JOURNAL OF PROPULSION AND POWER
Vol. 20, No. 3, May–June 2004

Ignition Delays of Heptane/O_2/Ar Mixtures in the 1300–1600 K Temperature Range

Bruno Imbert,* Laurent Catoire,† Nabiha Chaumeix,‡ and Claude Paillard§
Centre National de la Recherche Scientifique, and University of Orleans, F-45071 Orléans CEDEX 2, France

Ignition time measurements of lean, stoichiometric, and rich n-heptane/oxygen/argon mixtures have been studied behind reflected shock waves in the temperature range 1300–1600 K and pressure range 2–4 atm. The experimental data were compared to previously published results and have been found to be consistent with them. The experimental data were compared to ignition delay predicted using some of the kinetic models available in the literature. Discrepancies have been interpreted kinetically, thus leading to a slightly modified detailed kinetic model able to predict accurately high-temperature ignition delay such as encountered in the heptane/oxygen detonation wave.

Introduction

THE self-sustained detonation regime of heptane-air gaseous mixtures has never been studied. However, recent study reports that these mixtures can exhibit detonation-like regimes.[1] This is of interest, fundamentally, for safety reasons and also for applications such as the pulsed-detonation engines (PDE) because heptane is a product of decomposition of some fuels considered for applications because some aviation fuels and other propellants include fraction of liquid heptane and also because heptane is a reference fuel for engine knock rating in spark-ignition engines. Detonation properties of hydrocarbon/air or hydrocarbon/O_2 gas mixtures have been reported by several authors: Tieszen et al.,[2] Smirnov and Tyurnikov,[3] Sochet et al.,[4] Nettleton,[5] Beeson et al.,[6] Gelfand et al.,[7] Austin and Shepherd,[8] and Kaneshige and Shepherd,[9] among others. The Chapman–Jouguet detonation velocity can be calculated easily, but the detonation sensitivity can only be known through experiments because the Zeldovich, von Neumann, Döring (ZND) detonation model does not predict the proportionality factor A between the cell size λ and Δ, the induction distance in the detonation wave. The estimation of the induction distance Δ needs, in the frame of the ZND detonation model or a simplified form of it, reliable estimations of the high-temperature ignition delays, in the detonation wave, at the von Neumann temperature and pressure. Typical von Neumann temperature for a stoichiometric heptane/air mixture is 1540 K. These ignition delays at the von Neumann conditions can be estimated by using empirical ignition delays correlations (but in that case the chemistry is frozen) or, more efficiently, by using detailed kinetic model. Several investigators have studied high-temperature ignition delays of heptane/O_2/Ar mixtures.[10–15] Several ignition delays correlations have been reported to represent the experimental results.[11–13] Horning et al.[12] discussed recently all of these correlations and their respective interests. As well, several kinetic models, detailed, semidetailed, global or reduced,[16–27] have been proposed to explain the ignition delays of heptane/O_2 based mixtures. The aims of this study are as follows: 1) to obtain new experimental high-temperature ignition delay data; 2) to enlarge the limit of validity of the existing empirical correlations; 3) to compare these new experimental data with the predictions of some of the existing chemical kinetic models, detailed or reduced; 4) to suggest some kinetic ways to improve the predictive ability of the existing chemical kinetic models for accurate estimations of the ignition delays in the detonation wave; and 5) to perform a preliminary experimental study of the detonation properties of heptane/oxygen mixtures to assess both the interest of the present study and the possibility to use heptane for PDE engines.

Experimental Setup

Heptane is a liquid with a relatively low vapor pressure. Gaseous mixtures are prepared by the partial pressure method at ambient temperature. Liquid heptane (provided by ACROS ORGANICS) has a purity of 99%. The operating stainless-steel shock tube (78 mm i.d.) has a 1-m-long driver section filled with helium and a test section, about 4.50 m long, in which the test mixtures are introduced at ambient temperature T_1 and total pressure P_1. Several diagnostic instruments are located in the second half of the driven section: four piezoelectric pressure transducers, mounted flush with the inside wall, for shock wave and detonation velocity measurements, and a pair of calcium fluoride optical windows mounted at 10 mm from the end of the tube, associated with a monochromator, for following OH emission at 306 nm from which the ignition delays are deduced. The values of $\Delta T/T$ and $\Delta P/P$ behind the reflected shock wave are estimated to be about 1.5 and 2%, respectively. The overall uncertainty for the ignition delays is $\pm 10\ \mu s$.

Results and Discussion

Qualitative and Quantitative Comparisons Between Experimental Ignition Delays Presented Here and Literature

About 70 ignitions delays have been obtained in the 1293–1597 K temperature range and in the 269–717 kPa pressure range for equivalence ratios equal to 0.5, 1, and 1.5. The proportions of heptane in the mixture are 0.08-1 mol%. Most of the experimental points are around 450 kPa. Mixtures studied are given in Table 1. About all of the ignition delays τ determined experimentally are given in Fig. 1. For this figure, the ignition delays are defined as the time interval between the passing of the reflected shock and the initial rapid rise of OH emission (see Fig. 2). Other criteria exist (see following discussion and Figs. 2 and 3). Figure 1 also shows the effect of temperature, pressure, equivalence ratio, and mole fractions on the ignition delays. These effects are as observed by others. These delays can be expressed, by least-squares multiregression, without constraint, as

$$\tau(\mu s) = 1.206 \times 10^{-5}[\text{Heptane}]^{+0.92}[O_2]^{-1.41}[\text{Ar}]^{+0.09}e^{26922/T} \tag{1}$$

with an average accuracy of 25%. This expression has been obtained with the ignition delays defined against the initial rapid rise

---

Received 14 May 2003; revision received 27 November 2003; accepted for publication 27 November 2003.

*Ph.D. Student, Laboratoire de Combustion et Systèmes Réactifs, 1C, avenue de la Recherche Scientifique.

†Assistant Professor, Laboratoire de Combustion et Systèmes Réactifs, 1C, avenue de la Recherche Scientifique.

‡Senior Researcher, Laboratoire de Combustion et Systèmes Réactifs, 1C, avenue de la Recherche Scientifique.

§Professor, Laboratoire de Combustion et Systèmes Réactifs, 1C, avenue de la Recherche Scientifique.

Table 1 Heptane/oxygen/Ar mixtures studied in this work

Mixture	Mol% heptane	Mol% oxygen	Mol% argon	Equivalence ratio	Temperature range, K	Pressure range, bars	Number of points
A	0.08	0.92	99	1	1470–1593	4.03–4.89	27
B	0.6	4.4	95	1.5	1430–1597	4.09–4.78	13
C	0.42	4.58	95	1	1379–1480	4.48–4.87	10
D	0.22	4.78	95	0.5	1397–1497	4.14–4.58	5
E	0.42	4.58	95	1	1408–1521	2.55–2.85	7
F	0.42	4.58	95	1	1377	7.17	1
G	0.2	2.1	97.7	1	1422	4.59	1
H	1	11	88	1	1293–1380	4.60–4.86	5

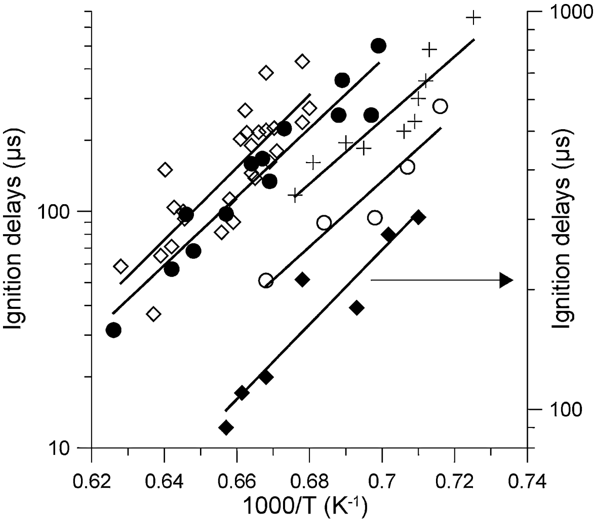


Fig. 1 Heptane/oxygen/argon ignition delays obtained experimentally (mixtures A–E). Ignition delays are defined here against the initial rapid rise of OH emission: ——, best fit; ◆ and corresponding best fit are to be read on the right axis. Other symbols and best fits are to be read on the left axis: ◇, mixture 0.0008 heptane + 0.0092 O_2 in Ar, $\phi = 1$, $4.03 < P$ (bars) < 4.89; ●, mixture 0.006 heptane + 0.044 O_2 in Ar, $\phi = 1.5$, $4.09 < P$ (bars) < 4.78; +, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $4.48 < P$ (bars) < 4.87; ○, mixture 0.0022 heptane + 0.0478 O_2 in Ar, $\phi = 0.5$, $4.14 < P$ (bars) < 4.58; and ◆, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $2.55 < P$ (bars) < 2.85.

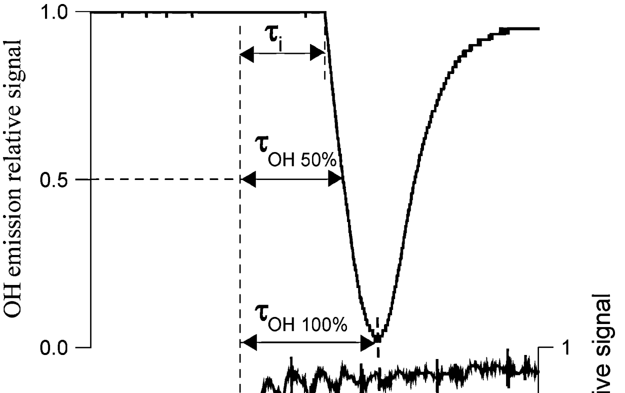


Fig. 2 Simultaneous records of OH emission signal and pressure signals. Mixture: 0.08 mol% heptane + 0.92 mol% O_2 + 99 mol% Ar, initial $T = 1593$ K, and initial $P = 4.33$ bars. τ_p, not measurable; $\tau_i = 58$ μs; τ_{OH} 50% = 70 μs; and τ_{OH} 100% = 94 μs.

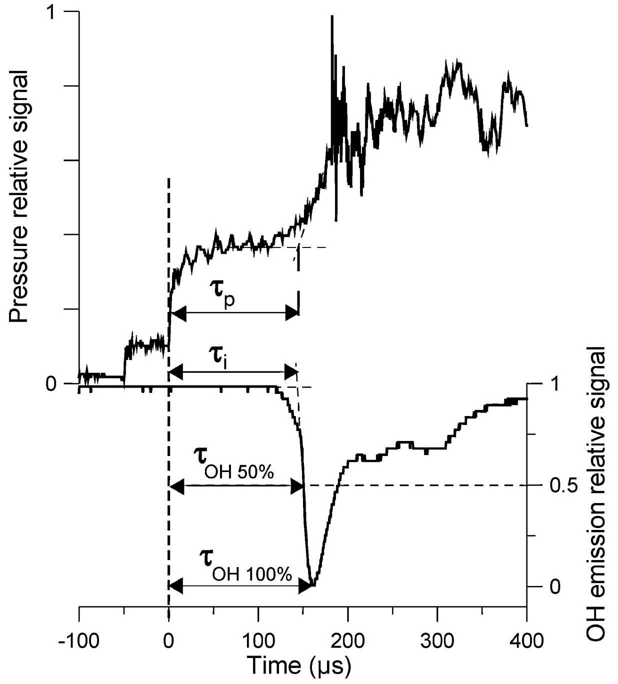


Fig. 3 Simultaneous records of OH emission signal and pressure signals. Mixture: 1 mol% heptane + 11 mol% O_2 + 88 mol% Ar; initial $T = 1354$ K; and initial $P = 4.86$ bars. τ_p, ignition delay defined against the pressure profile = 150 μs; τ_i, ignition delay defined against the initial rapid rise in OH emission = 145 μs; τ_{OH} 50%, ignition delay defined = 155 μs; and τ_{OH} 100%, ignition delay defined as = 165 μs.

of OH emission for all of the experiments (mixtures A–G), except five of them for which the ignition delay has been defined against the initial rapid rise of pressure signal (mixture H). However, experiments show that, for the less-diluted mixtures, both definitions lead to about the same ignition delay value (see Fig. 3). The concentrations are in moles m^{-3}. The units of T and τ are Kelvins and microseconds, respectively. The corresponding best-fit linear correlation (full line) is given in Fig. 4 with the experimental values (symbols). This correlation is given here mostly for its practical interest in its validity ranges. Outside the validity ranges of Eq. (1), the use of a detailed kinetic model is recommended. As usual for hydrocarbons/oxygen/diluant mixtures, correlations exhibit generally a small positive power dependence on the concentration of argon. Previous ignition time correlations are given in Table 2. Our correlation is qualitatively more consistent with the one proposed by Horning et al.[12] However, the individual value of each ignition delay cannot be compared quantitatively as is with the value estimated from the expression given in Table 2 because the ignition delays have been defined, in some occasions, against other criteria than the one taken here. Horning et al.[12] defined their ignition delays against the peak CH emission signal as either the maximum rate increase in the CH emission signal or the maximum of the CH emission signal. It is probably the case that both definitions lead to about the same value of the ignition delay. The question whether the peak

Table 2 Previous ignition delay data (concentrations are in moles per cubic centimeter)

Correlation	P, atm	T, K	Molar fraction of heptane	Equivalence ratio	References
$\tau(s) = 3.2 \times 10^{-12}[\text{Heptane}]^{+0.20}[O_2]^{-1.10}[\text{Ar}]^{+0.60}\, e^{17765/T}$	2–12	1100–1700	0.5–3	0.5–2	13
$\tau(s) = 6.76 \times 10^{-15}[\text{Heptane}]^{+0.40}[O_2]^{-1.20}[\text{Ar}]^{0}\, e^{20211/T}$	4–8	1200–1400	0.2	0.5, 1	11
$\tau(s) = 4.54 \times 10^{-14}[\text{Heptane}]^{+0.95}[O_2]^{-1.58}[\text{Ar}]^{0}\, e^{22647/T}$	1–6	1300–1700	0.2–1.8	0.5–2	12

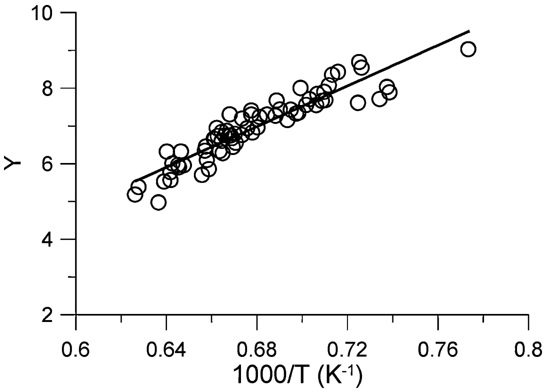


Fig. 4 Best-fit correlation obtained for experimental ignition delays τ_i in heptane/oxygen/Ar (mixtures A–H). $Y = \ell n$ (τ_i [Heptane]$^{-0.92}$ [O$_2$]$^{+1.41}$ [Ar]$^{-0.09}$).

CH emission signal and the peak OH emission signal lead to the same ignition delay value remains questionable. Nothing has been found in the literature concerning the experimental comparisons of the CH and OH emission signals. Studies performed by Davidson et al.[28] with iso-octane/oxygen mixtures show that the maximum in CH emission correspond approximately to about 50% of the maximum OH absorption. On pressure profile and CH emission signal profile given by Horning et al.[12] for ignition delays in butane/O_2/ar mixtures, it appears that the abrupt rise in pressure is consistent with the initial rapid rise in CH emission. This tends to show that in fact the initial rapid rise in CH emission and the initial rapid rise in OH emission should occur at about the same time. It is then possible to compare the ignition delays defined against the initial rapid rise in OH emission presented here with the corresponding estimated values according to the expression given by Horning et al.[12] (see Table 2).

Figure 5 shows that the experimental ignition delays defined against the initial rapid rise in OH emission are consistent with the predicted ignition delays with the expression of Horning et al.[12] Figure 5 includes the ignition delays obtained for the highly diluted mixture (mixture A) that was not considered for the establishment of the expression of Horning et al.[12] The agreement is generally better at higher temperatures than at lower temperature. The statement that the initial rapid rises in CH emission and in OH emission occur about at the same time appears to be reliable. The average activation temperature obtained in this study is around 27,000 K. This results in an activation energy of about 53 kcal mol^{-1}. Horning et al.[12] found an activation energy of 45 kcal mol^{-1}, whereas the correlations of Colket and Spadaccini,[11] Burcat et al.,[13] and Vermeer et al.[10] exhibit activation energies of 40.16 kcal mol^{-1}, 35.3 kcal mol^{-1} and 46.35 kcal mol^{-1}, respectively. The explanations for the discrepancy lead in the facts that the highly diluted experimental points (mixture A) are consistent with an activation energy of about 70 kcal mol^{-1} (see Table 3). The mixture 0.08% heptane + 0.9% O_2 in Ar (mixture A) is not included in the previously reported correlations for which the lowest amount in heptane was 0.2%. Once mixture A removed (42 remaining points), it is also possible to fit conveniently (average accuracy of 24%) the present ignition delays with an expression for which all of the exponents and the activation energy are constrained with the values deduced by Horning et al., that is, 0.95 for the exponent on heptane, −1.58 for the exponent on O_2, 0 for the exponent on argon and 22647 K for the activation temperature (see Fig. 6).

Table 3 Comparisons between activation energies experimentally observed and deduced from the kinetic models of Curran et al. and Golovitchev for mixtures A–E

Mixture	Experimental activation energy E, kcal mol^{-1}	Computed E with the model of Curran et al., kcal mol^{-1}	Computed E with the model of Golovitchev, kcal mol^{-1}
A	70.0	64.8	34.1
B	66.1	42.6	27.5
C	61.5	45.4	28.6
D	63.4	49.7	34.1
E	42.9	46.5	30.3

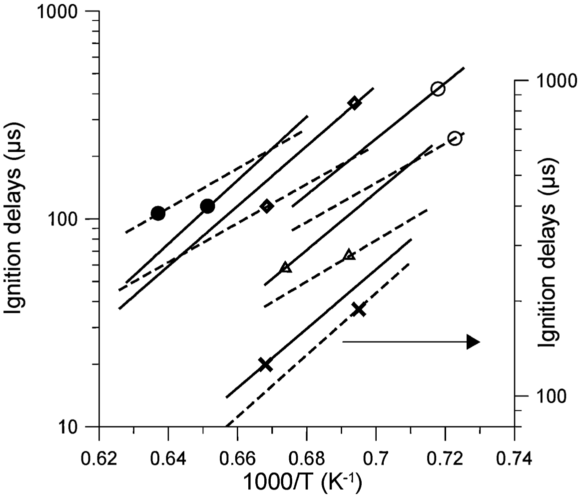


Fig. 5 Comparison between experimental ignitions delays (——, best fit) and predicted ignition delays (- - - -, best fit) with the expression of Horning et al.[12]; symbol and corresponding best fits are to be read on the right axis; ✖ and corresponding best fits are to be read on the left axis: ●, mixture 0.0008 heptane + 0.0092 O_2 in Ar, $\phi = 1$, $4.03 < P$ (bars) < 4.89; ◇, mixture 0.006 heptane + 0.044 O_2 in Ar, $\phi = 1.5$, $4.09 < P$ (bars) < 4.78; ○, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $4.48 < P$ (bars) < 4.87; △, mixture 0.0022 heptane + 0.0478 O_2 in Ar, $\phi = 0.5$, $4.14 < P$ (bars) < 4.58; and ✖, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $2.55 < P$ (bars) < 2.85.

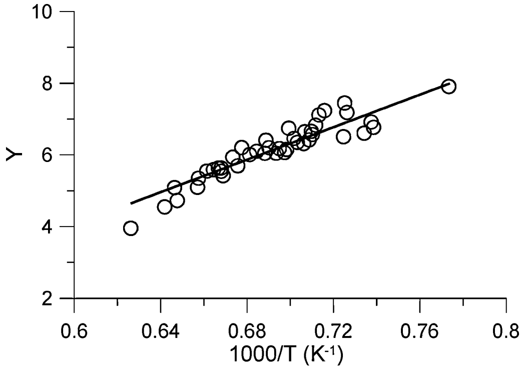


Fig. 6 Correlation obtained with the ignition delays presented here for mixtures B–H by constraining the activation energy and all of the exponents on concentrations to the one observed by Horning et al. $Y = \ell n$ (τ_i [Heptane]$^{-0.95}$ [O$_2$]$^{+1.58}$ [Ar]^{0}).

Comparison Between the Experimental and Computed Ignition Delays

Several kinetic models, detailed, semi-empirical or more and less reduced,[16–27] have been proposed to explain the ignition sequence of heptane/oxygen/diluent mixtures. The agreement between ignition delays and model predictions at high temperature (roughly above 1300 K) are found to be poor (with the experiments of Vermeer et al.[10]) or good (with the experiments of Coats and Williams) by Curran et al.[16] with their detailed kinetic model. Since then, Curran et al. modified and updated their heptane/oxygen/argon kinetic model.[29] This result in a better agreement between the calculations and the experiments of Vermeer et al.[10] The experiments of Burcat et al.[13] and Colket and Spadaccini[11] have not been considered by Curran et al.[16,29] Horning et al.[12] found a good agreement (generally better than a factor of two) between their high-temperature experimental data and the predictions of the model of Curran et al. Horning et al.[12] also found good agreement between their high-temperature experimental data and the predictions of the model of Lindstedt and Maurice,[22] although this kinetic model was not initially devoted to the simulations of ignition delays. The predictions of the semi-empirical model of Held et al.[19] are less accurate, but the agreement between predictions and the high-temperature experiments of Horning et al.[12] is generally better than a factor of three, and Colket and Spadaccini[11] found that the agreement between experimental data (Refs. 10, 11, 13, etc.) and the predictions is generally better than a factor of two. The agreement is generally worse when reduced kinetic models are used. Montgomery et al.[17] show that more than about 25 species are needed to simulate high-temperature n-heptane/O_2 ignition delays. The reduced kinetic model of Kim et al.[18] and the reduced kinetic model of Rente et al.[25] have been validated only with ignition delays obtained in the Negative Temperature Coefficient (NTC) region, and therefore further validation is needed at high-temperature.

In this study, our experimental data are compared to the predictions of the updated model of Curran et al.[16,29] and to the predictions of the reduced models of Rente et al.[25] and Montgomery et al.[17] Several other models can be considered, but it is beyond the scope of this study to decide which of the existing models is the most reliable. Moreover, Horning et al.[12] addressed this question recently. The model of Curran et al. is here considered as it is the most detailed one, and also the most widely validated, and therefore the most interesting to be confronted to new experimental data. Moreover, an other interesting experimental feature predicted by the model of Curran et al. is the high-temperature two-step ignition process of heptane. Figure 7 shows that a two-step ignition is observed at high temperature. According to Peters et al.,[27] in the high-temperature regime there should be no two-step ignition process (and therefore no first-stage ignition). Indeed, for the mixtures containing more than 0.2 mol% heptane in the mixture no first-stage ignition is observed in this study (as observed by others for such mixtures), and this first-stage ignition is only observed here for mixture containing 0.08 mol% heptane. Although it is beyond the scope of the present paper, a chemical kinetic interpretation of this phenomenon is possible as, interestingly, the model of Curran et al. reproduces this phenomenon, at least qualitatively, whereas the reduced model of Rente et al.[25] does not reproduce this observation (see Fig. 8). The model of Montgomery et al.[17] also reproduces these experimental features, but the second-stage ignition appears to be considerably delayed (see Fig. 8). Therefore the model of Curran et al. will be considered to study further the chemical kinetics of the high-temperature ignition of the heptane/oxygen system.

Nevertheless, the reduced model of Montgomery et al.[17] remains interesting because it is devoted to the high-temperature chemistry, the one of interest here. The model consists of 105 species and 808 reactions and has been found to predict correctly some of the experimental ignition delays of Vermeer et al.[10]

The reduced kinetic model of Rente et al.[25] is also interesting as it is obtained from the detailed kinetic model of Curran et al. As it consists of 60 species and 602 reactions, it can be considered, at least tentatively, as a reliably predictive reduced kinetic model following the statement of Montgomery et al.[17] concerning the number of species to be included in the reduced kinetic model. The SENKIN code[30] was used to compute the kinetic models. In all computations, the mixture is assumed to be at a constant volume over its reaction time. Comparisons between experiments and models are given in Table 4 for mixture H and in Figs. 9–11 for mixtures A–G. Basically, the updated model of Curran et al.[16,29] predicts ignition delays a

Table 4 Comparison between experimental ignition delays τ_{exp} (mixture H), predicted ignition delays τ_{pred} with the expression of Burcat et al.,[13] and computed ignition delays τ_{comp} by using the detailed kinetic model of Curran et al. (mixture: 1 mol% heptane + 11 mol% O_2 + 88 mol% Ar)

Temperature, K	Pressure, bars	τ_{exp}, μs	τ_{pred}, μs	τ_{comp}, μs
1354	4.86	187	136	128
1356	4.76	218	134	127
1362	4.60	161	128	122
1380	4.70	145	108	97
1293	4.73	582	251	284

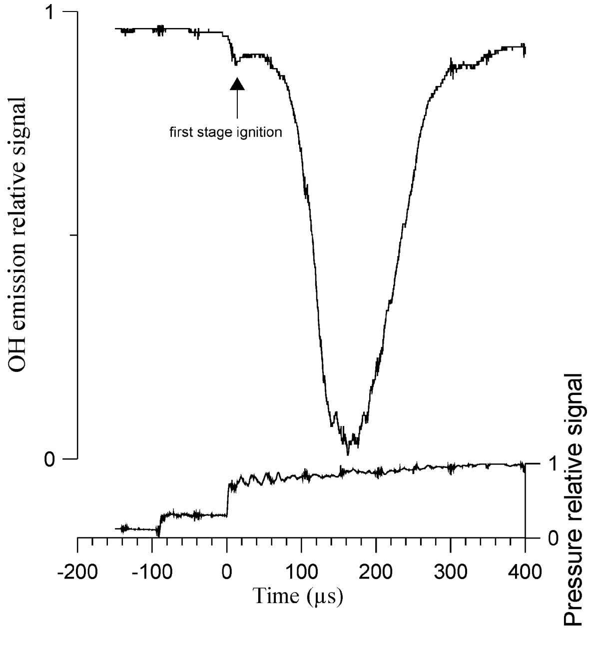


Fig. 7 OH emission signal showing a two-step ignition for high-temperature heptane/oxygen/argon ignition delays. Mixture: 0.08 mol% heptane + 0.92 mol% O_2 in Ar; $T = 1518$ K; and $P = 4.60$ bars.

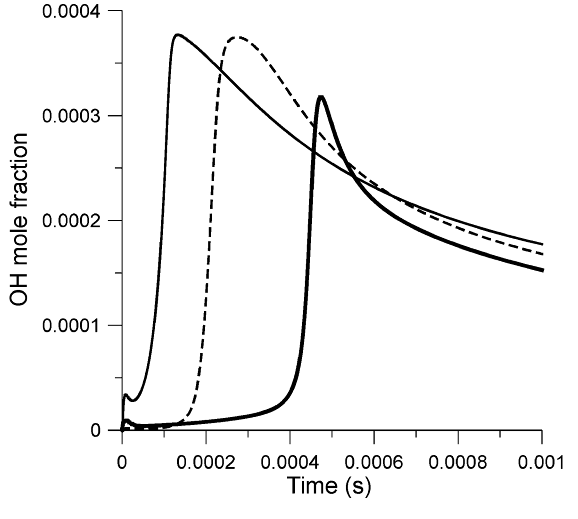


Fig. 8 Comparison between OH profiles predicted by different models. Mixture: 0.08 mol% heptane + 0.92 mol% O_2 in Ar; initial $T = 1518$ K; and initial $P = 4.60$ bars: ——, detailed kinetic model of Curran et al.; – – –, reduced kinetic model of Golovitchev; and ▬, reduced kinetic model of Montgomery et al.

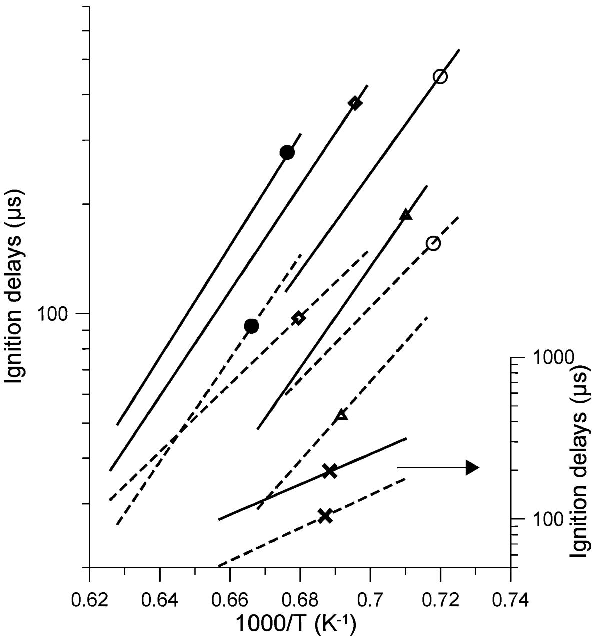


Fig. 9 Comparison between experimental ignitions delays (——, best fit) and computed ignition delays (– – –, best fit) with the kinetic model of Curran et al.: ●, mixture 0.0008 heptane + 0.0092 O_2 in Ar, $\phi = 1$, $4.03 < P$ (bars) < 4.89; ◆, mixture 0.006 heptane + 0.044 O_2 in Ar, $\phi = 1.5$, $4.09 < P$ (bars) < 4.78; ○, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $4.48 < P$ (bars) < 4.87; △, mixture 0.0022 heptane + 0.0478 O_2 in Ar, $\phi = 0.5$, $4.14 < P$ (bars) < 4.58; and ✖, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $2.55 < P$ (bars) < 2.85.

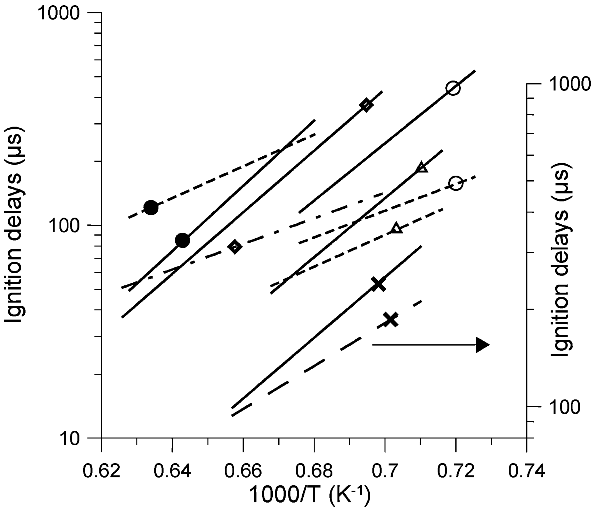


Fig. 10 Comparison between experimental ignitions delays (——, best fit) and computed ignition delays (– – –, best fit) with the reduced kinetic model of Golovitchev: ●, mixture 0.0008 heptane + 0.0092 O_2 in Ar, $\phi = 1$, $4.03 < P$ (bars) < 4.89; ◆, mixture 0.006 heptane + 0.044 O_2 in Ar, $\phi = 1.5$, $4.09 < P$ (bars) < 4.78; ○, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $4.48 < P$ (bars) < 4.87; △, mixture 0.0022 heptane + 0.0478 O_2 in Ar, $\phi = 0.5$, $4.14 < P$ (bars) < 4.58; and ✖, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $2.55 < P$ (bars) < 2.85.

factor of two (average value) shorter than observed for all of the mixtures whatever the temperature and pressure are in the validity ranges of the experiments presented here (see Fig. 9 and Table 4). This trend is also noticeable with the experiments performed by Horning et al.[12] (see Figs. 9–12 of the paper of Horning et al.). This led us to the conclusion that this systematic underprediction might be interpreted kinetically. It might be that the extrapolation of some rate constants from the low temperature region ($T < 1100$ K) up to the 1400–1600 K temperature region has to be reconsidered.

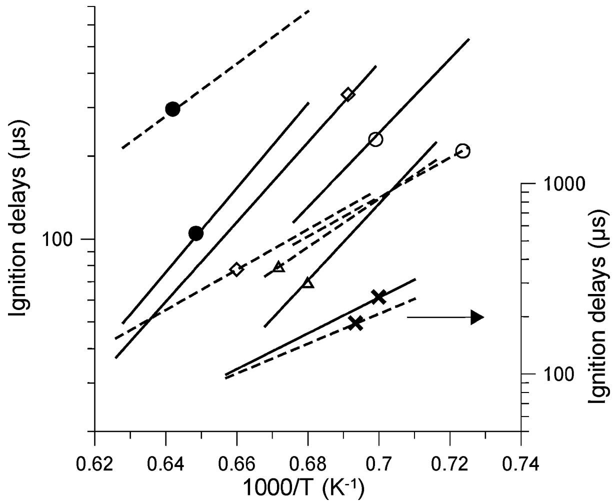


Fig. 11 Comparison between experimental ignitions delays (——, best fit) and computed ignition delays (– – –, best fit) with the reduced kinetic model of Montgomery et al.: ●, mixture 0.0008 heptane + 0.0092 O_2 in Ar, $\phi = 1$, $4.03 < P$ (bars) < 4.89; ◆, mixture 0.006 heptane + 0.044 O_2 in Ar, $\phi = 1.5$, $4.09 < P$ (bars) < 4.78; ○, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $4.48 < P$ (bars) < 4.87; △, mixture 0.0022 heptane + 0.0478 O_2 in Ar, $\phi = 0.5$, $4.14 < P$ (bars) < 4.58; and ✖, mixture 0.0042 heptane + 0.0458 O_2 in Ar, $\phi = 1$, $2.55 < P$ (bars) < 2.85.

The predictions of the model of Rente et al.[25] are better on average when comparing individual values as, except some ignition delays, most of them are within a factor of two (see Fig. 10). However, when comparing the activation energies for each mixture the situation appears more complex as the activation energy predicted by the model of Curran et al. is closer to the experimental ones (see Table 3). This is probably because some unimportant reactions for the NTC region, logically removed by Golovitchev, are probably important at high temperature. The predictions of the model of Montgomery et al. are quite comparable with the predictions of Golovitchev et al. except for the highly diluted mixture (0.08 mol% heptane) for which the predicted ignition delays are too long (see Fig. 11).

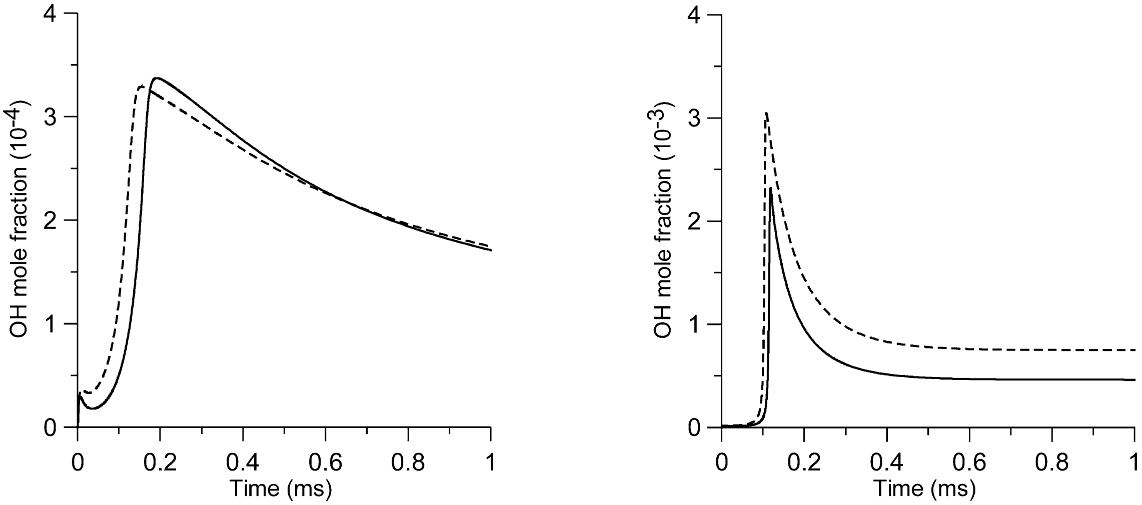
Sensitivity Analyses

A reduced kinetic model has been built from the model of Curran et al. to simulate the OH profiles of the high-temperature oxidation chemistry of heptane/oxygen mixtures. It consists of 70 species and 243 reactions. The agreement between the model of Curran et al. and the reduced model is shown in Fig. 12 for the OH profile for seven mixtures (mixtures A–E, mixture H, and one of the mixtures studied by Vermeer et al.). The reduced model also simulates the two-step ignition just described. It is however not stated here that this reduced kinetic model is a validated kinetic model for all of the species profiles. To tentatively explain the discrepancy between our experimental results and the predictions of the model of Curran, a first-order sensitivity analysis has been performed against OH radicals to focus on the reactions of importance for the OH profiles for the mixtures of Fig. 12. This reduced kinetic model is used here for the sensitivity analysis because such a study is too computationally expensive with the detailed kinetic model of Curran et al. As observed for hydrocarbons/oxygen ignition, $H + O_2 = O + OH$ (R1) exhibits the greatest sensitivity for all mixtures whatever the equivalence ratio, the dilution, the temperature, and the pressure. Then sensitivities have to be examined for each class of mixtures separately. Other reactions than (R1), which exhibit significant sensitivity against OH radicals, are reported in Table 5 for various mixtures studied here or studied by Vermeer et al.

Once the reactions sensitive to the OH radicals are known, rate constants and their respective uncertainty factors have to be considered to find a set of rate constants able to explain all of the experimental results. In fact, a huge number of sets can be found, and approaches have to be followed to limit the search.

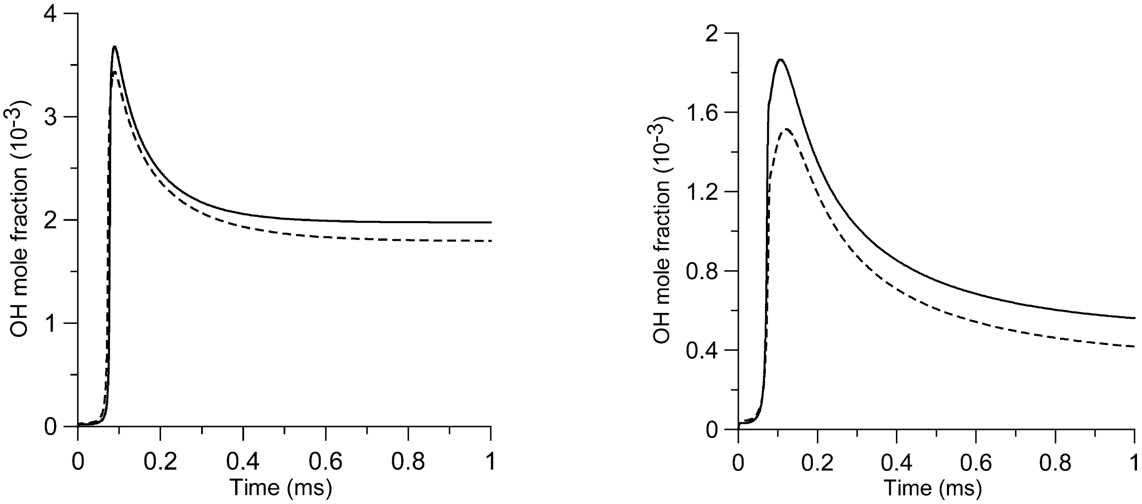
Table 5 Sensitivity analyses against OH radicals [for each mixture, (R1) is the most sensitive reaction]

Mixtures	Reactions	
Mixture studied by Vermeer et al.[10]	$C_2H_3 + O_2 = CH_2CHO + O$	(R2)
and less diluted mixtures studied here	$CH_3 + HO_2 = CH_3O + OH$	(R3)
[mixture H (see Table 1)]	$C_2H_4 + OH = C_2H_3 + H_2O$	(R4)
	$NC_7H_{16} + H = C_7H_{15} - 2 + H_2$	(R5)
	$NC_7H_{16} + H = C_7H_{15} - 3 + H_2$	(R6)
	$CH_3 + CH_3 + M = C_2H_6 + M$	(R7)
	$C_2H_3 + O_2 = C_2H_2 + HO_2$	(R8)
Rich mixture studied here (mixture B)	(R2), (R3), (R4), (R5), (R8)	
	$C_3H_6 = C_2H_3 + CH_3$	(R9)
	$HCO + M = H + CO + M$	(R10)
	$C_3H_6 = C_3H_5 - a + H$	(R11)
Lean mixture studied here (mixture D)	(R2), (R3), (R4)	
	$HCO + M = H + CO + M$	(R10)
	$C_3H_6 = C_3H_5 - a + H$	(R11)
	$HCO + O_2 = CO + HO_2$	(R12)
	$HO_2 + OH = H_2O + O_2$	(R13)
	$OH + H_2 = H + H_2O$	(R14)
Stoichiometric mixtures studied here	(R2) (R9) (R11) (R14)	
99 mol% Ar (mixture A)	$CH_3 + H + M = CH_4 + M$	(R15)
	$C_2H_4 + O = CH_3 + HCO$	(R16)
	$CH_2(S) + O_2 = CO + OH + H$	(R17)
	$CH_3 + OH = CH_2(S) + H_2O$	(R18)
Stoichiometric mixtures studied here	(R2), (R3), (R4), (R8), (R10),	
95 mol% Ar (mixtures C and E)	(R11), (R12), (R13)	



a) 0.08 mol% heptane + 0.92 mol% O_2 in Ar, $T = 1475$ K, $P = 4.43$ bar (mixture A)

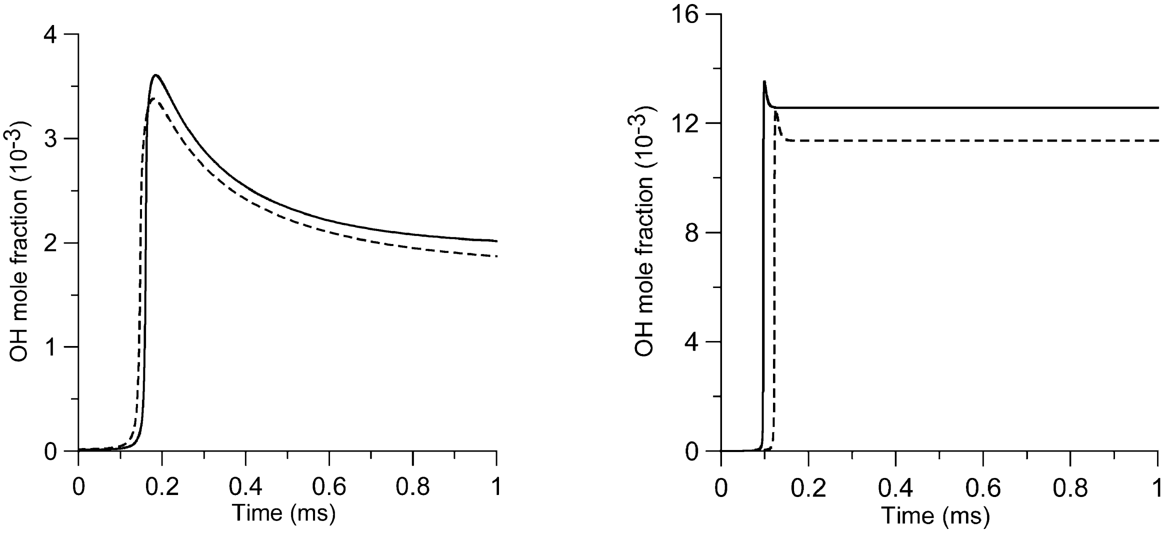
b) 0.6 mol% heptane + 4.4 mol% O_2 in Ar, $T = 1453$ K, $P = 4.09$ bar (mixture B)



c) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, $T = 1449$ K, $P = 4.49$ bar (mixture C)

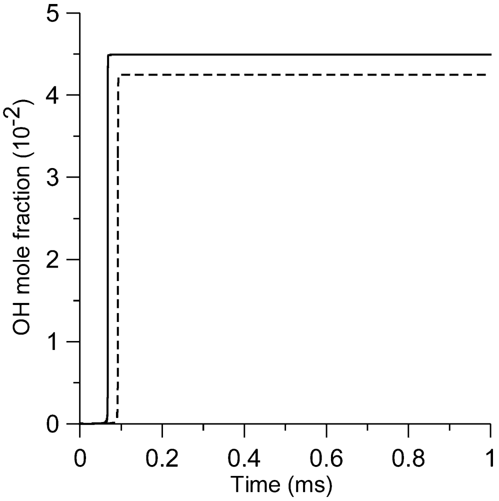
d) 0.22 mol% heptane + 4.78 mol% O_2 in Ar, $T = 1415$ K, $P = 4.30$ bar (mixture D)

Fig. 12 Comparison between the computed ignition delays with the detailed kinetic model of Curran et al. (——) and the reduced kinetic model (– – –) established for this study to allow computationally efficient sensitivity analyses.



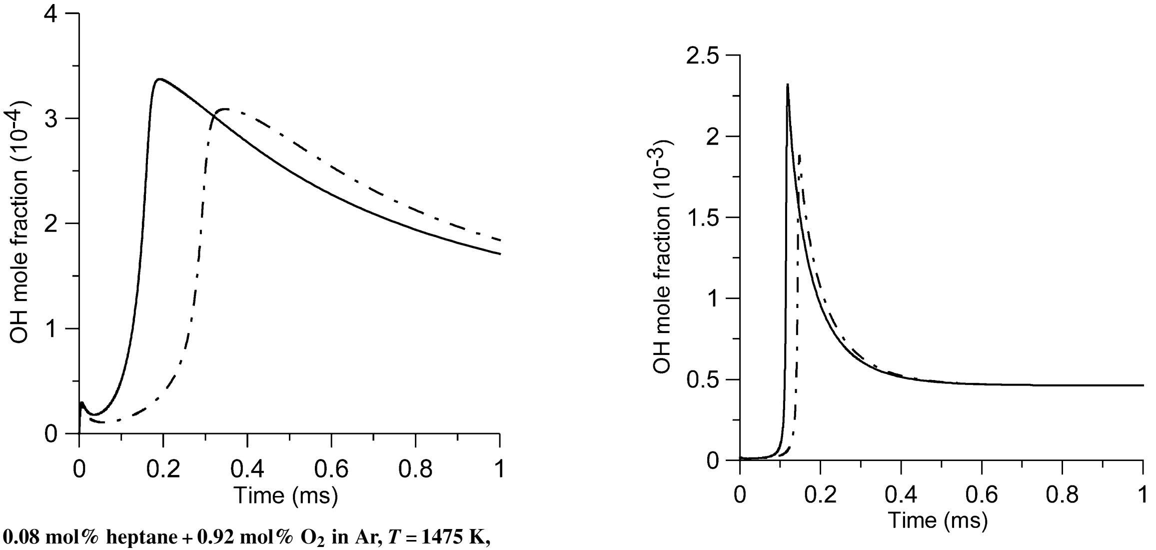
e) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, $T = 1408$ K, $P = 2.70$ bar (mixture E)

f) 1 mol% heptane + 11 mol% O_2 in Ar, $T = 1380$ K, $P = 4.70$ bar (mixture H)



g) 2.5 mol% heptane + 27.5 mol% O_2 in Ar, $T = 1415$ K, $P = 2.31$ bar (mixture of Vermeer et al.)

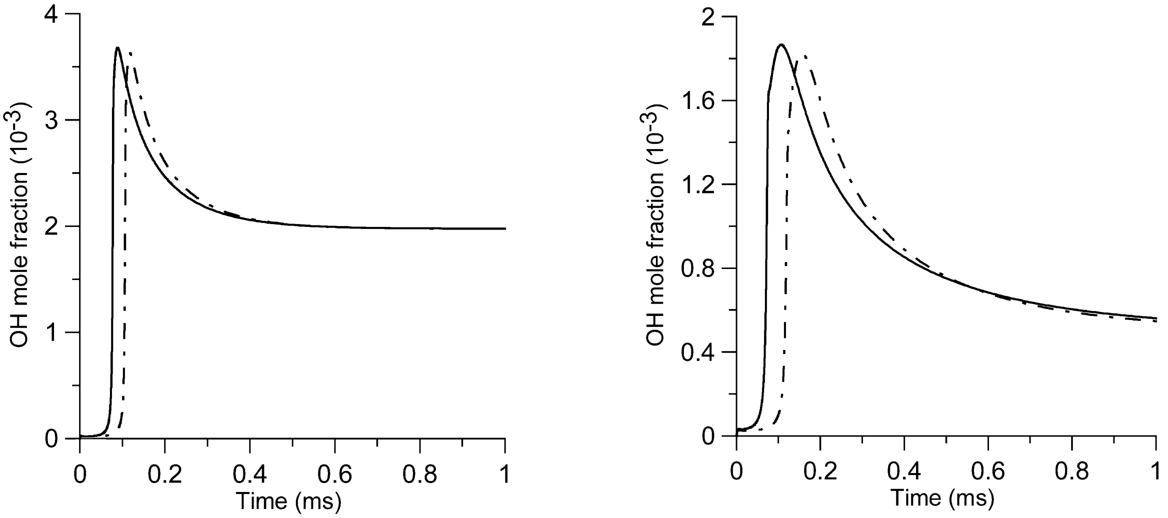
Fig. 12 Comparison between the computed ignition delays with the detailed kinetic model of Curran et al. (——) and the reduced kinetic model (– – –) established for this study to allow computationally efficient sensitivity analyses (continued).



a) 0.08 mol% heptane + 0.92 mol% O_2 in Ar, $T = 1475$ K, $P = 4.43$ bar, $\tau_{\mathrm{exp}} = 238$ μs, $\tau_{\mathrm{curran}} = 126$ μs, $\tau_{\mathrm{curranmod1}} = 258$ μs (mixture A)

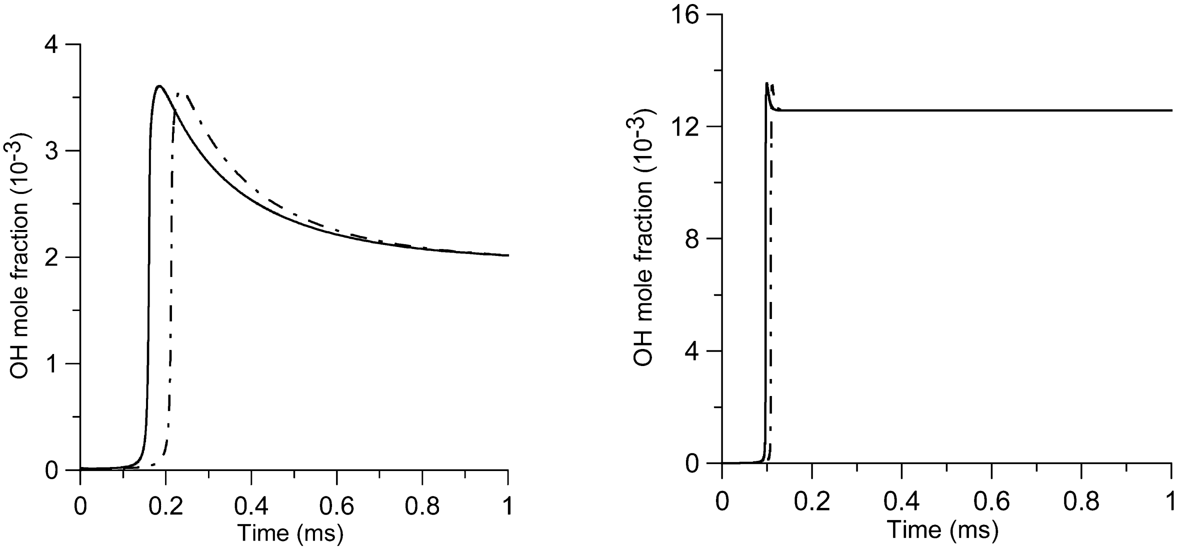
b) 0.6 mol% heptane + 4.4 mol% O_2 in Ar, $T = 1453$ K, $P = 4.09$ bar, $\tau_{\mathrm{exp}} = 255$ μs, $\tau_{\mathrm{curran}} = 110$ μs, $\tau_{\mathrm{curranmod1}} = 142$ μs (mixture B)

Fig. 13 Comparison between predicted ignition delays τ_{curran} with the detailed kinetic model of Curran et al. (——) and predicted ignition delays $\tau_{\mathrm{curranmod1}}$ (– – –) with the detailed kinetic model of Curran et al. for which rate constants of reactions (R10), (R12), (R13), (R15), and (R17) have been comprehensively changed (see text for details). Experimental ignition delays are noted τ_{exp}.



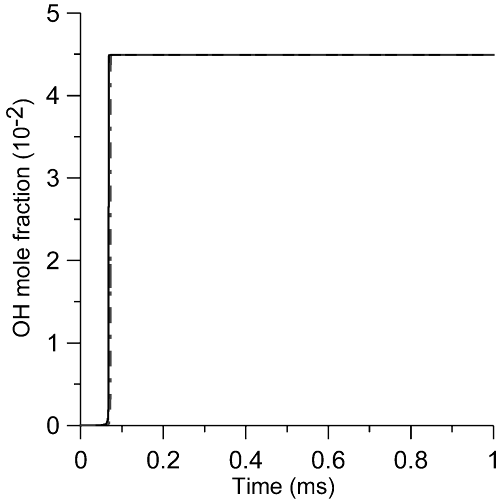
c) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, $T = 1449$ K, $P = 4.49$ bar, $\tau_{\mathrm{exp}} = 195$ μs, $\tau_{\mathrm{curran}} = 77$ μs, $\tau_{\mathrm{curranmod1}} = 105$ μs (mixture C)

d) 0.22 mol% heptane + 4.78 mol% O_2 in Ar, $T = 1415$ K, $P = 4.30$ bar, $\tau_{\mathrm{exp}} = 154$ μs, $\tau_{\mathrm{curran}} = 70$ μs, $\tau_{\mathrm{curranmod1}} = 117$ μs (mixture D)



e) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, $T = 1408$ K, $P = 2.70$ bar, $\tau_{\mathrm{exp}} = 304$ μs, $\tau_{\mathrm{curran}} = 160$ μs, $\tau_{\mathrm{curranmod1}} = 212$ μs (mixture E)

f) 1 mol% heptane + 11 mol% O_2 in Ar, $T = 1380$ K, $P = 4.70$ bar, $\tau_{\mathrm{exp}} = 145$ μs, $\tau_{\mathrm{curran}} = 97$ μs, $\tau_{\mathrm{curranmod1}} = 108$ μs (mixture H)



g) 2.5 mol% heptane + 27.5 mol% O_2 in Ar, $T = 1415$ K, $P = 2.31$ bar, $\tau_{\mathrm{exp}} = 80$ μs, $\tau_{\mathrm{curran}} = 67$ μs, $\tau_{\mathrm{curranmod1}} = 72$ μs (mixture of Vermeer et al.)

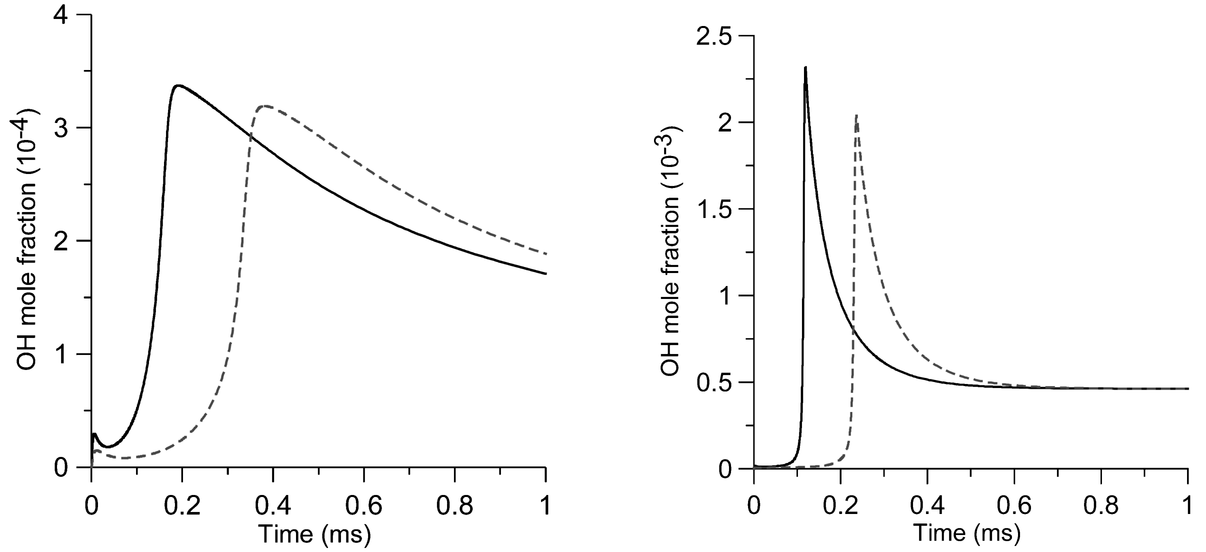
Fig. 13 Comparison between predicted ignition delays τ_{curran} with the detailed kinetic model of Curran et al. (——) and predicted ignition delays $\tau_{\mathrm{curranmod1}}$ (– – –) with the detailed kinetic model of Curran et al. for which rate constants of reactions (R10), (R12), (R13), (R15), and (R17) have been comprehensively changed (see text for details). Experimental ignition delays are noted τ_{exp} (continued).

Elementary Kinetics

One approach is to consider reactions other than (R1) to (R8) because the model of Curran et al. predicts reliable ignition delays for the less diluted mixtures (experiments of Vermeer et al.[10] and our experiments given in Table 4). The source for the uncertainty factors is the compilation of Baulch et al.[31] Therefore, rate constants will be modified such as the value retained is both consistent with the rate constant of Curran et al. and with the one of Baulch et al.[31] in the limit of the uncertainty factor recommended by Baulch.[31] Reactions for which rate constants taken by Curran et al. and recommended by Baulch et al. are not consistent will be let as given by Curran et al.

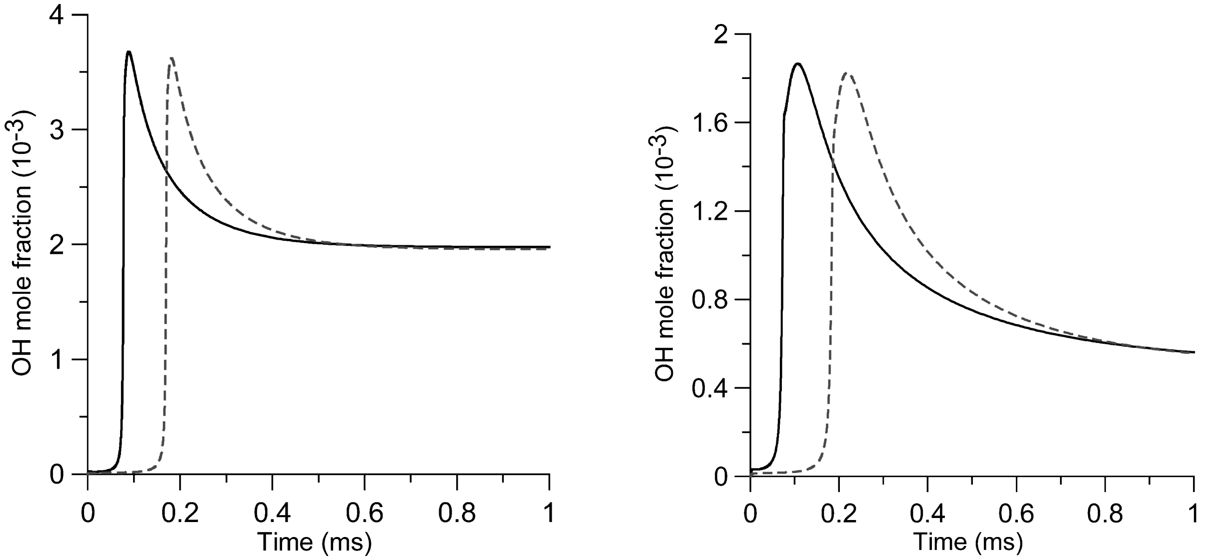
For all of the remaining mixtures, except the highly diluted one, reaction (R10) $HCO + M = H + CO + M$ seems to be one of the key reactions in this context. Curran et al.[29] considered a rate constant $k0$ ($cm^3\ mol^{-1}\ s^{-1}$) $= 1.86 \times 10^{17} \times T^{-1} \times \exp(-17000\ cal/RT)$, whereas Baulch et al. recommend in the 600–2500 K temperature range, with error limits $\Delta \log k = \pm 0.5$, $k0$ ($cm^3\ mol^{-1}\ s^{-1}$) $= 1.56 \times 10^{14} \times \exp(-15757\ cal/RT)$. The rate constant taken by Curran et al. is therefore a factor of about two lower, in the 1400–1600 K temperature range, than the one recommended by Baulch et al. If one consider the error limit of $\Delta \log k$ given by Baulch, this means that the range of values of k encompassed by these error limits can be found by multiplication and division of k by a factor three and that the rate constant of Curran et al. can be multiplied by a maximum factor of six or divided by a maximum factor of 1.5 to be consistent with the rate constant recommended by Baulch et al. once its uncertainty factor included in the analysis.

One other reaction potentially able to explain partially the discrepancies is reaction (R13) $HO_2 + OH = H_2O + O_2$, which is influential for all of the mixtures except the highly diluted one and the rich one. The rate constant taken in the model of Curran et al. for this reaction is exactly the same as the one recommended in the 300–2000 K temperature range by Baulch et al. Error limits given by Baulch et al. are $\Delta \log k = \pm 0.2$ at 300 K rising to ± 0.5 at 2000 K. In our temperature range (roughly 1300–1600 K), error limits of $\Delta \log k = \pm 0.4$ are therefore tenable. This represents an uncertainty factor of 2.5.



a) 0.08 mol% heptane + 0.92 mol% O_2 in Ar, T=1475 K, P = 4.43 bar, τ_{exp} = 238 μs, τ_{curran} = , $\tau_{curranmod2}$ = 290 μs (mixture A)

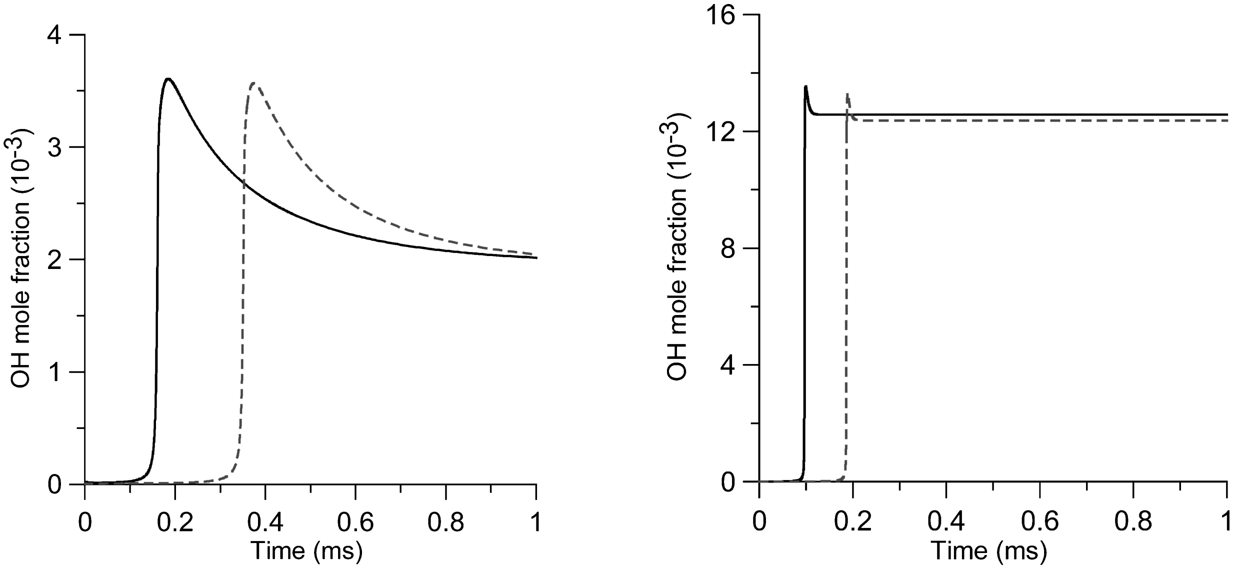
b) 0.6 mol% heptane + 4.4 mol% O_2 in Ar, T = 1453 K, P = 4.09 bar, τ_{exp} = 255 μs, τ_{curran} = 110 μs, $\tau_{curranmod2}$ = 230 μs (mixture B)



c) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, T = 1449 K, P = 4.49 bar, τ_{exp} = 195 μs, τ_{curran} = 77 μs, $\tau_{curranmod2}$ = 170 μs (mixture C)

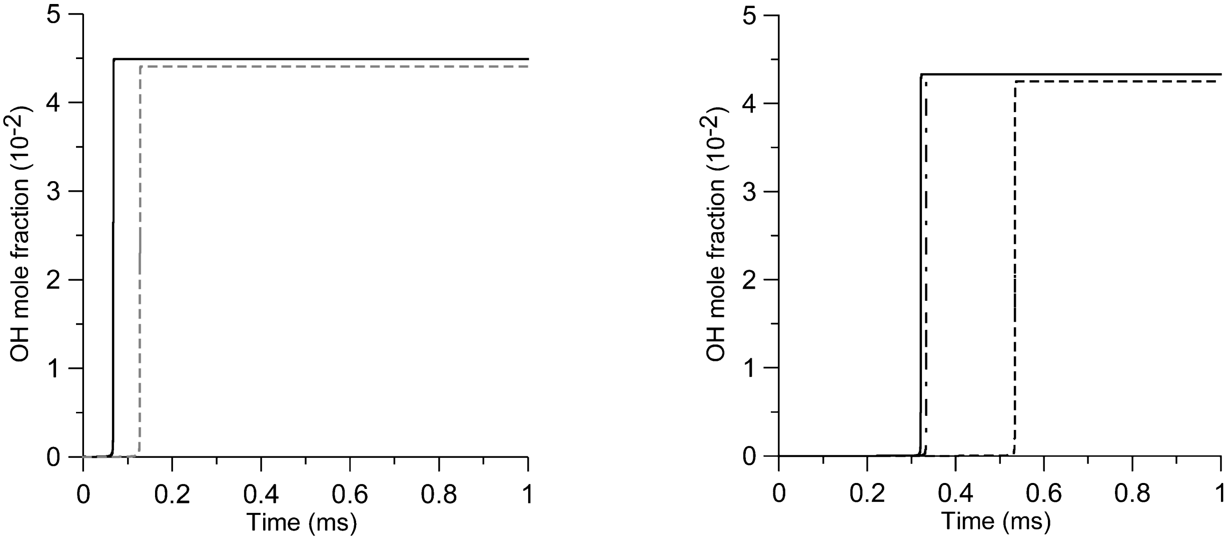
d) 0.22 mol% heptane + 4.78 mol% O_2 in Ar, T = 1415 K, P = 4.30 bar, τ_{exp} = 154 μs, τ_{curran} = 70 μs, $\tau_{curranmod2}$ = 180 μs (mixture D)

Fig. 14 Comparison between predicted ignition delays τ_{curran} with the detailed kinetic model of Curran et al. (——) and predicted ignition delays $\tau_{curranmod2}$ (– – –) with the detailed kinetic model of Curran et al. for which rate constants of reactions (R1), (R3), (R4), (R10), and (R13) have been comprehensively changed (see text for details). Experimental ignition delays are noted τ_{exp}.



e) 0.42 mol% heptane + 4.58 mol% O_2 in Ar, $T = 1408$ K, $P = 2.70$ bar, $\tau_{exp} = 304$ μs, $\tau_{curran} = 160$ μs, $\tau_{curranmod2} = 348$ μs (mixture E)

f) 1 mol% heptane + 11 mol% O_2 in Ar, $T = 1380$ K, $P = 4.70$ bar, $\tau_{exp} = 145$ μs, $\tau_{curran} = 97$ μs, $\tau_{curranmod2} = 187$ μs (mixture H)



g) 2.5 mol% heptane + 27.5 mol% O_2 in Ar, $T = 1415$ K, $P = 2.31$ bar, $\tau_{exp} = 80$ μs, $\tau_{curran} = 67$ μs, $\tau_{curranmod2} = 127$ μs (mixture of Vermeer et al.)

h) 2.5 mol% heptane + 27.5 mol% O_2 in Ar, $T = 1270$ K, $P = 2.95$ bar, $\tau_{exp} = 385$ μs, $\tau_{curran} = 322$ μs, $\tau_{curranmod1} = 333$ μs, $\tau_{curranmod2} = 533$ μs (mixture of Vermeer et al.)

Fig. 14 Comparison between predicted ignition delays τ_{curran} with the detailed kinetic model of Curran et al. (——) and predicted ignition delays $\tau_{curranmod2}$ (– – –) with the detailed kinetic model of Curran et al. for which rate constants of reactions (R1), (R3), (R4), (R10), and (R13) have been comprehensively changed (see text for details). Experimental ignition delays are noted τ_{exp} (continued).

Specific to the lean mixture, reaction (R12) $HCO + O_2 = CO + HO_2$ can potentially play a role. Baulch et al. in their recommendations only give a rate constant for the reaction $HCO + O_2 \rightarrow$ products with an uncertainty factor of two.

Reactions able to play specifically a role for the highly diluted mixture studied are as follows:

$$CH_3 + H + M = CH_4 + M \qquad (R15)$$

$$C_2H_4 + O = CH_3 + HCO \qquad (R16)$$

$$CH_2(S) + O_2 = CO + OH + H \qquad (R17)$$

$$CH_3 + OH = CH_2(S) + H_2O \qquad (R18)$$

Baulch et al.[31] recommended an uncertainty factor of three for the $k0$ and an uncertainty factor of two for the $k\infty$ for reaction (R15). Baulch et al. recommended a rate constant for reaction (R16) with an uncertainty factor of two, and there is however a factor four between the rate constant taken by Curran et al. and the recommendation of Baulch et al.

Baulch et al. only recommended a global rate constant for $CH_2(S) + O_2 \rightarrow$ products in the 300–1000 K temperature range with an uncertainty factor of three at 1000 K. The rate constant taken by Curran et al. for (R17) is about equal with the one recommended by Baulch et al. for the global reaction.

Curran et al. take a rate constant a factor of three different with the rate constant recommended by Baulch et al. for reaction (R18), this rate constant being recommended with an uncertainty factor of three.

Figure 13 shows the effect of modifications for five of the rate constants (only five on a total of 2538 in the detailed kinetic model of Curran et al.). The rate constants (R10) and (R17) have been divided (both forward and reverse) by a factor 1.5 and 2, respectively, whereas the forward and reverse rate constants (R12), (R13), and (R15) have been multiplied by a factor of 2. Figure 13 shows that it is possible to increase the computed ignition delays for the mixtures we studied without changing too much the predictions for the less-diluted mixtures studied by Vermeer et al. for which good agreement with the model of Curran et al. has been already demonstrated.

Another approach, among many others, is to modify, in their uncertainty limits, some of the most important reactions for ignition for all of the reactions studied, namely (R1), (R3), and (R4). For reaction (R1) $H + O_2 = OH + O$, the rate constant taken by Curran et al. in their detailed kinetic model is k (cm^3 mol^{-1} s^{-1}) $= 1.97 \times 10^{14} \exp(-16540/RT)$ with $R = 1.987$ cal K^{-1} mol^{-1}. However, Baulch et al. recommend an error limit of $\Delta \log k$ comprised between ± 0.1 (at 300 K) and ± 0.5 (at 5000 K) depending on the temperature ($\Delta \log k = \pm 0.2$ at 2500 K). If one considers the lowest error limit of $\Delta \log k$, this means that the range of values of k encompassed by these error limits can be found by multiplication and division of k by a factor of 1.25.

For reaction (R3) $CH_3 + HO_2 = CH_3O + OH$ in the model of Curran et al., a temperature-independent rate constant of 1.1×10^{13} cm^3 mol^{-1} s^{-1} is considered. Baulch et al. recommended about the same value (1.8×10^{13} cm^3 mol^{-1} s^{-1}) in the 300–2500 K temperature range. However the recommended error limit given by Baulch et al. for this rate constant is $\Delta \log k = \pm 0.7$ whatever the temperature is. This means that the values of k encompassed by these error limits can be found by multiplication and division of k by a factor of 5.

The forward rate constant taken for reaction (R4) $C_2H_4 + OH = C_2H_3 + H_2O$ by Curran et al. is exactly the same as the one recommended by Baulch et al. in the 650–1500 K temperature range. Error limits of $\Delta \log k = \pm 0.5$ are given by Baulch et al. for this reaction. This represents an uncertainty factor of 3.

Much more complicated appears the case of reaction (R2) $C_2H_3 + O_2 = CH_2CHO + O$. In fact, Baulch et al. give no recommendation for this reaction as several channels are globally responsible for the reaction $C_2H_3 + O_2 \rightarrow$ Products. Recent theoretical calculations[32] give a rate constant for the title reaction of k (cm^3 mol^{-1} s^{-1}) $= 3.03 \times 10^{11} \times T^{+0.29} \exp(-10$ cal$/RT)$ for the 300–3500 K temperature range, whereas Curran et al.[29] report a value of k (cm^3 mol^{-1} s^{-1}) $= 3.5 \times 10^{14} \times T^{-0.61} \times \exp(-5260$ cal$/RT)$. In the 1400–1600 K temperature range, the rate constant taken by Curran et al. is a factor 3.4 up to 3.9 lower than the rate constant theoretically calculated. In fact, the two rate constants, at a given temperature, are quite consistent if one considers an uncertainty factor of 3. No direct experimental determination of the rate constant $C_2H_3 + O_2 = CH_2CHO + O$ exists, and therefore the rate constant for reaction (R2) is let here as given by Curran et al.

Figure 14 shows the effect of modifications for five of the rate constants (only five on a total of 2538 in the detailed kinetic model of Curran et al.). In the detailed kinetic model of Curran et al., rate constants for reactions (R1), (R3), (R4), (R10), and (R13) have been replaced by the recommendation of Baulch et al. This does not change the predictions of the model. Then, the rate constants (R1), (R3), (R4), and (R10) have been divided by a factor 1.25, 5, 3, and 3, respectively, whereas the rate constant (R13) is multiplied by a factor of 2. Figure 14 shows that it is possible to increase the computed ignition delays for the mixtures we studied such as to obtain a very good agreement between the detailed model and all of the experiments performed for this study. This agreement is obtained furthermore without changing too much the predictions for the less diluted mixtures studied by Vermeer et al. (see Fig. 14g) and the one presented in this study (see Fig. 14f). However, for the lowest temperatures the set of changes just presented can induce too long ignition delays as shown in Fig. 14h, whereas the first set of changes presented predicts about the same ignition delay as the detailed model of Curran et al. Nevertheless, the predicted delays, although too long, always agree with the experiments within a factor of 2.

Detonation of Heptane/Oxygen Mixtures Behind an Incident Shock Wave

The conditions for the onset of a detonation wave behind an incident shock wave have been preliminarily examined. Figure 15 shows the variation of the experimental wave velocity V vs P_4 for the stoichiometric mixture heptane/oxygen at an initial pressure $P_1 = 2$ kPa, where P_4 is the pressure of helium in the driver section. For a critical value, named P_{4C}, the wave velocity suddenly increases, corresponding to the onset of the coupling between the incident shock wave and the reaction zone, which is the onset of detonation. In the critical zone, the wave velocity can reach very high values (here about 4.5 km s^{-1}), leading to a very unstable detonation. Once P_4 is increased past this critical zone, the wave tends to be a stable self-sustained detonation, with a constant velocity value D (here about 2.1 km s^{-1}), slightly lower than the theoretical Chapman–Jouguet detonation velocity. The Chapman–Jouguet detonation velocity has been calculated with the EQUIL code.[33]

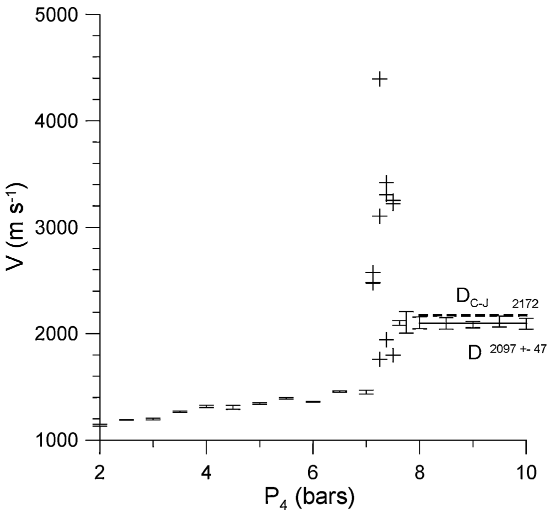


Fig. 15 Shock wave and detonation velocity vs helium pressure P_4 in the driver section for the stoichiometric heptane/oxygen mixture at an initial pressure $P_1 = 2$ kPa. Chapman–Jouguet detonation velocity D_{C-J} is 2172 m s^{-1} (– – –) and experimental detonation velocity D is 2097 m s^{-1} (——).

Conclusions

This study shows the following:

1) A two-step ignition process also exists at high temperatures for the mixture 0.08 mol% heptane/0.92 mol% oxygen/99 mol% argon, and this two-step ignition process does not exist for the other mixtures studied.

2) The experimental results presented here are in reasonable agreement with the previous results reported in the literature.

3) The high-temperature ignition delays predicted by the model of Curran et al. are about a factor of 2 shorter on average that the ignition delays experimentally observed.

4) Some smooth, physically meaningful, modifications (approach number 1) of the detailed chemical kinetic mechanism are able to explain conveniently all of the (past and present, highly or less diluted mixtures, rich, lean or stoichiometric mixtures) experimental high-temperature ignition delay data. It is also shown that other modifications (approach number 2) are also possible. Although approach number 2 is physically realistic, approach number 1 is preferred. It can be concluded that the only way to go further in that way is to use an optimization procedure.

5) There is a lack for elementary kinetic data for some important reactions here such as, for instance, $CH_3 + HO_2 = CH_3O + OH$.

6) The modifications proposed here do not alter the predictions at low temperature because the changes suggested are only devoted to temperatures above about 1250 K.

7) Self-sustained detonations can propagate in heptane/O_2 mixtures.

Acknowledgments

The authors would like to thank H. J. Curran, V. I. Golovitchev, and C. J. Montgomery for the supplying of their kinetic models and

N. Peters and D. F. Davidson for the supplying of some of their very recent articles.

References

[1] Frolov, S. M., Basevich, V. Ya., Aksenov, V. S., and Polikhov, S. A., "Initiation of Homogeneous and Heterogeneous Detonation by Successive Triggering of Electric Discharges," Abstract of the German-Russian Workshop on Reactive Flows, Inst. of Energy Engineering, Technical Univ. of Berlin, Germany 2002.

[2] Tieszen, S. R., Stamps, D. W., Westbrook, C. K., and Pitz, W. J., "Gaseous Hydrocarbon-Air Detonations," *Combustion and Flame*, Vol. 84, Nos. 3–4, 1991, pp. 376–390.

[3] Smirnov, N. N., and Tyurnikov, M. V., "Experimental Investigation of Deflagration to Detonation Transition in Hydrocarbon-Air Gaseous Mixtures," *Combustion and Flame*, Vol. 100, No. 4, 1995, pp. 661–668.

[4] Sochet, I., Aminallah, M., and Brossard, J., "Detonability of Fuel-Oxygen and Fuel-Air Mixtures," *Shock Waves*, Vol. 7, No. 3, 1997, pp. 163–174.

[5] Nettleton, M. A., "Recent Work on Gaseous Detonation," *Shock Waves*, Vol. 12, No. 1, 2002, pp. 3–12.

[6] Beeson, H. D., McClenagan, R. D., Bishop, C. V., Benz, F. J., Pitz, W. J., Westbrook, C. K., and Lee, J. H. S., "Detonability of Hydrocarbon Fuels in Air," *Progress in Astronautics and Aeronautics*, Vol. 133, 1990, pp. 19–36.

[7] Gelfand, B. E., Frolov, S. M., and Nettleton, M. A., "Gaseous Detonations—a Selective Review," *Progress in Energy and Combustion Science*, Vol. 17, No. 4, 1991, pp. 327–371.

[8] Austin, J. M., and Shepherd, J. E., "Detonation in Hydrocarbon Fuel Blends," California Inst. of Technology, GALCIT, TR FM99-6, July 2000.

[9] Kaneshige, M., and Shepherd, J. E., "Detonation Database," California Inst. of Technology, GALCIT, TR FM97-8, July 1997.

[10] Vermeer, D. J., Meyer, J. W., and Oppenheim, A. K., "Auto-Ignition of Hydrocarbons Behind Reflected Shock Waves," *Combustion and Flame*, Vol. 18, No. 3, 1972, pp. 327–336.

[11] Colket, M. B., and Spadaccini, L. J., "Scramjet Fuels Autoignition Study," *Journal of Propulsion and Power*, Vol. 17, No. 2, 2001, pp. 315–323.

[12] Horning, D. C., Davidson, D. F., and Hanson, R. K., "Study of the High-Temperature Autoignition of n-Alkane/O_2/Ar Mixtures," *Journal of Propulsion and Power*, Vol. 18, No. 2, 2002, pp. 363–371.

[13] Burcat, A., Farmer, R. F., and Matula, R. A., "Shock Initiated Ignition in Heptane-Oxygen-Argon Mixtures," *Proceedings of the Thirteenth International Symposium on Shock Tubes and Waves*, State Univ. of New York Press, Albany, 1981, pp. 826–833.

[14] Coats, C. M., and Williams, A., "Investigation of the Ignition and Combustion of n-Heptane-Oxygen Mixtures," *Proceedings of the Seventeenth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1979, pp. 611–621.

[15] Levinson, G. S., "High Temperature Preflame Reactions of n-Heptane," *Combustion and Flame*, Vol. 9, No. 1, 1965, pp. 63–72.

[16] Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K., "A Comprehensive Modeling Study of n-Heptane Oxidation," *Combustion and Flame*, Vol. 114, Nos. 1–2, 1998, pp. 149–177.

[17] Montgomery, C. J., Cremer, M. A., Chen, J. Y., Westbrook, C. K., and Maurice, L. Q., "Reduced Chemical Kinetic Mechanisms for Hydrocarbon Fuels," *Journal of Propulsion and Power*, Vol. 18, No. 1, 2002, pp. 192–198.

[18] Kim, H., Pae, S., and Min, K., "Reduced Chemical Kinetic Model for the Ignition Delay of Hydrocarbon Fuels and DME," *Combustion Science and Technology*, Vol. 174, No. 8, 2002, pp. 221–238.

[19] Held, T. J., Marchese, A. J., and Dryer, F. L., "A Semi-Empirical Reaction Mechanism for n-Heptane Oxidation and Pyrolysis," *Combustion Science and Technology*, Vol. 123, Nos. 1–6, 1997, pp. 107–146.

[20] El Bakali, A., Delfau, J. L., and Vovelle, C., "Kinetic Modeling of a Rich, Atmospheric Pressure, Premixed n-Heptane/O_2/N_2 Flame," *Combustion and Flame*, Vol. 118, No. 3, 1999, pp. 381–398.

[21] Chevalier, C., Pitz, W. J., Warnatz, J., Westbrook, C. K., and Melenk, H., "Hydrocarbon Ignition: Automatic Generation of Reaction Mechanisms and Applications to Modeling of Engine Knock," *Proceedings of the Twenty-Fourth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1992, pp. 93–101.

[22] Lindstedt, R. P., and Maurice, L. Q., "Detailed Kinetic Modelling of n-Heptane Combustion," *Combustion Science and Technology*, Vol. 107, 1995, pp. 317–353.

[23] Chakir, A., Bellimam, M., Boettner, J. C., and Cathonnet, M., "Kinetic Study of N-Heptane Oxidation," *International Journal of Chemical Kinetics*, Vol. 24, No. 4, 1992, pp. 385–410.

[24] Bollig, M., Pitsch, H., Hewson, J. C., and Seshadri, K., "Reduced n-Heptane Mechanism for Non-Premixed Combustion with Emphasis on Pollutant-Relevant Intermediate Species," *Proceedings of the Twenty-Sixth International Symposium on Combustion*, Combustion Inst., Symposium, Pittsburgh, PA, Vol. 1, 1996, pp. 729–737.

[25] Rente, T., Golovitchev, V. I., and Denbratt, I., "Numerical Study of n-heptane Spray Auto-Ignition at Different Levels of Pre-Ignition Turbulence," *Proceedings of the Fifth International Symposium on Diagnostics and Modeling Combustion in Internal Combustion Engines*.

[26] Glaude, P. A., Warth, V., Fournet, R., Battin-Leclerc, F., Côme, G. M., Scacchi, G., Dagaut, P., and Cathonnet, M., "Modélisation de l'Oxydation de Mélanges de n-Heptane et d'Iso-Octane à l'Aide d'un Mécanisme Généré Automatiquement," *Combustion*, Vol. 1, No. 2, 2000, pp. 123–139.

[27] Peters, N., Paczko, G., Seiser, R., and Seshadri, K., "Temperature Cross-Over and Non-Thermal Runaway at Two-Stage Ignition of N-Heptane," *Combustion and Flame*, Vol. 128, Nos. 1–2, 2002, pp. 38–59.

[28] Davidson, D. F., Oehlschlaeger, M. A., Herbon, J. T., and Hanson, R. K., "Shock Tube Measurements of Iso-Octane Ignition Times and OH Concentration Time Histories," *Proceedings of the Twenty-Ninth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, Pt. 1, 2002, pp. 1295–1301.

[29] Curran, H. J., Gaffuri, P., Pitz, W. J., and Westbrook, C. K., "A Comprehensive Modeling Study of Iso-Octane Oxidation, " *Combustion and Flame*, Vol. 129, No. 3, 2002, pp. 253–280.

[30] Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., and Adigun, O., CHEMKIN Collection, Release 3.6, Reaction Design, Inc., San Diego, CA, Dec. 2001.

[31] Baulch, D. L., Cobos, C. J., Cox, R. A., Frank, P., Hayman, G., Just, Th., Kerr, J. A., Murrels, T., Pilling, M. J., Troe, J., Walker, R. W., and Warnatz, J., "Summary Table of Evaluated Kinetic Data for Combustion Modeling: Supplement 1," *Combustion and Flame*, Vol. 98, Nos. 1–2, 1994, pp. 59–79.

[32] Mebel, A. M., Diau, E. W. G., Lin, M. C., and Morokuma, K., "Ab Initio and RRKM Calculations for Multichannel Rate Constants of the $C_2H_3 + O_2$ Reaction," *Journal of the American Chemical Society*, Vol. 118, No. 40, 1996, pp. 9759–9771.

[33] Kee, R. J., Rupley, F. M., Miller, J. A., Coltrin, M. E., Grcar, J. F., Meeks, E., Moffat, H. K., Lutz, A. E., Dixon-Lewis, G., Smooke, M. D., Warnatz, J., Evans, G. H., Larson, R. S., Mitchell, R. E., Petzold, L. R., Reynolds, W. C., Caracotsios, M., Stewart, W. E., Glarborg, P., Wang, C., and Adigun, O., CHEMKIN Collection, Release 3.6, Reaction Design, Inc., San Diego, CA, Dec. 2001.