Experimental and modeling study of 1-hexene oxidation behind reflected shock waves

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Abstract

The auto-ignition delay times τ_i of 1-C_6H_{12}/O_2/Ar mixtures have been measured between 1270 and 1700 K using shock tube technique for 3 equivalence ratios ($\Phi = 0.5$, 1, and 1.5) at a pressure of about 0.2 MPa. At higher temperatures (>1400 K), the logarithm of τ_i varies linearly as a function of the temperature inverse for a given value of equivalence ratio. The apparent activation energy, E_a, is approximately equal to 230 kJ mol^{-1}. At lower temperature (<1400 K), E_a strongly decreases and becomes equal to about 120 kJ mol^{-1} around 1300 K. A correlation between τ_i, reactant concentrations, and temperature behind reflected shock waves was proposed for each temperature range. These correlations give an estimation of τ_i with an accuracy better than 12%. A detailed chemical mechanism of the 1-hexene oxidation has been developed with the "EXGAS" program. The agreement between computed and measured values of τ_i was correct at high temperatures (>1400 K). The major channels of the chemical species fluxes have been discussed: at low temperatures, 1-hexene is mainly consumed by retro-ene reaction to give propene and, in a smaller ratio, by unimolecular decomposition to give allyl and 1-propyl radicals. At high temperature, unimolecular decomposition becomes more important than retro-ene reaction. The change in E_a below 1400 K is not explained by the model. The auto-ignition delay times of 1-hexene have been compared to those of other unsaturated hydrocarbons. For stoichiometric mixtures diluted by 99 mol% of argon at a pressure of 200 kPa, the shortest delays were obtained for 1-octene while the longest delays were obtained for propene. With iso-butene and ethylene, the delay times are closer to 1-hexene in the low temperature side and to propene in the high temperature one.
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1. Introduction

Olefins are a family of hydrocarbons that are present in gasoline up to 20%. Many studies were carried out on the oxidation of alkanes, while relatively few were conducted on the oxidation of alkenes. In some conditions, their ability to react in air is superior to that of alkanes as well as to that of aromatic compounds [1]. To reduce the emission of pollutants and to increase the engine efficiency, the composition of fuels could be modified. In particular, fuels could be adapted to the working conditions of homogeneous charge

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compression ignition (HCCI) engines. Unlike engines controlled by spark ignition, HCCI engines use fuels with a weak octane number. The main problems of HCCI engines are the control of ignition delay and burn rate [2]. Heptane could be a reference fuel for this type of engine. A rapid compression machine study showed that ignition delay times of hydrocarbon mixtures containing heptane in air were a function of the *n*-heptane/O_2 ratio [3]. The auto-ignition of numerous fuels is characterized by a 2-stage ignition (*n*-heptane, *n*-heptene, etc.). The first stage is mainly due to peroxy radical formation by addition to O_2 of alkyl radicals: $R + O_2 \rightarrow RO_2$. In the low temperature range ($T < 800$ K), peroxy radicals lead to the hydroperoxide compound formation, such as ketohydroperoxide, $HOOQ=O$, which can easily decompose and involve a multiplication of the radical number. When the temperature increases ($T > 800$ K), alkyl radicals start to decompose to give smaller alkyl radicals and olefins and their reaction with O_2 leads mainly to conjugated olefins and HO_2. The multiplication of the radical number decreases and the related temperature rise drops steeply. The reaction run-away occurs in the second stage after a more or less long period. This delay time corresponding to the second stage is due to high temperature mechanism, the multiplication of radicals being performed by branching reactions, such as $H + O_2 \rightarrow O + OH$ or $H_2O_2 \rightarrow 2OH$. The intermediate species of the auto-ignition of alkanes are generally identified as olefins. While small amounts of 1-hexene are obtained from *n*-heptane–air mixtures [4], this compound is one of the major olefins formed during the oxidation of higher alkanes, such as *n*-decane [5] or *n*-hexadecane [6]. 1-Hexene can also be obtained by thermal decomposition of alkanes and cyclanes (*n*-heptane steam cracking [7], cyclohexane and *n*-heptane pyrolysis around 1000 K [8]).

The auto-ignition of the *n*-heptane in the presence of oxygen diluted with argon was largely studied [9–13]. However, very few kinetic studies were performed on the oxidation of 1-hexene at high temperature, unlike lighter olefins, which were the object of several studies at low temperatures ($T < 1000$ K), as well as at high temperatures ($T > 1000$ K). The most studied olefin was ethene for which a mechanism of oxidation was proposed [14,15]. Propene, 1-butene, iso-butene, and 1-pentene were also the object of detailed studies [16–22].

The purpose of this article was to determine the ignition delay times of 1-hexene, which can be considered as representative of the unbranched alkenes in gasoline, at high temperature ($T > 1000$ K), to compare these delay times to those obtained with other alkenes and to validate the kinetic model obtained on the bases of a self-generated mechanism.

2. Experimental method

Experiments were carried out behind reflected shock waves in shock tube with a 2 m long metallic driver section and a 9 m-pyrex driven section with a 50 mm i.d. Both of the 2 shock tube parts were evacuated using 2 primary vacuum pumps. The shock velocity was measured via 4 pressure transducers equally spaced by 150 mm, flush mounted into the inner surface of the tube, the last one being 10 mm before the shock tubes end-wall. A fused silica window (9 mm optical diameter and 6 mm thickness) is mounted across a monochromator centred at 306 nm (characteristic of OH emission) and equipped with a UV-sensitive photomultiplier tube R928 HAMAMATSU. Both pressure and emission signals are transferred and registered on a numerical oscilloscope. Reflected shock conditions were calculated from standard procedure [23]. The ignition delay time is defined as the time between the passage of the reflected shock wave, indicated by pressure jump, monitored by pressure transducer, and 50% of the maximum OH emission signal at 306 nm. In case of less diluted mixtures, the OH emission corresponds to the run-away of the explosive reaction detected by a small pressure signal increase. The error on the temperature is estimated to be less than 1% while that on the pressure is 1.3%. With regard to the error on the auto-ignition delay time, the estimated error depends on the temperature range and is the highest on the high temperature side, varying between 2% and 14%.

The reactive gas mixtures were prepared using 1-hexene (Aldrich 99+%), oxygen (Air liquide 99,999%), and argon (Air liquide 99,999%) in a 10 L pyrex glass bulb. The liquid hydrocarbon was degassed several times before the mixtures were prepared. The mixtures were mixed one to 2 h to ensure homogeneous composition. The fuel and oxygen molar percent are given in Table 1, the rest being argon in all cases.

3. Modelling

A detailed chemical kinetic reaction mechanism has been developed with the "EXGAS" program, which allows the automatic generation of mechanisms of oxidation and combustion [24,25]. The recent development of this system for the combustion of alkenes has been previously

Table 1
Experimental conditions, the remaining gas being argon

1-C_6H_{12}%mol	O_2%mol	Φ	T_5 (K)	P_5 (kPa)
0.1	1.8	0.5	1346–1760	194–225
0.1	0.9	1	1418–1752	180–236
0.1	0.6	1.5	1399–1711	192–230
0.4	3.6	1	1345–1729	198–223

described [26] for propene and 1-butene. The mechanism has been written according to the rules, which are briefly described here. The comprehensive primary mechanism contains the reactions of 1-hexene and free radicals that it produces. Since the model was built for high temperature conditions, additions of alkyl, alkenyl, and allylic free radicals to O_2 are ignored. The reaction rules accounted for are: unimolecular retro-ene molecular elimination yielding 2 molecules of propene, initiations by breaking a C–C or a C–H bond, bimolecular initiations between C_6H_{12} and O_2 or two C_6H_{12}, addition of H, O, OH, CH_3, and HO_2 radicals to the double bond, radical isomerizations, decompositions of radicals by β-scission, oxidations of alkyl, allyl, and alkenyl radicals with O_2 yielding alkenes or dienes and HO_2 radicals, H-abstraction by small radicals, combination of resonance stabilized and alkyl radicals among themselves and small radicals. Because of the very high temperatures of the experiments, few modifications have been made to the previous model [26]. The rate constant for the retro-ene molecular elimination is that measured by Tsang for 1-hexene [8] ($k = 4 \times 10^{12} \exp(-29{,}040/T)s^{-1}$). The unimolecular initiations by breaking a C–C bond are calculated using the KINGAS software [27]. In the case of the formation of allyl and propyl radicals from 1-hexene molecule, the rate constant is $k = 1.8 \times 10^{15} \exp(37{,}770/T)s^{-1}$. The unimolecular initiations by breaking a C–H bond are written in the reverse direction; the rates of the combination of radicals with H-atom are $10^{14} \, cm^3 \, mol^{-1} \, s^{-1}$ as recommended by Allara and Shaw [28]. The isomerizations of alkyl radicals through a 4-member cyclic transition state are included, while they are usually neglected because of their high ring strain (26 kcal mol^{-1}) in comparison with larger rings (6.3 kcal mol^{-1} for a 5-membered ring). The kinetic parameters are calculated as explained in [26].

A lumped secondary mechanism includes the molecular primary product reactions. For reducing the reactant number, the different primary molecular product isomers are lumped into one unique species, this is the case for butenes, pentenes or molecules yielded in combination steps. The different hexadiene isomers are distinguished because of the importance of this specific product. Species reacting in the C_0–C_6 reaction base are not lumped either. The subsequent reactions are not elementary steps, but global reactions that produce molecules or radicals, whose reactions are included in the C_0–C_6 reaction bases [29,30]. Alkenes and dienes react by H-abstraction or addition of small radicals. The formation of secondary resonance stabilized free radicals has been considered and their combination included. A C_0–C_6 reaction base includes all the reactions involving radicals or molecules containing less than 3 carbon-atoms [29], together with a C_3–C_6 sub-

mechanism that contains the reactions of multi-unsaturated hydrocarbons [30], such as propyne, allene or butadiene, including reactions leading to the formation of benzene. Thermochemical data for molecules or radicals have been automatically computed and stored according to CHEM-KIN II [31]. These data were calculated using THERGAS software [32], based on group additivity. The C–H bond dissociation energies used for calculating the enthalpy of radicals have been updated for alkyl and allylic radicals [33]. The 1-hexene sub-mechanism involves 174 species and 822 reactions, and the whole model 246 species and 1545 reactions. The mechanism cannot be extensively displayed here but is available on request. The calculations have been performed with the SENKIN-CHEMKIN-II package [31].

4. Results and discussion

4.1. Experimental auto-ignition delay times

Ignition delay times of 1-hexene/oxygen mixtures diluted with argon were measured for different initial hydrocarbon molar fractions in the mixture. The experiments were conducted at 3 different equivalence ratios (0.5, 1, and 1.5). The total pressure behind reflected shock waves was kept constant around 200 kPa. Figure 1 shows typical OH emission signals (306 nm) recorded by oscilloscope. Instead of recording a unique peak corresponding to the OH production, 2 peaks of unequal intensity were observed. The first emission appears at early times, followed by a second one corresponding to the main exothermic step of the reaction.

This phenomenon was also reported by Davidson et al. [34] in the case of iso-octane ignition delay time measurements. According to them, the first OH emission is due to the initial decomposition of the fuel molecule during the induction period. This early OH population is quickly suppressed by the scavenging effect of iso-octane and its decomposition products. However, in the low temperature region only one peak remains. The ignition delay time has been defined from the OH emission based on the 2nd peak.

The evolution of the auto-ignition delay times as a function of the temperature inverse is reported in Fig. 2. As one can see, the auto-ignition delay time decreases as the temperature rises and also when the oxygen concentration increases. Figure 3 shows that decreasing the concentration of the diluent induces shorter auto-ignition delay times. An important feature has to be pointed out: the logarithm of the auto-ignition delay times does not vary linearly with the temperature inverse, a change in the activation of energy is observed for temperature below a critical one: the ignition delay times are shorter than those
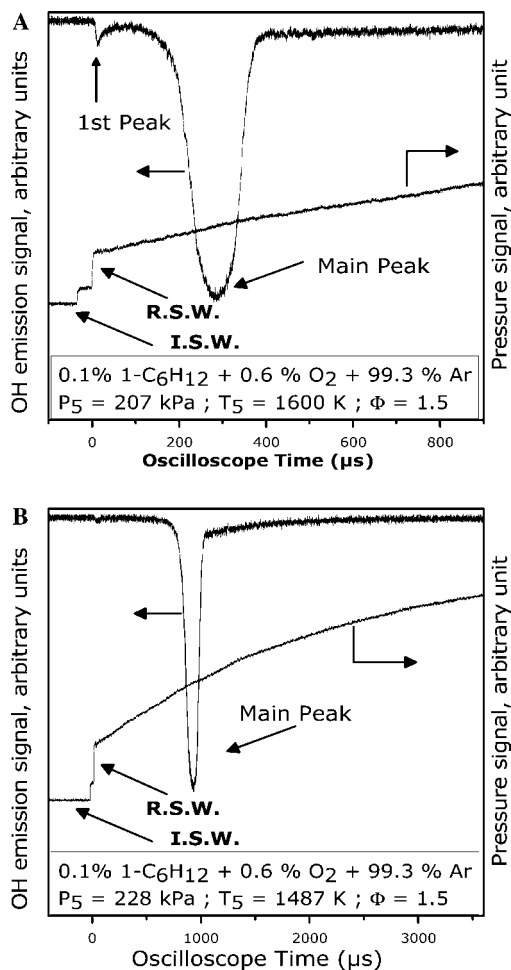
Fig. 1. Signal examples recorded during the oxidation of 1-hexene behind reflected shock waves. (A) $\tau_{50\%} = 227$ μs; (B) $\tau_{50\%} = 842$ μs.

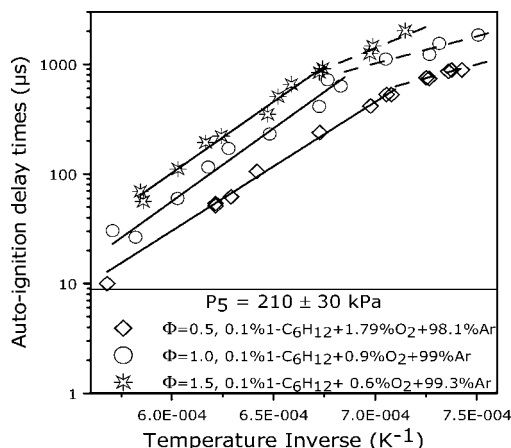Fig. 2. Auto-ignition delay times of 1-C$_6$H$_{12}$/O$_2$/Ar versus the temperature inverse for different equivalence ratios.
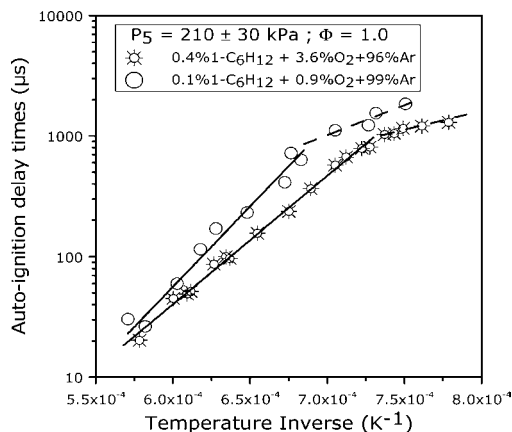

Fig. 3. Auto-ignition delay times of 1-C$_6$H$_{12}$/O$_2$/Ar versus the temperature inverse for 2 different fuel concentrations at an equivalence ratio of 1.

predicted by the first slope that corresponds to the high temperature side (Figs. 2 and 3). The temperature at which the change in activation energy is observed varies slightly with the oxygen content in the mixture. For an equivalence ratio of 0.5, the critical temperature is equal to 1410 K while it increases up to 1460 and 1480 K as the equivalence ratios are set equal to 1 and 1.5, respectively. At an equivalence ratio of 1, an increase in the initial 1-hexene concentration induces a reduction of the critical temperature from 1460 to 1370 K. The same behaviour was also reported by Herzler et al. [35] in the case of propane-air auto-ignition delay times measured behind reflected shock waves, for an equivalence ratio of 0.5 and a reflected shock pressure of 10 bar, the critical temperature at which the activation energy changes was found equal to 1050 K. Similar results were also reported by Peterson et al. [36] in the case of methane oxidation at high pressure and low temperature conditions.

A multiple regression correlation was applied on the experimental results to obtain a modified Arrhenius expression of τ_i as a function of the initial conditions of temperature, pressure, and concentrations. The following expression was obtained in the temperature range of 1410–1700 K for $\Phi = 0.5$, and 1460–1700 K for $\Phi = 1$, 1480–1700 K for $\Phi = 1.5$ (molar fraction of 1-hexene = 0.001), and in the temperature range of 1370–1700 K for $\Phi = 1$ with a molar fraction of 1-hexene = 0.004:

$$\tau_i = 1.14 \times 10^{-13} [\text{1-C}_6\text{H}_{12}]^{0.77} [\text{O}_2]^{-1.24} \exp(27{,}900/T),$$

where τ_i is in seconds, concentrations in mol/cm^3, and the temperature in K.

The average error between the experimental data and the correlated ones is equal to 12%. As expected from the variation of the delay time

versus the fuel or oxygen concentrations, a positive exponent over the fuel concentration was derived, which expresses the inhibitor effect of the fuel over its own oxidation, while a negative one was derived for the oxygen concentration assessing the promoter effect of oxygen during the oxidation process. Despite the few data that were obtained in the low temperature side, an expression of the auto-ignition delay times was also derived, in the temperature range of 1340–1410 K for $\Phi = 0.5$, 1330–1460 K for $\Phi = 1$, and 1380–1480 K for $\Phi = 1.5$ (molar fraction of 1-hexene = 0.001), and in the temperature range of 1280–1370 K: for $\Phi = 1$ with a molar fraction of 1-hexene = 0.004:

$$\tau_i = 3.32 \times 10^{-10} [\text{1-C}_6\text{H}_{12}]^{0.53} [\text{O}_2]^{-0.93} \exp(13{,}960/T),$$

where the ignition delay time is in seconds, concentrations in mol/cm^3, and the temperature in K.

The average error between the experimental data and the correlated ones is equal to 10%. In the low temperature side, the activation energy is half that of the high temperature side. The effect of fuel on the auto-ignition delay time is less pronounced in the low temperature region than in the high temperature one (the fuel coefficient increases from 0.527 up to 0.766). The same conclusion can be drawn from the variation the coefficient of oxygen, which increases from -1.24 up to -0.93.

To compare the auto-ignition delay times of 1-hexene to those of other unsaturated hydrocarbons, Fig. 4 shows the variation in the auto-ignition delay times of ethylene [14], propene [16], iso-butene [37], 1-octene [38], and 1-hexene (this work) in the case where the mixture is diluted by 99% of argon for an equivalen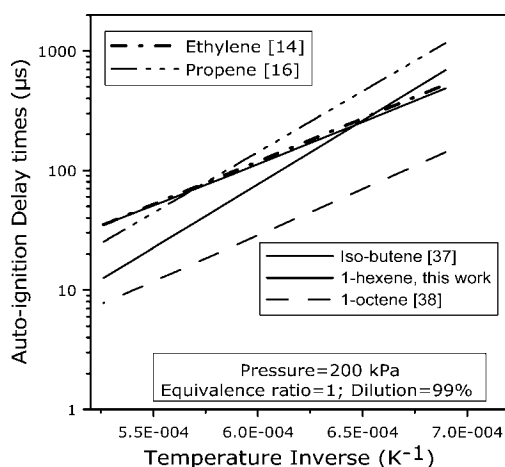ce ratio of 1 and a pressure behind reflected shock waves of 200 kPa. As it is expected, the auto-ignition delay time is inversely proportional to the number of carbon atoms in the fuel. The shortest delays are obtained for 1-octene while the longest are obtained for propene. Iso-butene and ethylene exhibit similar ignition delay times, which are closer to 1-hexene in the low temperature side and to propene in the high temperature one.

4.2. Computed auto-ignition delay times

Figure 5 presents a comparison between the computed and the experimental delays times for a fuel concentration of 1% and for the 3 different equivalence ratios (0.5, 1, and 1.5). Simulated delay times are derived from the computed profiles of OH radicals. While the computed τ_i do vary monotonically with the temperature inverse, the agreement obtained is globally acceptable, with a difference always lower than a factor of 1.5. The change in apparent activation energy below 1400 K is not explained by the model. We have tried making many changes to our mechanism, but unsuccessfully. Apart from the additions of alkyl, alkenyl, and allylic free radicals to O$_2$, all known reaction paths of oxidation of 1-hexene and propene have been considered. It must also be pointed out that reactions of small peroxy radicals CH$_3$O$_2$ and C$_2$H$_5$O$_2$, included in the reaction base, do not explain such a kinetic effect. Reactions of H$_2$O$_2$ are also included in the model with recent rate expressions, which are those usually used in the oxidation models available in the literature.

Figure 6 presents the major channels of the fluxes analysis, Fig. 7 displays an analysis of the sensitivity of some important reactions, and Fig. 8 shows profiles of some species of interest; these
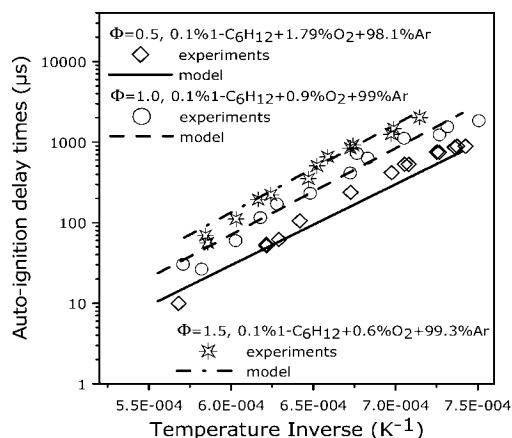

Fig. 4. Auto-ignition delay times of different olefins/O$_2$/Ar versus the temperature inverse at an equivalence ratio of 1. The total pressure behind reflected shock waves is set equal to 200 kPa.

Fig. 5. Auto-ignition delay times of 1-C$_6$H$_{12}$/O$_2$/Ar versus the temperature inverse for different equivalence ratios. Comparison between the model and the experiments.
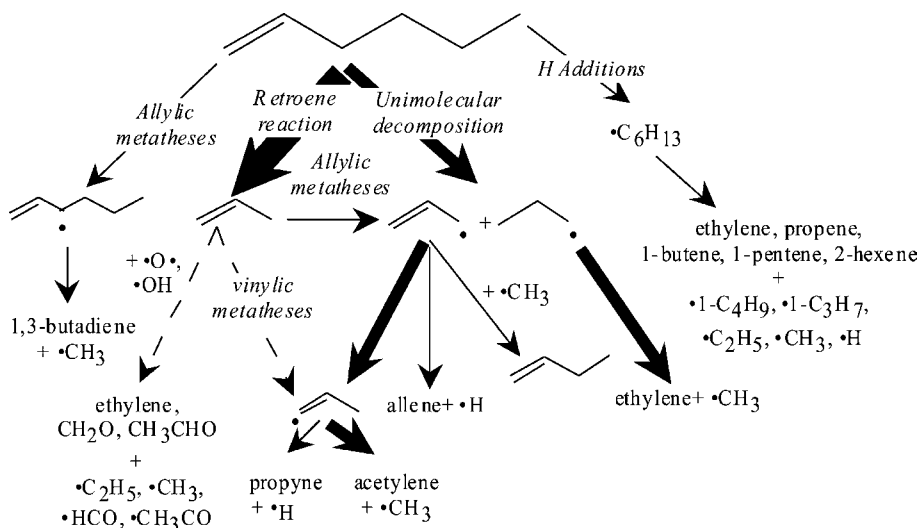
Fig. 6. Flow rate analysis (the sizes of arrows are proportional to the net global fluxes) at 1300 K.
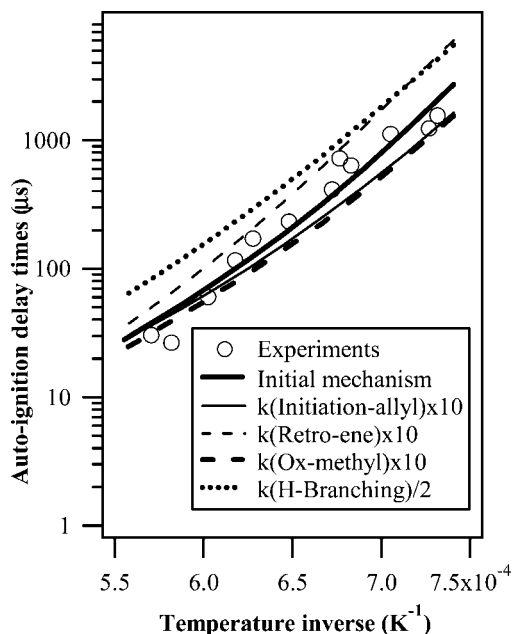

Fig. 7. Sensitivity analysis at 1300 K for some reactions described in the text.

Fig. 8. Temporal profiles of 1-hexene, propene, methyl, and hydroxyl radicals at 1300 K.

3 figures have been computed at 1300 K, for an equivalence ratio of 1 and for 50% conversion.

4.2.1. Main consumption pathways of 1-hexene molecules

As shown in Fig. 6, at 1300 K, 1-hexene is mainly consumed by retro-ene reaction (48% of its consumption) to give propene and by unimolecular decomposition (17% of its consumption)
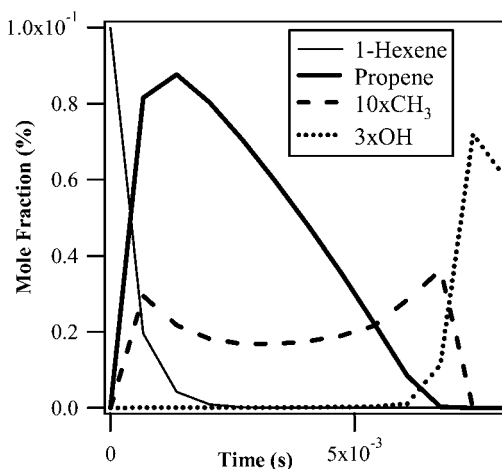
to give allyl and 1-propyl radicals. At 1750 K, the repartition between these 2 major channels changes, as unimolecular decomposition accounts for 45% of the consumption of reactant, while retro-ene reaction accounts for 21%. Figure 7 also demonstrates the importance of these reactions, as simulations have been performed by multiplying the rate constant of each of these reactions by a factor of 10. Retro-ene reaction has a strong inhibiting effect, while the initiation giving allyl and 1-propyl radicals (initiation-allyl) has a slight promoting effect.

The importance of the retro-ene reaction makes propene as the major primary product of the oxidation of 1-hexene. This is consistent with Fig. 8, which shows that the concentration of

1-hexene decreases when that of propene increases. Allyl radicals mainly isomerize to produce s-C_3H_5 radicals. 1-Propyl and s-C_3H_5 radicals decompose by β-scission and mainly lead to the formation of methyl radicals, and ethylene and acetylene, respectively. The importance of the unimolecular decomposition involves that methyl radicals are rapidly formed when 1-hexene is consumed, as shown in Fig. 8. As methyl radicals mainly lead to termination reactions among themselves or with allyl radicals, this unimolecular initiation does not promote much the multiplication of radicals leading to auto-ignition. Nine percentage of 1-hexene also react by additions of hydrogen atoms to give C_6-alkyls radicals that decompose by β-scission to give smaller alkenes and alkyl radicals (see Fig. 6), and 9% by allylic metatheses to give resonance stabilized propylallyl radicals that rapidly decompose to produce 1,3-butadiene and methyl radicals. Minor consumption channels of 1-hexene, not included in Fig. 6, include the 2 other unimolecular decompositions and the 3 possible alkylic metatheses.

4.2.2. Main consumption pathways of propene molecules

Retro-ene reactions are not possible for propene and unimolecular initiations, which involve the formation of vinyl radicals, are more difficult than for 1-hexene. The rate of consumption of propene is lower than that of 1-hexene, as shown in Fig. 8. As shown in a previous study [26], propene mainly reacts by H-abstraction of allylic hydrogen atoms by H atoms and OH radicals to give resonance stabilized allyl radicals. This leads to an additional production of methyl radicals by the channels previously described and explains why the temporal profile of this species presents 2 maxima in Fig. 8. Minor consumption channels include vinylic metatheses to form s-C_3H_5 radicals and additions of O atoms and OH radicals to the double bond.

4.2.3. Main formation pathways of hydroxyl radicals

Figure 8 presents the temporal profile of hydroxyl radicals, which was used to determine the computed ignition delay. The fact that this profile is not as steep as the experimental emission, which is related to excited hydroxyl radicals, is a source of error in the determination of the simulated delay. A flow rate analysis performed for a residence time just before the start of the auto-ignition shows that the formation of these radicals was mainly derived from the reactions of methyl radicals. Apart from termination step, methyl radicals react with O_2 to yield formaldehyde and hydroxyl radicals, $CH_3 + O_2 \rightarrow CH_2O + OH$ (Ox-methyl); Fig. 7 shows the promoting influence of this reaction. As in our previous modeling of auto-ignition in a shock tube [26], the most promoting reaction

is the branching step between hydrogen atoms and oxygen molecules to give hydroxyl radicals and oxygen atoms, $H + O_2 \rightarrow O + OH$ (H-Branching), as shown in Fig. 7 by dividing its rate constant by a factor of 2. Hydrogen atoms are mainly formed from ethyl radicals and butenyl radicals.

5. Conclusion

The ignition delay times of 1-hexene/O_2/Ar mixtures have been measured between 1250 and 1700 K for 3 equivalence ratio values ($\Phi = 0.5$, 1, and 1.5) at a pressure of about 0.2 MPa. The ignition delay time, τ_i, varies differently according to the temperature domain:

(1) At higher temperatures, greater than 1400 K, the logarithm of τ_i varies linearly as a function of the temperature inverse for a given value of equivalence ratio. The apparent activation energy is approximately equal to 230 kJ mol^{-1}. The ignition delay times (s) can be correlated to the reactant concentration (mol cm^{-3}) and to the temperature (K):

$$\tau_i = 1.14 \times 10^{-13} [1\text{-}C_6H_{12}]^{0.77} [O_2]^{-1.24} \exp(27,900/T).$$

With this expression the delay time is estimated with an accuracy better than 12%.

(2) At lower temperature, less than 1400 K, the apparent activation energy strongly decreases and becomes equal to about 120 kJ mol^{-1}. The correlation between τ_i, reactant concentration and temperature between 1280 ant 1400 K becomes:

$$\tau_i = 3.32 \times 10^{-10} [1\text{-}C_6H_{12}]^{0.53} [O_2]^{-0.93} \exp(13,960/T).$$

In this case, τ_i is estimated with an accuracy of about 10%.

A detailed chemical mechanism of the 1-hexene oxidation has been developed with the "EXGAS" program including recent results on the oxidation models of propene and 1-butene. The agreement between computed and measured values of τ_i was globally acceptable and can be estimated with an accuracy better than 50%. The major channels of the chemical species fluxes and an analysis of the sensitivity of some important reactions have been discussed: at low temperature, 1-hexene is mainly consumed by retro-ene reaction to give propene and, in a smaller ratio, by unimolecular decomposition to give allyl and 1-propyl radicals. At high temperature, the repartition between these 2 major channels changes: unimolecular decomposition becomes more important than retro-ene one. However, the change in the activation energy below 1400 K was not explained by the detailed model. The auto-ignition delay times of 1-hexene have been compared to those of other unsaturated hydrocarbons for stoichiometric mixtures diluted by 99 mol% of argon at a pressure of 200 kPa. The shortest delays are obtained

for 1-octene while the longest ones are obtained for propene. With iso-butene and ethylene, the ignition delay times are closer to 1-hexene in the low temperature side and to propene in the high temperature one.

Acknowledgments

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Comments

Wing Tsang, NIST, USA. In your slide on C-C bond cleavage you give a rate expression 1.2×10^{15} exp $(-37580/T)$ s^{-1} which is clearly in error. Indeed you use a value for the retroene process that was given in that paper. The real problem is that your number calls into question the KINGAS program for calculating rate parameters for bond breaking reactions.

Reply. The proposed rate constant for the unimolecular decomposition of 1-hexene, $k = 1.8 \times 10^{15}$ exp$(-37770/$ T$)$ s^{-1} (there was a misprint in the A factor of the slide), has been calculated by KINGAS at a temperature of 1400 K, close to the temperature used in the experimental study, while the value proposed by W. Tsang, $k = 7.9 \times 10^{15}$ exp$(-35720/T)$ s^{-1} (Ref. [8] in paper), has been measured around 1000 K.

The software KINGAS estimates the A factor of dissociation from that of the reverse recombination using thermo-chemistry. The A factor of the recombination is obtained from the modified collision theory.

$A = 1/4$ Zo P, with

- Zo, the collision number, which very slightly increases with temperature (T**0.16),
- P, the steric factor, which depends on the nature of the bond created and on temperature; for the reaction studied, $P = 0.067$ at 1000 K, and $P = 0.033$ at 1400 K.

The thermo-chemical relationships between the direct and the reverse kinetic parameter depends also on temperature and, finally, the rate constant calculated by KINGAS at 1000 K is, $A = 5.1 \times 10^{15} \exp(-35730/T)$ s^{-1}, which is in a rather good agreement with the experimental value.

●

Joel M. Hall, University of Central Florida, USA. In a sample emission trace, you pointed out a small rise before the main ignition for a 99.3% dilute mixture. Did you observe this effect in mixtures of lower dilution, and if not, could it be due to dilution level and/or impurities?

Reply. The small peak that was observed at 306 nm before the main emission corresponding to explosive reaction probably is not due to impurities. 1-hexene was of high purity (+99 %) and such a small peak was observed with other hydrocarbon/oxygen mixtures by other researchers [1,2]. In the presence of iso-octane, the first emission would be controlled by the reaction $C_3H_7 \rightarrow CH_3 + C_2H_4$ [3]. In our case, C_3H_7 could be produced by the unimolecular decomposition that becomes more important than the retroene reaction at high temperature. Indeed, it was observed that the relative importance of first emission mainly depends on the temperature domain.

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