$) in long chain alkanes. The generalized differential equation over a single site for the first stage ignition can then be written as:

$$\begin{bmatrix} \frac{d[\text{RO}_2]}{dt} \\ \frac{d[\text{OQ}'\text{OOH}]}{dt} \end{bmatrix} = \begin{bmatrix} -\left((1-\alpha) + \frac{(1-\beta)}{\beta}\right) \theta k_{14} & (1+\gamma) \alpha k_{17} \\ \theta k_{14} & -k_{17} \end{bmatrix} \begin{bmatrix} [\text{RO}_2] \\ [\text{OQ}'\text{OOH}] \end{bmatrix} \quad (49)$$

In the above equation, θ , k_{14} and k_{17} correspond to the parameters for the secondary RO₂ radical.

The positive eigenvalue for the above system of equation is given by:

$$\lambda_{1B} = \frac{k_{17}}{2} \left(- \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right) + \sqrt{4 \frac{((2+\gamma)\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right)^2} \right) \quad (50)$$

It is worth noting that in contrast to propane where approximately 50% of the OH radicals are lost to the *i*-propyl channel, for large *n*-alkanes the loss of OH radicals is effectively only due to secondary chemistry (i.e reactions with aldehydes, alkenes, cyclic ethers). Thus, within the single site assumption in the initial stages of the ignition where intermediates and secondary products have relatively small concentrations, the value of α will be close to unity.

The time for first stage ignition delay is given approximately by the following expression:

$$\tau_{OOH_{peak}} \approx \frac{1}{\lambda_{1B}(T_0)} \ln \left(\frac{T_{stage-1,max} - T_0}{\frac{\Delta H_{eff} x_{0,RH}}{c_V} X_{0,B}} \right) \quad (51)$$

where λ_{1B} is given by equation (50), with β and θ needed to evaluate λ_{1B} are given by the expressions (12) and (13) respectively. Table 2 gives the rate coefficients for the respective alkanes needed to evaluate λ_{1B} . The value for α is assumed to be 1 for long alkanes. The critical temperature $T_{stage-1,max}$ for long chain alkanes is obtained by solving:

$$\frac{\theta(T_{stage-1,max}, P_0, [O_2]_0) k_{14}(T_{stage-1,max}, P_0)}{\theta(T_{stage-1,max}, P_0, [O_2]_0) k_{14}(T_{stage-1,max}, P_0) + k_{12}(T_{stage-1,max}, P_0)} = \frac{1}{(2+\gamma)} \quad (52)$$

Table 3 gives the calculated critical temperatures for $\gamma = 0$ and $\gamma = 1$ for various alkanes. We note that $T_{stage-1,max}$ is conceptually and mathematically similar to the cross-over temperature discussed by Peters et al. [10] for the case of heptane, but because Peters et al.'s heptane model

did not include the reactions $\text{RO}_2 \rightarrow \text{alkene} + \text{HO}_2$, now known to be very important, it is hard to compare our results with the results in [10]. Beeckmann et al. [13] recently developed analytical expression for low temperature ignition delay for dimethyl-ether mixtures. However a direct comparison cannot be made since the controlling mechanism in ether is significantly different than alkanes; the chain branching is controlled by either the QOOH radical undergoing β -scission or second O_2 addition. Since the fate of $\text{OQ}'\text{O}$ is uncertain in the current chemical mechanisms, we assume the value of $\gamma = 1$ for the rest of the section. More research is needed to identify the proper value of γ for various alkanes. The fuel conversion at the end of the incubation period ($X_{0,B}$) which appears in equation (51), was kept fixed for all alkanes at the value obtained for full model simulations of propane $\sim 3\text{E-}7$. Sensitivity analysis showed that this term does not have a large effect on the predicted ignition.

The rate coefficients in Table 2 come from published chemical kinetic mechanisms for each n-alkane. This table highlights significant discrepancies between these literature mechanisms. For example the $\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$ rate is faster for heptane than for pentane, butane and propane. Also the $\text{RO}_2 \rightarrow \text{alkene} + \text{HO}_2$ rate has a very non-Arrhenius behavior probably because it comes from a pressure dependent calculation, but the form should be different for different size molecules. Figure 15 provides a comparison of the overall ignition delay for the full model simulations of propane, *n*-butane (Healy et al. [59]), *n*-pentane (Mehl et al. [3]) and *n*-heptane (Mehl et al. [3]) with that predicted for the first stage ignition delay using (51). The predicted ignition delay ($T < 700\text{K}$) is within a factor of 2-3 of the full model simulation for most fuels. The value of α will not be unity as the secondary products grow in as the reaction proceeds. Notably, even decreasing the value of α to 0.9 (10% loss of OH radicals to

secondary chemistry, which was the typical loss seen from full model simulations) or alternatively γ to 0.7 markedly improves the agreement between the predicted and simulated ignition delays as shown by the dashed-dotted lines in Figure 15. The good agreement suggests that the approximations (*e.g.* lumping of all the different type of carbon sites in the molecule to a single site) used to calculate $\tau_{\text{OO}^\bullet\text{OOH}_{\text{peak}}}$ are reasonably accurate.

Table 2: Arrhenius rate coefficient parameters for reactions required to calculate the first stage ignition delay using equation (51). The parameters come from the 10 atm PLOG fits for *n*-propyl pathway from Goldsmith et al. [30], from the detailed model of Healey et al. [59] for propane + OH and butane and the detailed model by Mehl et al. [3] for pentane and heptane.

Reaction	Fuel	A (cm ³ /mol-s) or s ⁻¹	n	E _a (kcal / mol)
RH + OH → R + H ₂ O	Heptane	4.9E+06	2.0	-0.59
	Pentane	9.3E+07	1.61	-0.035
	Butane	9.3E+07	1.61	-0.035
	Propane	1.0E+10	0.97	1.59
RO ₂ ⇌ QOOH ^a	Heptane	2.5E+10	0.0	20.5
	Pentane	2.5E+10	0.0	20.8
	Butane	3.8E+10	0.0	24.4
	Propane	1.01	3.38	18.9
RO ₂ → alkene + HO ₂	Heptane	20.0E+42	-9.4	42.5

	Pentane	20.0E+42	-9.4	42.5
	Butane	20.0E+42	-9.4	42.5
	Propane	2.6E+16	-1.2	32.8
$\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}^{\text{a}}$	Heptane	7.5E+12	0.0	0.0
	Pentane	7.5E+12	0.0	0.0
	Butane	4.5E+12	0.0	0.0
	Propane	2.2E+27	-4.8	4.0
$\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH}$	Heptane	1.2E+10	0.0	17.5
	Pentane	1.2E+10	0.0	17.5
	Butane	2E+11	0.0	26.4
	Propane	4.5E+11	-0.5	18.4
$\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$	Heptane	1.0E+16	0.0	39.0
	Pentane	1.5E+16	0.0	42.0
	Butane	1.5E+16	0.0	41.6
	Propane	5.2E+43	-8.7	51.5

*Note: (a) The reverse rate coefficients were obtained from the respective thermodynamic parameters of the species and are provided in a separate file.

Figure 15: Comparison of the numerically simulated full-model adiabatic isochoric overall ignition delays with the first stage ignition delay predicted by Eqs. (50)-(52), for different n-alkanes with initial conditions $P_0 = 10$ bar and $\Phi = 1$ in air. The parameters are tabulated in Table 2 and Table 3. The value of γ is uncertain for fuels larger than propane, here we plot results using $\gamma = 1$ and $\gamma = 0.7$.

6.1.1. Implications for chemistry of first-stage ignition

In this section we analyze how different chemical kinetic parameters and mixture composition affect first stage ignition delay. Since the time for first stage ignition is inversely proportional to the rise rate, parameters that affect the eigenvalue necessarily affect the first-stage ignition delay. The rise rate (λ_{IB}) for long straight chain alkanes is given by equation (50), and for $\gamma = 1$ this equation reduces to equation (22). As discussed previously, λ_{IB} is a function of α the fraction of OH radicals that participates in the chain-branching process by producing viable alkyl radicals, and β , which is the fraction of RO_2 radicals that can go on to participate in the peroxy cycle. The third parameter, θ , is the ratio of flux through $O_2QOOH \rightarrow OQ'OOH + OH$ over the flux for $RO_2 \rightarrow QOOH$. The rise rate is independent of the fuel concentration ($[RH]$), however the fuel concentration will affect the initial condition of the system via the $RH + O_2$ reaction which forms the initial radical pool. Changing the fuel concentration at constant C_v also

proportionally affects the temperature rise. However as seen from equation (51) the first stage ignition delay has only a logarithmic dependence on fuel mole fraction $x_{0,RH}$. Hence, increasing the fuel concentration modestly decreases the first stage ignition delay. The oxygen dependence of the first stage ignition delay is via $RH+O_2$, similar to the fuel dependence discussed above, but more significantly via θ . As discussed in Section 5.1, θ for propane tends to 1 for $T < 600$ K and $P > 10$ bar so the rise rate will become independent of the oxygen concentration. Under these conditions the reaction $nRO_2 \rightarrow QOOH$ is the rate limiting step. However for $T > 650$ K and low pressures, θ is no longer 1 and the rise rate is a function of $\theta^{0.5}$. As the temperature is increased or pressure is decreased (i.e. oxygen concentration is decreased) a larger fraction of O_2QOOH will dissociate back to O_2 and $QOOH$. An increase in temperature also increases the reverse rate of $RO_2 \rightarrow QOOH$ and consequently the reaction $O_2QOOH \rightarrow OQ'OOH + OH$ becomes rate limiting. The parameter θ can be approximated by:

$$\theta \approx \frac{k_{16}K_{15}x_{O_2}P / RT}{k_{-14} + k_{16}K_{15}x_{O_2}P / RT} \quad (53)$$

where x_{O_2} is the mole fraction of oxygen. The parameter θ also affects the $T_{stage1,max}$ through β . As the pressure is increased a smaller fraction of RO_2 radicals are lost via $RO_2 \rightarrow \text{alkene} + HO_2$ causing the critical temperature ($T_{stage1,max}$) to increase.

Table 3 gives $T_{stage1,max}$ as function of pressure for various straight chain alkanes. Both of these effects lead to first stage ignition delay having a modest dependence on the oxygen concentration at higher temperatures (the Supplemental Material provides predictions for propane first stage ignition delay under varying equivalence ratios and pressures). The above analysis is specific to

fuel/air mixtures (or mixtures that are close to fuel/air mixtures) and should not be used for very dilute or rich mixtures.

Table 3: Critical temperature ($T_{stage-I,max}$) calculated for stoichiometric mixture of fuel in air. The range in $T_{stage-I,max}$ corresponds to γ values of 0 and 1 respectively. For propane the fate of $OO^{\bullet}O$ is well understood and $\gamma = 1$.

Fuel	$T_{stage-I,max}$ (K)		
	$P_0 = 1$ bar	$P_0 = 10$ bar	$P_0 = 50$ bar
Propane	650	690	760
Butane	680 - 710	710 - 750	740 - 810
Pentane	760 - 800	860 - 930	930 - 1030
Heptane	790 - 830	890 - 950	970 - 1070

6.1.2. Overall activation energy of first-stage ignition for long chain alkanes

It has often been observed that the low-temperature portion of a measured ignition delay for long-chain fuels can be well represented by an Arrhenius expression. Using the expression derived above (51), we can determine the overall activation energy. For long straight-chain alkanes, as a first approximation, during pre-ignition we can assume $\alpha \approx 1$ (this was verified using full model simulations for n -alkanes). For $T < 600$ K and $P > 10$ bar it is reasonable to further approximate $\beta \approx 1$ (alkene + HO_2 is negligible) and $\theta \approx 1$ (the back reaction of $RO_2 \rightleftharpoons QOOH$ is insignificant compared to the rate at which $QOOH$ reacts away to O_2QOOH). The ignition time given by equation (52) scales as follows (See Supplemental Material for details):

$$\tau_{OO^{\bullet}OOH_{peak}} \propto \frac{1}{\sqrt{2k_{14}k_{17}}} \quad (54)$$

Such that the ignition delay can be expressed as an Arrhenius expression

$$\ln(\tau_{OQ'OOH_{peak}}) = -\left(\ln A_{eff} - \frac{E_{eff}}{T}\right) \quad (55)$$

where

$$E_{eff} \approx \frac{1}{2}(E_{14} + E_{17}) \quad (56)$$

The above equation has an important implication that the overall activation energy E_{eff} for the first stage ignition delay $\tau_{OQ'OOH_{peak}}$ is dependent not only on the activation energy of the isomerization between RO_2 (secondary carbon) and $QOOH$ (radical on the secondary carbon), as stated by Zhao and Law [12], but also on the activation energy of the ketohydroperoxide decomposition. Zhao and Law [12], obtained their correlation by simply comparing their fitted E_{eff} with the activation energy of different reactions in their mechanism. Since the decomposition of ketohydroperoxide controls the release of OH radicals it is reasonable to expect this term to affect the activation energy of the ignition. Table 4 provides the overall activation energy E_{eff} for the first stage ignition delay $\tau_{OQ'OOH_{peak}}$ for different fuels in the temperature range of 550 – 650 K as obtained via Arrhenius expressions fitted to full model simulations, equation (56) and $E_{eff} = E_{a,RO2=QOOH}$. Clearly equation (56) provides a better prediction of the overall activation energy than does $E_{eff} = E_{a,RO2=QOOH}$.

Table 4: Overall activation energy (kcal/mol) for first stage ignition delay for different n-alkanes for stoichiometric mixture of fuel and air at $P_0 = 10$ bar.

Fuel	Activation Energy (Full model)	Activation Energy Eq (56)	E_a ($RO_2 \rightleftharpoons QOOH$)
Butane	35.0	32.6	24.4

Pentane	33.9	31.0	20.8
Heptane	28.6	29.3	20.5

*Note: The overall activation energy from the full model is obtained by linear least square fit of the simulated full model first stage ignition delay to the temperature ($\ln(\tau_{\text{OQ}\cdot\text{OOH}_{\text{peak}}}) = A + E/RT$). The temperature range was limited to $T < 650$ K.

7. Concluding remarks

Using a detailed propane model we analyze the controlling chemistry for the first-stage ignition of propane. The analysis demonstrates that low-temperature auto-ignition of straight-chain alkanes is a multi-stage process. The experimentally observed first-stage ignition can be divided into two stages. In stage-1A, both OH and HO₂ radicals abstract hydrogen atoms from the fuel, and the resulting alkyl radicals initiate a peroxy radical cycle, which leads to chain branching via the thermal decomposition of ketohydroperoxides. This process causes the OH and HO₂ concentrations to rise exponentially and continues until the concentration of HO₂ is sufficiently large that the recombination reaction, $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$, becomes competitive with the rate of HO₂ formation. Once this occurs, which marks the beginning of stage-1B, the [OH]/[HO₂] ratio rises sharply and the vast majority of fuel consumption occurs through OH. Fuels that do not produce a significant amount of HO₂ (*e.g.* long straight-chain alkanes) will not show this “multistage” phenomenon so distinctly, but instead stage-1A and stage-1B will be observed as a single stage driven by OH radicals.

Several phenomena occur as the first-stage ends. First, oxidation products such as aldehydes, alkenes and H₂O₂ accumulate, diverting some of the OH radicals from chain branching pathways. An increasing fraction of the nRO₂ radicals also get consumed by the growing secondary chemistry (CH₂O and HO₂). Most importantly the increase in temperature of the system speeds up the loss due to the concerted elimination of RO₂ to alkene + HO₂. This

diversion of the OH and $n\text{RO}_2$ radicals reduces the gain of the autocatalytic cycle to < 1 . The combination of these effects causes the ketohydroperoxide concentration to first rise exponentially, then peak and drop rapidly, leading to the point of inflection in the temperature profile that has often been used to mark the end of first-stage ignition. The peak in ketohydroperoxide concentration, which occurs when $\text{gain} \approx 1$, is used here as a convenient chemical marker for the end of first-stage ignition.

The analysis also clarifies which species are in quasi steady-state. From these approximations, analytical expressions for first-stage ignition delay were derived: equations (22), (40) and (41) for propane, and equations (50) - (52) for longer n -alkanes. The accuracy of these analytical expressions emphasizes that first-stage ignition delay depends on the rate coefficients of only about a dozen reactions, not on the hundreds or thousands of other reactions in the mechanism. Furthermore, from the dependence of $\tau_{\text{OQ'OOHpeak}}$ on important rate coefficients and mixture composition, the following observations can be made:

1. The first-stage ignition delay is nearly independent of the fuel and oxygen concentration for low temperatures ($T < 650\text{K}$) and high pressure ($P > 50$ bar).
2. The first-stage ignition delay however will have a weak $[\text{O}_2]$ dependence for lower pressures and higher temperatures ($T > 650$ K).
3. The overall activation energy of first-stage ignition delay is dependent on the activation energy of isomerization of RO_2 to QOOH and the activation energy of the decomposition of the ketohydroperoxide. For large alkanes at high oxygen partial pressures and low temperatures < 650 K, the global activation energy for the ignition delay time can be estimated through the following equation:

$$E_{eff} \approx \frac{1}{2} (E_{ROO=QOOH} + E_{OQ'OOHdecmp})$$

4. The first-stage ignition delay is determined by the competition between pathways that go on to chain branch versus those that go onto chain terminate. The major branch points are
  - a. Fuel + OH selectivity towards fuel radicals with different reactivity e.g. *n*-propyl vs *iso*-propyl radicals. We denote this branching ratio by α . For propane only *n*-propyl radicals contribute to chain branching and $\alpha \sim 0.5$. For longer *n*-alkanes all alkyl radicals can contribute to radical generation and we use a value of $\alpha \sim 1$.
  - b. Peroxy radical (RO_2) that are lost by decomposition to alkene + HO_2 and by reaction with oxidation products (e.g. HO_2 , H_2O_2 , carbonyl compounds). This decomposition is often the major loss term and it increases with increasing temperature leading to longer ignition delays. We denote this branching ratio by β . The value of β is a strong function of temperature for all alkanes.
  - c. What fraction of the carbonyl (acyl-oxy) radicals formed by ketohydroperoxide decomposition go on to form OH or otherwise initiate new autocatalytic cycles. We denote this branching ratio by γ . For propane, which forms 2-formyl ethoxy radicals, there is a consensus that $\gamma \sim 1$, but for longer *n*-alkanes the value of γ is unclear, different literature models give different values [3, 46].

5. Above a critical fuel specific temperature ($T_{\text{stage-1,max}}$) the QOOH cycle is ineffective at creating additional radicals (gain - $f_{\text{OH}} = (2 + \gamma)\alpha\beta \approx 1$).

The results obtained from the present simple model for the first-stage of propane ignition were extended to longer straight chain fuels under the approximation of a single effective (average) site. This simplifying assumption gives reasonable agreement of the predicted $\tau_{\text{stage-1}}$ with the numerical solutions of large reaction mechanisms.

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Appendix A. Supplementary Material

Supplementary content associated with this article can be found, in the online version, at <http://XXXX>. This includes the full propane model in CHEMKIN format, validation of that full model versus experiments [74], derivations of several of the equations, and comparisons between the full-model simulations and the simple analytic formulas for several cases.

9. Supplementary Material

9.1 Validation of the Full Propane Model

The full propane model used in this work gives reasonable predictions against low temperature ignition delay data obtained using rapid compression machine as seen from Fig below

Figure 16: Comparison of experimental measured overall (filled symbols) and simulated (line) ignition delays in a rapid compression machine (RCM) for propane [74] at $P_0=30$ bar, $\phi=1$ and $\phi=0.5$. The simulations are performed using the constant volume assumption and do not account for the heat loss.

The reduced model provided in Table 1 provides reasonable predictions of the first-stage ignition delay for propane as illustrated in Figure 17.

Figure 17: Comparison of the predicted first-stage ignition delay for constant volume adiabatic simulations using the full and reduced propane model, for $P_0 = 10$ bar, stoichiometric mixture of propane in air. The $\tau_{\text{stage-1}}$ was obtained using the first inflection in the temperature profile.

9.1.1. Derivation for explosive eigenvalue using reduced model for stage-1A

The following set of ODE's can be constructed from the reduced model

$$\frac{d[nR]}{dt} = k_1[RH][O_2] + k_3[RH][OH] + k_5[RH][HO_2] - k_7[nR][O_2] + k_{-7}[nRO_2] - k_9[nR][O_2] + k_{-9}[QOOH] - k_{10}[nR][O_2] \quad (S\ 1)$$

$$\frac{d[iR]}{dt} = k_2[RH][O_2] + k_4[RH][OH] + k_6[RH][HO_2] - k_8[iR][O_2] + k_{-8}[iRO_2] - k_{11}[iR][O_2] \quad (S\ 2)$$

$$\frac{d[nRO_2]}{dt} = k_7[nR][O_2] - k_{-7}[nRO_2] - k_{12}[nRO_2] - k_{14}[nRO_2] + k_{-14}[QOOH] \quad (S\ 3)$$

$$\frac{d[iRO_2]}{dt} = k_8[iR][O_2] - k_{-8}[iRO_2] - k_{13}[iRO_2] \quad (S\ 4)$$

$$\begin{aligned} \frac{d[QOOH]}{dt} &= k_9[nR][O_2] - k_{-9}[nRO_2] + k_{14}[nRO_2] - k_{-9}[OQOOH] - k_{-14}[QOOH] \\ &- k_{15}[QOOH][O_2] + k_{-15}[O_2QOOH] \end{aligned} \quad (S\ 5)$$

$$\frac{d[O_2QOOH]}{dt} = k_{15}[QOOH][O_2] - k_{-15}[O_2QOOH] - k_{16}[O_2QOOH] \quad (S\ 6)$$

$$\frac{d[OQ'OOH]}{dt} = k_{16}[O_2QOOH] - k_{17}[OQ'OOH] \quad (S\ 7)$$

$$\frac{d[OQ'O]}{dt} = k_{17}[OQ'OOH] - k_{18}[OQ'O] \quad (S\ 8)$$

$$\frac{d[\text{CH}_2\text{CHO}]}{dt} = k_{18}[\text{OQ'O}] - k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] \quad (\text{S } 9)$$

$$\begin{aligned} \frac{d[\text{OH}]}{dt} = & -k_1[\text{RH}][\text{OH}] - k_2[\text{RH}][\text{OH}] + k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ'OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] \\ & + 2k_{25}[\text{H}_2\text{O}_2] \end{aligned} \quad (\text{S } 10)$$

$$\begin{aligned} \frac{d[\text{HO}_2]}{dt} = & k_1[\text{RH}][\text{O}_2] + k_2[\text{RH}][\text{O}_2] - k_5[\text{RH}][\text{HO}_2] - k_6[\text{RH}][\text{HO}_2] + k_{10}[\text{nR}][\text{O}_2] + k_{11}[\text{iR}][\text{O}_2] \\ & + k_{12}[\text{nRO}_2] + k_{13}[\text{iRO}_2] + k_{21}[\text{CH}_2\text{O}][\text{O}_2] + k_{22}[\text{HCO}][\text{O}_2] + k_{23}[\text{H}_2\text{O}_2][\text{OH}] - 2k_{24}[\text{HO}_2]^2 \end{aligned} \quad (\text{S } 11)$$

$$\frac{d[\text{CH}_2\text{O}]}{dt} = k_{18}[\text{OQ'O}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] - k_{20}[\text{CH}_2\text{O}][\text{OH}] - k_{21}[\text{CH}_2\text{O}][\text{O}_2] \quad (\text{S } 12)$$

After the induction period, several radical species will be in QSS including nR, iR, OH, QOOH, O₂QOOH, OQ'O and CH₂CHO

$$[\text{nR}] = \frac{(k_1[\text{O}_2] + k_3[\text{OH}] + k_5[\text{HO}_2])[\text{RH}] + k_{-7}[\text{nRO}_2] + k_{-9}[\text{QOOH}]}{(k_7 + k_9 + k_{10})[\text{O}_2]} \quad (\text{S } 13)$$

$$[\text{iR}] = \frac{(k_2[\text{O}_2] + k_4[\text{OH}] + k_6[\text{HO}_2])[\text{RH}] + k_{-8}[\text{iRO}_2]}{(k_8 + k_{11})[\text{O}_2]} \quad (\text{S } 14)$$

$$[\text{QOOH}] = \frac{k_9[\text{nR}][\text{O}_2] + k_{14}[\text{nRO}_2] + k_{-15}[\text{O}_2\text{QOOH}]}{k_{-9} + k_{-14} + k_{15}[\text{O}_2]} \quad (\text{S } 15)$$

$$[\text{O}_2\text{QOOH}] = \frac{k_{15}}{k_{-15} + k_{16}}[\text{O}_2][\text{QOOH}] \quad (\text{S } 16)$$

$$[\text{OQ'O}] = \frac{k_{17}[\text{OQ'OOH}]}{k_{18}} \quad (\text{S } 17)$$

$$[\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ}'\text{OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] + 2k_{25}[\text{H}_2\text{O}_2]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{23}[\text{H}_2\text{O}_2]} \quad (\text{S } 18)$$

$$[\text{CH}_2\text{CHO}] = \frac{k_{18}[\text{OQ}'\text{O}]}{k_{19}[\text{O}_2]} \quad (\text{S } 19)$$

We make the following simplifications:

1. For pressures greater than one atmosphere, the vast majority of QOOH is formed via isomerization from RO₂, such that the chemically activated production of QOOH from R + O₂ is sufficiently small that its contribution can be considered negligible.
2. Similarly the contributions of reaction 10 and 11 are also negligible, as confirmed by flux analysis with the complete model.
3. For temperatures less than 800 K (those considered here) the decomposition of H₂O₂ to OH is not significant during stage-1 and can be neglected.

Applying these simplifications to (S 13)-(S 19):

$$[\text{nR}] = \frac{(k_1[\text{O}_2] + k_3[\text{OH}] + k_5[\text{HO}_2])[\text{RH}] + k_{-7}[\text{nRO}_2]}{k_7[\text{O}_2]} \quad (\text{S } 20)$$

$$[\text{iR}] = \frac{(k_2[\text{O}_2] + k_4[\text{OH}] + k_6[\text{HO}_2])[\text{RH}] + k_{-8}[\text{iRO}_2]}{(k_8 + k_{11})[\text{O}_2]} \quad (\text{S } 21)$$

$$[\text{QOOH}] = \frac{k_{14}[\text{nRO}_2] + k_{-15}[\text{O}_2\text{QOOH}]}{k_{-14} + k_{15}[\text{O}_2]} \quad (\text{S } 22)$$

$$[\text{O}_2\text{QOOH}] = \frac{k_{15}}{k_{-15} + k_{16}}[\text{O}_2][\text{QOOH}] \quad (\text{S } 23)$$

$$[\text{OQ}'\text{O}] = \frac{k_{17}[\text{OQ}'\text{OOH}]}{k_{18}} \quad (\text{S } 24)$$

$$[\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + k_{17}[\text{OQ}'\text{OOH}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{23}[\text{H}_2\text{O}_2]} \quad (\text{S } 25)$$

$$[\text{CH}_2\text{CHO}] = \frac{k_{18}[\text{OQ}'\text{O}]}{k_{19}[\text{O}_2]} \quad (\text{S } 26)$$

Substituting for O_2QOOH (S 23) in (S 22) and solving gives

$$[\text{O}_2\text{QOOH}] = \frac{k_{14} \frac{k_{15}}{k_{-15} + k_{16}} [\text{O}_2]}{k_{-14} + \frac{k_{15}k_{16}}{k_{-15} + k_{16}} [\text{O}_2]} [\text{nRO}_2] \quad (\text{S } 27)$$

Substituting for QOOH (S 22) in (S 23) and solving gives:

$$[\text{QOOH}] = \frac{k_{14}}{k_{-14} + \frac{k_{15}k_{16}}{k_{-15} + k_{16}} [\text{O}_2]} [\text{nRO}_2] \quad (\text{S } 28)$$

Substituting for CH_2CHO (S 24) and (S 26) in the expression (S 25) for OH :

$$[\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + 2k_{17}[\text{OQ}'\text{OOH}]}{(k_3 + k_4)[\text{RH}] + k_{20}[\text{CH}_2\text{O}] + k_{23}[\text{H}_2\text{O}_2]} \quad (\text{S } 29)$$

Initially during stage-1 the concentrations of intermediates and products is sufficiently small that their contributions to OH consumption can be neglected. However this assumption breaks down as the fuel is consumed, which leads to the production of secondary products.

$$[\text{OH}] = \frac{k_{16}[\text{O}_2\text{QOOH}] + 2k_{17}[\text{OQ}'\text{OOH}]}{(k_3 + k_4)[\text{RH}]} \quad (\text{S } 30)$$

We can simplify the notation by introducing three non-dimensional parameters:

$$\alpha = \frac{k_3}{k_3 + k_4} \quad (\text{S } 31)$$

$$\beta = \frac{\theta k_{14}}{\theta k_{14} + k_{12}} \quad (\text{S } 32)$$

$$\theta = \frac{\frac{k_{15}k_{16}}{k_{-15} + k_{16}}[O_2]}{k_{-14} + \frac{k_{15}k_{16}}{k_{-15} + k_{16}}[O_2]} \quad (\text{S } 33)$$

Using (S 27) in ODE for OQ'OOH (S 7):

$$\frac{d[\text{OQ'OOH}]}{dt} = k_{14}\theta[\text{nRO}_2] - k_{17}[\text{OQ'OOH}] \quad (\text{S } 34)$$

Using (S 20), (S 28) and (S 30) in (S 3):

$$\frac{d[\text{nRO}_2]}{dt} = \alpha(k_{16}[\text{O}_2\text{QOOH}] + 2k_{17}[\text{OQ'OOH}]) + (k_1[\text{O}_2] + k_5[\text{HO}_2])[\text{RH}] - k_{12}[\text{nRO}_2] - k_{14}\theta[\text{nRO}_2] \quad (\text{S } 35)$$

Using (S 27) in (S 35) and simplifying:

$$\frac{d[\text{nRO}_2]}{dt} = 2\alpha k_{17}[\text{OQ'OOH}] + (k_1[\text{O}_2] + k_5[\text{HO}_2])[\text{RH}] + ((\alpha - 1)k_{14}\theta - k_{12})[\text{nRO}_2] \quad (\text{S } 36)$$

Using (S 14) and (S 30) in (S 4):

$$\frac{d[\text{iRO}_2]}{dt} = (1 - \alpha)(k_{16}[\text{O}_2\text{QOOH}] + 2k_{17}[\text{OQ'OOH}]) + (k_2[\text{O}_2] + k_6[\text{HO}_2])[\text{RH}] - k_{13}[\text{iRO}_2] \quad (\text{S } 37)$$

Using (S 27) in (S 37) and simplifying:

$$\frac{d[\text{iRO}_2]}{dt} = (1 - \alpha)(\theta[\text{nRO}_2] + 2k_{17}[\text{OQ'OOH}]) + (k_2[\text{O}_2] + k_6[\text{HO}_2])[\text{RH}] - k_{13}[\text{iRO}_2] \quad (\text{S } 38)$$

The ODE for HO_2 after ignoring contributions from R10 and R11 is given by:

$$\begin{aligned} \frac{d[\text{HO}_2]}{dt} = & k_1[\text{RH}][\text{O}_2] + k_2[\text{RH}][\text{O}_2] - k_5[\text{RH}][\text{HO}_2] - k_6[\text{RH}][\text{HO}_2] \\ & + k_{12}[\text{nRO}_2] + k_{13}[\text{iRO}_2] + k_{21}[\text{CH}_2\text{O}][\text{O}_2] + k_{22}[\text{HCO}][\text{O}_2] + k_{23}[\text{H}_2\text{O}_2][\text{OH}] - 2k_{24}[\text{HO}_2]^2 \end{aligned} \quad (\text{S } 39)$$

At early times the concentration of secondary product (CH_2O , H_2O_2) can be considered negligibly small. The HO_2 concentration is also sufficiently small that the rate of its self- reaction can be neglected, which allows for simplification of (S 39) to:

$$\frac{d[\text{HO}_2]}{dt} = k_1[\text{RH}][\text{O}_2] + k_2[\text{RH}][\text{O}_2] - k_5[\text{RH}][\text{HO}_2] - k_6[\text{RH}][\text{HO}_2] + k_{12}[\text{nRO}_2] + k_{13}[\text{iRO}_2] \quad (\text{S } 40)$$

We can also neglect the consumption terms for CH_2O simplifying (S 12) to

$$\frac{d[\text{CH}_2\text{O}]}{dt} = k_{18}[\text{OQ'O}] + k_{19}[\text{CH}_2\text{CHO}][\text{O}_2] \quad (\text{S } 41)$$

The above equation can be simplified using (S 24) and (S 26) to (S 42), which is valid during early times when the concentration of CH_2O has not grown significantly

$$\frac{d[\text{CH}_2\text{O}]}{dt} \approx 2k_{17}[\text{OQ'OOH}] \quad (\text{S } 42)$$

During stage-1 the concentration of the fuel and oxygen remains nearly constant such that

$$[\text{RH}][\text{O}_2] \approx [\text{RH}]_0[\text{O}_2]_0 \quad (\text{S } 43)$$

Since α , β and θ are approximately constants, equations (S 34), (S 36), (S 38) and (S 40) are linear ODE's which can be solved using eigenvalue analysis

$$\begin{bmatrix} \frac{d[\text{nRO}_2]}{dt} \\ \frac{d[\text{iRO}_2]}{dt} \\ \frac{d[\text{HO}_2]}{dt} \\ \frac{d[\text{OQ'OOH}]}{dt} \end{bmatrix} = \begin{bmatrix} -\left((1-\alpha) + \frac{(1-\beta)}{\beta}\right)\theta k_{14} & 0 & k_5[\text{RH}]_0 & 2\alpha k_{17} \\ (1-\alpha)\theta k_{14} & -k_{13} & k_6[\text{RH}]_0 & 2(1-\alpha)k_{17} \\ \frac{(1-\beta)\theta k_{14}}{\beta} & k_{13} & -(k_5 + k_6)[\text{RH}]_0 & 0 \\ \theta k_{14} & 0 & 0 & -k_{17} \end{bmatrix} \begin{bmatrix} [\text{nRO}_2] \\ [\text{iRO}_2] \\ [\text{HO}_2] \\ [\text{OQ'OOH}] \end{bmatrix} + \begin{bmatrix} k_1[\text{RH}]_0[\text{O}_2]_0 \\ k_2[\text{RH}]_0[\text{O}_2]_0 \\ (k_1 + k_2)[\text{RH}]_0[\text{O}_2]_0 \\ 0 \end{bmatrix} \quad (\text{S } 44)$$

The system of linear ODE's can be written in terms of a concentration vector $\underline{C}$, coefficient matrix $\underline{M}$ and source term $\underline{R}$.

$$\frac{d\underline{C}}{dt} = \underline{M}\underline{C} + \underline{R} \quad (\text{S } 45)$$

For which $\underline{M}$ can be decomposed into an eigenvector matrix, $\underline{V}$ and eigenvalue matrix, $\underline{\Lambda}$ as

$$\underline{M} = \underline{V}\underline{\Lambda}\underline{V}^{-1}$$

$$\frac{d\underline{C}}{dt} = \underline{V}\underline{\Lambda}\underline{V}^{-1}\underline{C} + \underline{R} \quad (\text{S } 46)$$

Transforming variables from the concentration vector to the eigenvectors, $\underline{Z} = \underline{V}^{-1}\underline{C}$ diagonalizes the equation

$$\frac{d\underline{Z}}{dt} = \underline{\Lambda}\underline{Z} + \underline{E} \quad (\text{S } 47)$$

$$\text{where } \underline{E} = \underline{V}^{-1}\underline{R}$$

Another change of variables to $\underline{Y} = \underline{\Lambda}\underline{Z} + \underline{E}$ further simplifies the equation to

$$\frac{d\underline{Y}}{dt} = \underline{\Lambda}\underline{Y} \quad (\text{S } 48)$$

This has a general solution of the form

$$\underline{Y} = \exp(\underline{\Lambda}t)\underline{Y}_0 \quad (\text{S } 49)$$

Substituting for C we get back

$$\underline{C} = \underline{V} \exp(\underline{\Lambda} t) \underline{Y}_0 - \underline{V} \underline{\Lambda}^{-1} \underline{V}^{-1} \underline{R} \quad (\text{S } 50)$$

where the value of $\underline{Y}_0$ can be obtained from $\underline{R}$ and the true initial conditions $\underline{C}_0(t=0)$

$$\underline{Y}_0 = \underline{V}^{-1} \underline{C}_0 + \underline{\Lambda}^{-1} \underline{V}^{-1} \underline{R} \quad (\text{S } 51)$$

Hence if the complete eigenvectors and the true initial conditions $\underline{C}_0(t=0)$ are used, then the numerical solutions to the above can be found exactly (without any further approximations).

Since only one of the eigenvalues (λ_1) has a positive real number, after a brief induction period of time C can be approximated as

$$C_i \approx y_{0,i} V_{i,1} \exp(\lambda_1 t) \text{ where we assume } \text{real}(\lambda_1) > 0 \quad (\text{S } 52)$$

The initial conditions for HO_2 , RO_2 and OQ'OOH in stage-1A is given by

$$C_{i0,A} \approx y_{0,i} V_{i,1} \quad (\text{S } 53)$$

Initial conditions for all other species will just be linear combinations of HO_2 , RO_2 and OQ'OOH .

If desired we can take the ratio of concentrations to eliminate the initial condition

$$\frac{C_{i+1}}{C_i} \approx \frac{V_{i+1,1}}{V_{i,1}} \quad (\text{S } 54)$$

Figure 18 compares the ratio of concentrations obtained from the eigenvectors (S 54) and the full model simulation.

Figure 18: Predictions (dotted lines) for relative concentrations of species involved in first-stage ignition (stage-1A) by eigen mode analysis for simulations at $P_0=10$ bar and $T_0=650$ K for a stoichiometric mixture of propane in air. The solid lines are obtained from full model simulations, the dotted lines are the ratio of the eigenvector elements $V_{(\text{species})}/V_{(\text{OQ'OOH})}$ corresponding to the positive eigenvalue in stage-1A.

9.1.2. Analytical solution for the explosive eigenvalue for stage-1A

An analytical solution to the system of linear ODE's, equation (S 44), can be achieved if the quartic system is reduced to a cubic equation by making the following assumption for HO_2

$$\frac{d[\text{HO}_2]}{dt} = 2k_{17}[\text{OQOOH}] - \frac{d[\text{nRO}_2]}{dt} - \frac{d[\text{iRO}_2]}{dt} \approx 2k_{17}[\text{OQ'OOH}] \quad (\text{S } 55)$$

The left hand side of the above expression comes from rearranging (S 40) using (S 37) and (S 38).

Figure 19 gives the comparison of the net HO_2 flux and the flux estimated by the approximation made in (S 55). As seen from Figure 19 the approximation provides a satisfactory reproduction of the net HO_2 flux until the HO_2 self-reaction becomes a significant contributor to HO_2 consumption near the end of stage-1A.

Figure 19: Comparison of the net HO₂ flux (from the full model simulation) and the approximation $2k_{\text{OQ'OOHdecmp}}[\text{OQ'OOH}]$ for $P_0=10$ bar and $T_0=650$ K.

This approximation effectively decouples iRO₂ from the system of differential equations (S 44), reducing it to a cubic system.

$$\begin{bmatrix} \frac{d[\text{nRO}_2]}{dt} \\ \frac{d[\text{HO}_2]}{dt} \\ \frac{d[\text{OQ'OOH}]}{dt} \end{bmatrix} = \begin{bmatrix} -\left((1-\alpha) + \frac{(1-\beta)}{\beta}\right)\theta k_{14} & k_5[\text{RH}]_0 & 2\alpha k_{17} \\ 0 & 0 & 2k_{17} \\ \theta k_{14} & 0 & -k_{17} \end{bmatrix} \begin{bmatrix} [\text{nRO}_2] \\ [\text{HO}_2] \\ [\text{OQ'OOH}] \end{bmatrix} + \begin{bmatrix} k_1[\text{RH}]_0[\text{O}_2]_0 \\ (k_1 + k_2)[\text{RH}]_0[\text{O}_2]_0 \\ 0 \end{bmatrix} \quad (\text{S } 56)$$

The eigenvalues are roots of the following cubic characteristic equation

$$\lambda^3 + \left(\left((1-\alpha) + \frac{(1-\beta)}{\beta} \right) \theta k_{14} + k_{17} \right) \lambda^2 + \left((1-3\alpha) + \frac{(1-\beta)}{\beta} \right) \theta k_{14} k_{17} \lambda - 2\theta k_{14} k_{17} k_5 [\text{RH}] = 0 \quad (\text{S } 57)$$

The characteristic equation is a general cubic of the form $x^3 + bx^2 + cx + d = 0$ and will have three roots.

$$\lambda_1 = -\frac{b}{3} + \frac{\sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}}{3\sqrt[3]{2}}$$

$$- \frac{\sqrt[3]{2}(3c - b^2)}{3\sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}} \quad (\text{S } 58)$$

$$\lambda_2 = -\frac{b}{3} - \frac{(1-i\sqrt{3})\sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}}{6\sqrt[3]{2}}$$

$$+ \frac{(1+i\sqrt{3})(3c - b^2)}{3 \times 2^{\frac{2}{3}} \sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}} \quad (\text{S } 59)$$

$$\lambda_3 = -\frac{b}{3} - \frac{(1+i\sqrt{3})\sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}}{6\sqrt[3]{2}}$$

$$+ \frac{(1-i\sqrt{3})(3c - b^2)}{3 \times 2^{\frac{2}{3}} \sqrt[3]{\left(-2b^3 + 3\sqrt{3}\sqrt{4b^3d - b^2c^2 - 18bcd + 4c^3 + 27d^2} + 9bc - 27d\right)}} \quad (\text{S } 60)$$

where

$$b = \left((1-\alpha) + \left(\frac{1-\beta}{\beta} \right) \right) \theta k_{14} + k_{17}$$

$$c = \left((1-3\alpha) + \left(\frac{1-\beta}{\beta} \right) \right) \theta k_{14} k_{17}$$

$$d = -2\theta k_{14} k_{17} k_5 [RH]$$

Table 5: Comparison of the positive eigenvalue (λ_{1A}) obtained solving (S 44) numerically and the positive root of the cubic equation (S 57) for $P_0 = 10$ bar, stoichiometric mixture of propane in air.

T_0 (K)	λ_{1A} (Numerical)	λ_{1A} (Cubic approx.)
550	0.7	0.9
600	8.5	9.8
650	55.4	61.0

9.1.3. Simplification of the explosive eigenvalue for stage-1B

The expression for the explosive eigenvalue for a general fuel (for $\gamma = 1$) is given by:

$$\lambda_{1B} = \frac{k_{17}}{2} \left(- \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right) + \sqrt{4 \frac{(3\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right)^2} \right) \quad (\text{S } 61)$$

$$\lambda_{1B} = \frac{k_{17}}{2} \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right) \left(-1 + \sqrt{4 \frac{(3\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right)^2} + 1 \right) \quad (\text{S } 62)$$

The above expression can be further approximated as

$$\lambda_{1B} \approx \frac{k_{17}}{2} \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right) \left(\sqrt{4 \frac{(3\alpha\beta-1)\theta k_{14}}{\beta k_{17}} + \left(1 + \frac{(1-\alpha\beta)\theta k_{14}}{\beta k_{17}} \right)^2} \right) \quad (\text{S } 63)$$

$$\lambda_{1B} \approx \left(\sqrt{\frac{(3\alpha\beta-1)\theta k_{14} k_{17}}{\beta}} \right) \quad (\text{S } 64)$$

For high pressures and low temperature and high pressures ($T < 600$ K, $P > 10$ bar) $\theta \rightarrow 1$, which yields

$$\lambda_{1B} \approx \left(\sqrt{\frac{(3\alpha\beta - 1)k_{14}k_{17}}{\beta}} \right) \quad (\text{S } 65)$$

For $\alpha = 1$ and $\beta = 1$ we get

$$\lambda_{1B} \approx \sqrt{2k_{14}k_{17}} \quad (\text{S } 66)$$

Note this approximation has significant error in the absolute value of λ_{1B} and not recommended to be used above the limited temperature and pressure range.

9.1.4. Prediction for first-stage ignition delay for propane under varying equivalence ratios and pressure

Figure 20 provides the comparison of first-stage ignition delay for propane under varying equivalence ratios in air for $P_0 = 10$ bar. The first-stage ignition delay does not change significantly with fuel concentration.

Figure 20: Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first-stage ignition delay for various equivalence ratios of propane in air. All simulations are for $P_0 = 10$ bar. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first-stage ignition delay (dashed line) is obtained using equation (41).

Figure 21 provides the comparison of first-stage ignition delay for propane under varying pressure for $\phi = 1$. The first-stage ignition delay is a function of pressure (or oxygen concentration) as the temperature is increased ($T > 650$ K).

Figure 21: Comparison of the simulated adiabatic isochoric overall ignition delay with the predicted first-stage ignition delays for various pressures. All simulation are for stoichiometric mixture of propane in air. The overall ignition delay (solid line) is obtained from the full model simulations, while the predicted first-stage ignition delay (dashed line) is obtained using equation (41).

Table 6: Comparison of important parameters used in predicting first-stage ignition delay for propane under varying T_0 , P_0 and equivalence ratio.

	$T_0 = 600 \text{ K}$		$T_0 = 650 \text{ K}$	
$\varphi = 1$	$P_0 = 10 \text{ bar}$	$P_0 = 50 \text{ bar}$	$P_0 = 10 \text{ bar}$	$P_0 = 50 \text{ bar}$
$\alpha(T_0)$	0.5	0.5	0.5	0.5
$\beta(T_0)$	0.94	0.95	0.85	0.9
$\theta(T_0)$	0.75	0.93	0.46	0.8
$\lambda_{IA}(T_0) \text{ (s}^{-1}\text{)}$	8.5	13.1	55.4	102.9
$\lambda_{IB}(T_0) \text{ (s}^{-1}\text{)}$	3.0	3.2	25.3	37.5
$\tau_{\text{stage-1A}} \text{ (s)}$	1.2	0.7	0.2	0.1
$\tau_{\text{OQ'OOHpeak}} \text{ (s)}$	3.2	1.8	0.4	0.2
$T_{\text{stage-1,max}} \text{ (K)}$	690	760	690	760
	$T_0 = 600 \text{ K}$		$T_0 = 650 \text{ K}$	
$\varphi = 0.5$	$P_0 = 10 \text{ bar}$	$P_0 = 50 \text{ bar}$	$P_0 = 10 \text{ bar}$	$P_0 = 50 \text{ bar}$
$\alpha(T_0)$	0.5	0.5	0.5	0.5
$\beta(T_0)$	0.94	0.95	0.85	0.9
$\theta(T_0)$	0.75	0.93	0.46	0.8
$\lambda_{IA}(T_0) \text{ (s}^{-1}\text{)}$	7.0	11.4	46.1	87.3
$\lambda_{IB}(T_0) \text{ (s}^{-1}\text{)}$	3.0	3.2	25.5	37.6
$\tau_{\text{stage-1A}} \text{ (s)}$	1.5	0.8	0.24	0.11
$\tau_{\text{OQ'OOHpeak}} \text{ (s)}$	4.0	2.1	0.51	0.25
$T_{\text{stage-1,max}} \text{ (K)}$	690	760	690	760

9.1.5. First-stage ignition delay under isothermal conditions for propane

Under isothermal conditions, the criticality of the system will be completely determined by the concentrations of CH_2O and HO_2 . Substituting (33) and (34) in (30) and solving for the OQ'OOH concentration yields:

$$[\text{OQ'OOH}]_{\text{peak}} = \frac{C_{\text{OQ'OOH,B}}}{k_{26}C_{\text{CH}_2\text{O,B}}} \left((3\alpha - 1)\theta k_{14} - k_{12} \right) + \frac{k_{27}C_{\text{OQ'OOH,B}}^2}{k_{26}^2C_{\text{CH}_2\text{O,B}}^2} \left(\frac{k_{27}k_{17}}{2k_{24}} + \sqrt{\frac{k_{26}C_{\text{CH}_2\text{O,B}}}{C_{\text{OQ'OOH,B}}} \frac{k_{17}}{k_{24}} \left((3\alpha - 1)\theta k_{14} - k_{12} \right) + \frac{k_{27}^2k_{17}^2}{4k_{24}^2}} \right) \quad (\text{S } 67)$$

The first-stage ignition delay under isothermal conditions is then approximated by:

$$\tau_{\text{OQ'OOHpeak}} \approx \frac{1}{\lambda_{1\text{B}}(T_0)} \ln \left(\frac{[\text{OQ'OOH}]_{\text{peak}}}{C_{\text{OQ'OOH,B}}} \right) + \tau_{\text{stage-1A}} \quad (\text{S } 68)$$

where $\lambda_{1\text{B}}(T_0)$ is the rise rate at start of stage-1B. Figure 22 gives a comparison between various estimates for $\tau_{\text{OQ'OOHpeak}}$ obtained from 1) the time at which OQ'OOH peaks in the full model simulation, 2) the time at which the simulated OH multiplication factor is equal to 1, where f_{OH} is defined as:

$$f_{\text{OH}} = 3\alpha \left(1 + \frac{\sum k_{\text{ROOH} \rightarrow \text{RO} + \text{OH}} [\text{ROOH}]}{3(k_{\text{O}_2\text{QOOH} \rightarrow \text{OQ'OOH} + \text{OH}} [\text{O}_2\text{QOOH}])} \right) \beta \quad (\text{S } 69)$$

3) the time when the system becomes subcritical using the time predicted by equation (S 68).

The predictions are within a factor of 2 for the entire low temperature regime and the accuracy increases as we approach the negative temperature coefficient (NTC) region.

Figure 22: Comparison of the $\tau_{OQOOHpeak}$ obtained from 1) the OQOOH peak computed numerically from the full model, 2) the time at which criterion set by equation (30) is met using reaction fluxes obtained from full-model simulations, 3) the time predicted by equation (S 68), all for an isothermal isochoric simulation of a stoichiometric mixture of propane and air.

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Tables

Table 1: Simplified reaction mechanism for low-temperature propane ignition.

Label	Reaction	Rate coefficient	Reference
R1	$\text{RH} + \text{O}_2 \rightarrow \text{nR} + \text{HO}_2$	k_1	[46]
R2	$\text{RH} + \text{O}_2 \rightarrow \text{iR} + \text{HO}_2$	k_2	[46]
R3	$\text{RH} + \text{OH} \rightarrow \text{nR} + \text{H}_2\text{O}$	k_3	[46]
R4	$\text{RH} + \text{OH} \rightarrow \text{iR} + \text{H}_2\text{O}$	k_4	[46]
R5	$\text{RH} + \text{HO}_2 \rightarrow \text{nR} + \text{H}_2\text{O}_2$	k_5	[66]
R6	$\text{RH} + \text{HO}_2 \rightarrow \text{iR} + \text{H}_2\text{O}_2$	k_6	[66]
R7	$\text{nR} + \text{O}_2 \rightleftharpoons \text{nRO}_2$	k_7, k_{-7}	[30]
R8	$\text{iR} + \text{O}_2 \rightleftharpoons \text{iRO}_2$	k_8, k_{-8}	[30]
R9	$\text{nR} + \text{O}_2 \rightleftharpoons \text{QOOH}$	k_9, k_{-9}	[30]
R10	$\text{nR} + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{10}	[30]
R11	$\text{iR} + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{11}	[30]
R12	$\text{nRO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{12}	[30]
R13	$\text{iRO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{HO}_2$	k_{13}	[30]
R14	$\text{nRO}_2 \rightleftharpoons \text{QOOH}$	k_{14}, k_{-14}	[30]
R15	$\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}$	k_{15}, k_{-15}	[30]
R16	$\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH}$	k_{16}	[30]
R17	$\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$	k_{17}	[30]
R18	$\text{OQ}'\text{O} \rightarrow \text{CH}_2\text{CHO} + \text{CH}_2\text{O}$	k_{18}	[30]
R19	$\text{CH}_2\text{CHO} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{CO} + \text{OH}$	k_{19}	[67]
R20	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O}$	k_{20}	[68]
R21	$\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO} + \text{HO}_2$	k_{21}	[69]

R22	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	k_{22}	[70]
R23	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$	k_{23}	[71]
R24	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	k_{24}	[71]
R25	$\text{H}_2\text{O}_2 \rightarrow 2 \text{OH}$	k_{25}	[71]
R26	$n\text{RO}_2 + \text{CH}_2\text{O} \rightarrow n\text{ROOH} + \text{HCO}$	k_{26}	[46]
R27	$n\text{RO}_2 + \text{HO}_2 \rightarrow n\text{ROOH} + \text{O}_2$	k_{27}	[46]

Table 2: Arrhenius rate coefficient parameters for reactions required to calculate the first stage ignition delay using equation (51). The parameters come from the 10 atm PLOG fits for *n*-propyl pathway from Goldsmith et al. [30], from the detailed model of Healey et al. [59] for propane + OH and butane and the detailed model by Mehl et al. [3] for pentane and heptane.

Reaction	Fuel	A ($\text{cm}^3/\text{mol-s}$ or s^{-1})	n	E _a (kcal / mol)
$\text{RH} + \text{OH} \rightarrow \text{R} + \text{H}_2\text{O}$	Heptane	4.9E+06	2.0	-0.59
	Pentane	9.3E+07	1.61	-0.035
	Butane	9.3E+07	1.61	-0.035
	Propane	1.0E+10	0.97	1.59
$\text{RO}_2 \rightleftharpoons \text{QOOH}^a$	Heptane	2.5E+10	0.0	20.5
	Pentane	2.5E+10	0.0	20.8
	Butane	3.8E+10	0.0	24.4
	Propane	1.01	3.38	18.9
$\text{RO}_2 \rightarrow \text{alkene} + \text{HO}_2$	Heptane	20.0E+42	-9.4	42.5
	Pentane	20.0E+42	-9.4	42.5
	Butane	20.0E+42	-9.4	42.5

	Propane	2.6E+16	-1.2	32.8
$\text{QOOH} + \text{O}_2 \rightleftharpoons \text{O}_2\text{QOOH}^{\text{a}}$	Heptane	7.5E+12	0.0	0.0
	Pentane	7.5E+12	0.0	0.0
	Butane	4.5E+12	0.0	0.0
	Propane	2.2E+27	-4.8	4.0
$\text{O}_2\text{QOOH} \rightarrow \text{OQ}'\text{OOH} + \text{OH}$	Heptane	1.2E+10	0.0	17.5
	Pentane	1.2E+10	0.0	17.5
	Butane	2E+11	0.0	26.4
	Propane	4.5E+11	-0.5	18.4
$\text{OQ}'\text{OOH} \rightarrow \text{OQ}'\text{O} + \text{OH}$	Heptane	1.0E+16	0.0	39.0
	Pentane	1.5E+16	0.0	42.0
	Butane	1.5E+16	0.0	41.6
	Propane	5.2E+43	-8.7	51.5

*Note: (a) The reverse rate coefficients were obtained from the respective thermodynamic parameters of the species and are provided in a separate file.

Table 3: Critical temperature ($T_{stage-1,max}$) calculated for stoichiometric mixture of fuel in air. The range in $T_{stage-1,max}$ corresponds to γ values of 0 and 1 respectively. For propane the fate of OQ^*O is well understood and $\gamma = 1$.

Fuel	$T_{stage-1,max}$ (K)		
	$P_0 = 1$ bar	$P_0 = 10$ bar	$P_0 = 50$ bar
Propane	650	690	760
Butane	680 - 710	710 - 750	740 - 810
Pentane	760 - 800	860 - 930	930 - 1030
Heptane	790 - 830	890 - 950	970 - 1070

Table 4: Overall activation energy (kcal/mol) for first stage ignition delay for different n-alkanes for stoichiometric mixture of fuel and air at $P_0 = 10$ bar.

Fuel	Activation Energy (Full model)	Activation Energy Eq (56)	E_a ($RO_2 \rightleftharpoons QOOH$)
Butane	35.0	32.6	24.4
Pentane	33.9	31.0	20.8
Heptane	28.6	29.3	20.5

*Note: The overall activation energy from the full model is obtained by linear least square fit of the simulated full model first stage ignition delay to the temperature ($\ln(\tau_{OQ^*OOH_{peak}}) = A + E/RT$). The temperature range was limited to $T < 650$ K.

Figures

Figure 1: Experimental measured overall (filled symbols) and first-stage (open symbols) ignition delays in a rapid compression machine (RCM) for methylcyclohexane (MCH) [50] and dimethylether (DME) [51] at $P_0=15$ bar, $\phi(\text{MCH})=1$ and $\phi(\text{DME})=0.75$. For low temperatures the measured first-stage ignition delay is almost equal to the overall measured ignition delay. For higher temperatures the later stages of ignition contribute more to the overall ignition delay.

clarity some well-skipping pathways and reactions of HO_2 are omitted from the figure.

Figure 4: OH and HO_2 mole fraction profile (on semi-log scale) and temperature profile for isochoric (constant-volume) adiabatic simulation for a stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650\text{K}$. τ_{overall} is the overall ignition delay of the fuel. $\tau_{\text{stage-1}}$ is the first-stage ignition delay of the fuel, the time when the temperature (or pressure) of the system makes a small jump prior to the main ignition event. The first-stage ignition delay can be further divided into two stages A and B that are characterized by different time constants for the exponential rise of the OH concentration. $\tau_{\text{stage-1A}}$ is the time when the early exponential rise in OH concentration ends.

Figure 5: Fraction of propane consumed by each reaction during stage-1A (0.1s) and stage-1B (0.39s). HO_2 reaction with the fuel is significant during stage-1A, but negligible during stage-1B.

Figure 6: Magnitudes of the rates of important reactions producing or consuming HO_2 , for stoichiometric mixture of propane and air initially at $P_0 = 10$ bar and $T_0 = 650\text{K}$. The transition from stage-1A to stage-1B occurs when HO_2 recombination becomes comparable to other reactions.

Figure 7: Evolution of key species during isochoric adiabatic reaction of stoichiometric mixture of propane:air at $P_0=10$ bar and $T_0=650$ K. It should be noted that OQ'OOH peaks shortly before $\tau_{\text{stage-1}}$. The full scale values of H₂O₂, CH₂O and OQ'OOH were chosen to be of twice the maximum value reached in the simulation.

Figure 8: Arrhenius plot for adiabatic isochoric stoichiometric mixture of propane in air initially at $P_0 = 10$ bar comparing $\tau_{\text{OQ'OOHpeak}}$ to $\tau_{\text{stage-1}}$ (determined by inflection in temperature). The $\tau_{\text{OQ'OOHpeak}}$ is a good estimate of $\tau_{\text{stage-1}}$.

Figure 9: a) Net rate of production for reactions involved in *n*-propyl (nR) peroxy cycle, for adiabatic isochoric simulations ($P_0 = 10$ bar, $T = 650$ K) of stoichiometric mixture of propane and air using the full propane model. The arrows indicate the time when the species come into quasi-steady state, most species are in quasi-steady state after $t \sim 5$ ms. b) Inset of plot 5a) - the rate of $O_2QOOH \rightarrow OQ'OOH + OH$ and $OQ'OOH \rightarrow OQ'O + OH$ are significantly different indicating $OQ'OOH$ is not in quasi-steady state. For reference $\tau_{\text{stage-1A}}$, $\tau_{OQ'OOH}$ and $\tau_{\text{stage-1}}$ are ~ 0.2 , ~ 0.44 and ~ 0.56 s respectively

Figure 10: Effect of temperature on θ (equation (13)) at three different pressures for oxygen mole fraction of 0.2. As the temperature increases, the fraction of nRO_2 that participates in the chain branching sequence approaches zero. The fraction of nRO_2 that participates in the chain branching sequence is higher at higher pressures.

Figure 11: Comparison of the predicted and the simulated OH mole fraction profiles, for adiabatic isochoric simulations at $P = 10$ bar, $T = 650$ K and stoichiometric mixture of propane: air using the full model. The red line corresponds to the stage-1A prediction while the black line corresponds to the stage-1B prediction. The predictions are made using the equation $[\text{OH}] = C_{\text{OH},x} \exp(\lambda_{1x}t)$ where $\lambda_{1A} = 55.4 \text{ s}^{-1}$ and $\lambda_{1B} = 25.3 \text{ s}^{-1}$.

Figure 12: Simulated OH loss terms α and β as function of time for stoichiometric mixture of propane at $T_0 = 650$ K and $P_0 = 10$ bar under adiabatic conditions. The dashed grey line indicates the time when OQ'OOH peaks in the simulation.

Figure 13: Comparison of the first-stage ignition delays ($\tau_{\text{OQOOHpeak}}$) obtained from 1) the time of the inflection point in the temperature profile from full model simulation, 2) the time of the OQOOH peak in the full model simulation 3) the time for $f_{\text{OH}} = 1$ predicted from the solution to equations (31)-(36) and 4) the time for $f_{\text{OH}} = 1$ predicted by equation (41) for adiabatic, isochoric simulations of stoichiometric mixtures of propane and air, $P_0 = 10$ bar.

stage ignition delay predicted by Eqs. (50)-(52), for different n-alkanes with initial conditions $P_0 = 10$ bar and $\Phi = 1$ in air. The parameters are tabulated in Table 2 and

Table 3. The value of γ is uncertain for fuels larger than propane, here we plot results using $\gamma = 1$ and $\gamma = 0.7$.