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**Oxidation and combustion of the n-hexene isomers: a wide
range kinetic modeling study**

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Abstract

A detailed chemical kinetic mechanism has been developed to study the oxidation of the straight-chain isomers of hexene over a wide range of operating conditions. The main features of this detailed kinetic mechanism, which includes both high and low temperature reaction pathways, are presented and discussed with special emphasis on the main classes of reactions involved in alkene oxidation. Simulation results have been compared with experimental data over a wide range of operating conditions including shock tube, jet stirred reactor and rapid compression machine. The different reactivities of the three isomers have been successfully predicted by the model. Isomerization reactions of the hexenyl radicals were found to play a significant role in the chemistry and interactions of the three n-hexene isomers. A comparative reaction flux analysis is used to verify and discuss the fundamental role of the double bond position in the isomerization reactions of alkenyl radicals, as well as the impact of the allylic site in the low and high temperature mechanism of fuel oxidation.

Introduction

The increasing costs of fuel and the impact of combustion processes on the environment represent nowadays a critical and challenging issue. Deeper understanding of the basic mechanisms of combustion processes, and the capability to reproduce them by means of detailed kinetic models, represent a powerful tool to improve both the fuel quality and the design of combustion devices, burners and engines.

While extensive literature exists for the combustion of alkanes, unsaturated hydrocarbon oxidation still needs a more thorough investigation and a better knowledge. This is illustrated by the limited number of works concerning alkene oxidation which are available. Pitz et al. [1] performed an early experimental and modeling study of the oxidation of butenes in motored engines. Other contribution came from Minetti et al. [2], who carried out a Rapid Compression Machine (RCM) study on 1-pentene at low temperature, and from Prabhu et al. [3], who investigated it in a plug flow reactor between 654 and 716 K. Despite of this scarce literature, alkenes are important decomposition intermediates in the pyrolysis and combustion of large alkanes and they are also added to commercial gasoline to improve the octane rating. The importance of a proper understanding of alkene oxidation mechanisms appears evident when analyzing Fig. 1, where research and motor octane numbers (RON and MON) are reported and compared for different alkanes and alkenes. The octane number (ON) of an alkene is higher when compared to the value of the corresponding alkane, as a result of its lower reactivity. Different isomers show a different reactivity and 1-alkenes are the most reactive while 3-alkenes show the highest ON. The differences between RON and MON rating of alkenes is discussed elsewhere [4-5]

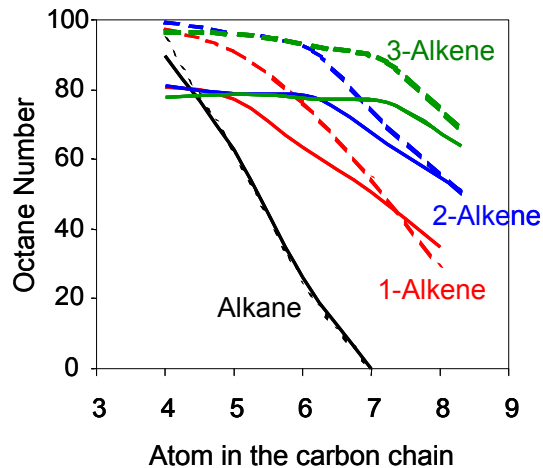


Figure 1: RON (dashed) and MON (solid) values for different classes of hydrocarbons

Decomposition and combustion of alkenes are also important in the pyrolysis and oxidation of cyclo-alkanes. This is because ring opening and isomerization reactions of cyclo-alkyl radical form different 1-alkenyl radicals [6]. Tsang [7] also noted this fact in his kinetic study of the decomposition and isomerization of 1-pentenyl radicals. However, the basic knowledge concerning alkene oxidation mechanisms is still an open issue and both experimental and modeling studies are needed to fill the gap compared to the more complete understanding of normal and branched alkane fuels. This is particularly true when considering large alkenes with more than four carbon atoms, where the position of the double bond in the carbon skeleton modifies the role of the different reaction paths.

In recent studies of alkenes, Vanhove et al. [8] investigated the autoignition of 1-, 2-, and 3-hexene in the Lille RCM in the temperature range 630 - 850 K for stoichiometric mixtures. Different diluents of N_2 , CO_2 and Ar were used to achieve a range of

compression temperatures while the O₂ concentration was maintained to that of air. They found that the reactivity of the different isomers is related to the double bond position, the type and number of C–H bonds, the stability of intermediate radicals, and the cyclic strain of the transition state of isomerization reactions. 1-hexene reacts with the typical features of alkanes and shows a two-stage ignition with a cool flame and a well defined negative temperature coefficient region, while 3-hexene only shows a single stage ignition and 2-hexene has an intermediate behavior. This behaviour is typical also of heptene isomers, as experienced by Tanaka [9] who observed a two stage ignition in the oxidation of 1- and 2- heptane in a rapid compression machine while only a single stage ignition was shown by 3-heptene.

In other recent works Yahyaoui et al. [10] studied the auto-ignition delay times of 1-C₆H₁₂/O₂/Ar mixtures between 1270 and 1700 K using shock tube technique for rich and lean mixtures at a pressure of about 0.2 MPa. A detailed chemical mechanism of the 1-hexene oxidation was also developed with the “EXGAS” program. A more complete discussion on the kinetic mechanisms for the oxidation of 1-pentene and 1-hexene at low temperature was then presented by Touchard et al. [11]. Namely, important improvements of the kinetic rules used by the EXGAS system for the automatic generation are discussed and the definition of the specific generic reactions involving alkenes and their free radicals, together with the relating rate values, were introduced. These detailed kinetic mechanisms at low temperature were also validated using experimental data obtained in a rapid compression machine between 600 and 900 K. The study confirms the significant role played in autoignition delays by the reaction of addition of hydroxyl radicals to the double bond and by the specific reactivity of the

allylic radical. The important role played by the reactions of allylic and alkenyl radicals with O_2 to produce dienes is also emphasized. Yahyaoui et al. [12] extended the previous kinetic study in the shock tube and investigated the 1-hexene oxidation in the jet-stirred reactor (JSR) between 750 and 1200 K, at a pressure of 1 MPa, and 0.1% of fuel diluted in N_2 by also varying the equivalence ratios.

Chemical Kinetic Model

The kinetic scheme discussed here represents an extension of the previous widely tested mechanism of alkanes combustion. Due to the hierarchical concept and modularity characterizing the adopted approach, a limited set of reactions specific to the considered class of species are necessary to characterize the oxidative behavior of the alkenes. The core of the model is comprised of a detailed sub-mechanism for C_1 - C_4 species [13-14] and the characteristic modular structure allows the introduction of different reaction subsystems, necessary to describe the oxidation and the pyrolysis of higher hydrocarbons at different conditions. Assuming rules for analogous reactions, only a few fundamental kinetic parameters are needed to extend the scheme to heavier species. These fundamental rate parameters define the main classes of reactions, appropriate to the different temperature ranges. This method is here applied to the definition of the rate parameters typical of unsaturated hydrocarbon reactivity. In the following paragraphs the attention mainly is focused on the definition of such rules for species containing double bonds.

A detailed approach has been applied to hexene mechanism, because of the need of a deeper understanding of the unsaturated hydrocarbon reactivity. The detailed model for hexenes developed here will later be reduced with lumping procedures so that it will have

the level of detail as the overall model of C1-C16 combustion. The general approach considered here is the natural extension of the methods developed and successfully applied by Milano, LLNL and Nancy groups. [13, 15-16].

The thermodynamic properties of all the species included in the mechanism were evaluated using the THERM program developed by Ritter and Bozzelli, implementing Benson's group additivity method [17-18].

The hexene submodel, including both the high and low temperature mechanism of the three isomers was added to the existing C1-C16 mechanism. The combined mechanism contains a total of about 350 species and 8000 reactions, while the hexene module only involves about 100 species. The thermodynamic properties and the chemical kinetic mechanism are available in Chemkin format.

[<http://www.chem.polimi.it/CRECKModeling/>]

This general mechanism is intended to be applied to the simulation of complex systems like internal combustion engines, for this reason the number of chemical species in large hydrocarbon sub-schemes is generally limited to reduce the computational efforts. Lumping procedures can be used to meet this requirement, as described in previous works [19].

Alkene Reactivity

Like saturated species, the oxidation of long chain alkene species is characterized by low and high temperature reactions. The high temperature oxidation starts typically with the homolytic cleavage of the molecules and proceeds through the interaction of smaller radicals with oxygen. Obviously the double bond influences the preferential breaking

sites. Other relevant pathways and peculiar behaviors are described in the following paragraphs. Low temperature oxidation follows similar pathways of alkanes. Experimental studies evidenced that these mechanisms assume a key role especially when the saturated portion of the fuel is longer, while, generally speaking, the double bond appears to be a hindrance to the low temperature ignition of hydrocarbons. The kinetic mechanism is here discussed focusing the attention on the role of the allylic position and the structural effects of unsaturation on the ketohydroperoxide formation process.

The main results of this study are then summarized in a limited set of kinetic parameters that are intended to represent a basic resource for the extension of the approach to other large unsaturated species.

High Temperature Reactivity

Initiation Reactions

The first stage of high temperature oxidation of hydrocarbons involves the homolytic cleavage of the fuel into two radicals. This step affects the composition of the radical pool and the initial reactivity of the system. When considering unsaturated hydrocarbons, the most favored site for this initiation reaction is generally the one resulting in a resonantly stabilized radical and an alkyl one, with an activation energy (E_a) of about 71000 kcal/kmol [20]. The lower pre-exponential factor is applied in this case where an allyl radical is being formed is likely due to resonance and a corresponding loss of a rotor in the transition state (Table 1). All the other possible initiation breakages of the hexene molecule have also been taken into account, including the cleavage of the relatively weak

H-C allyl bond ($E_a = 82000$ kcal/kmol). It is interesting to observe how the position of the double bond inside the chain can influence the formation of allyl, ethyl or methyl radicals. The relative proportions of these radicals are important in determining the reactivity of the system. Both the methyl and the allyl radicals are relatively unreactive, while the ethyl increases the global reactivity decomposing into ethylene and an H radical that can easily attack the double bond and is a chain branching promoter.

Obviously the cleavage of the double bond is practically negligible in most of the operating conditions, because of the higher activation energy required for this breakage.

Table 1 reports a set of reference values used for this class of reactions as well as some literature values.

	This Work	Reference
Allyl C-C bond	$8 \times 10^{15} e^{-71000/RT}$	$7.94 \times 10^{15} e^{-70740/RT}$ [20].
Sec. C-C bond	$3 \times 10^{16} e^{-82500/RT}$	$2.51 \times 10^{16} e^{-82070/RT}$ [21]
Pri. Allyl C-H bond	$2 \times 10^{15} e^{-84000/RT}$	$3.98 \times 10^{15} e^{-85050/RT}$ [22]
Sec. Allyl C-H bond	$2 \times 10^{15} e^{-82000/RT}$	$1.26 \times 10^{15} e^{-82470/RT}$ [22]

Table 1: Adopted and literature values of rate constants for initiation reactions (kcal-s-kmole-m³ units)

Molecular Dissociation

These molecular reactions, known also as retroene reactions, involve the decomposition of the fuel in two smaller alkenes. These reactions are normally important in alkene pyrolysis [23]. Unlike initiation reactions, no radical species are produced. Also in this case the position of the double bond in the molecule is a conditioning factor: while 1- and

2-hexene can undergo retroene reaction, that is prohibitive for 3-hexene. The minimum requirement of this kind of decomposition is a residual alkyl chain of 3 saturated carbon atoms because of the 6 member transition state involved in the reaction. The reference value adopted for the decomposition of 1-hexene in two propylene molecules is $4 \times 10^{12} \exp(-58000/RT) \text{ s}^{-1}$, as reported by King [20].

Radical Addition

As already mentioned, unlike alkane molecules, alkenes can easily undergo radical addition reactions on the double bonds. This is one of the most important features of alkenes. At high temperature the adducts formed rapidly decompose to products, while in the low temperature region they can undergo successive oxidative reactions.

	This Work	Reference
H addition	$3 \times 10^{10} e^{-1500/RT}$	$1.3 \times 10^{10} e^{-1560/RT}$ [24]
OH addition	$6 \times 10^9 e^{-1000/RT}$	9.91×10^9 [25]
HCO addition	$3 \times 10^8 e^{-6000/RT}$	$1.02 \times 10^8 e^{-5000/RT}$ [26]
CH ₃ addition	$1 \times 10^9 e^{-7600/RT}$	$.78 \times 10^8 e^{-7050/RT}$ [27]
C ₃ H ₅ addition	$1 \times 10^8 e^{-14000/RT}$	$3.55 \times 10^8 e^{-16890/RT}$ [28]

Table 2: Adopted and literature values of rate constants for additions reactions (kcal-s-kmole-m³ units)

Typical activation energies for this class of reactions range from being almost negligible for the most reactive radicals (such as O and OH) up to 12000 kcal/kmol in the case of

the relatively stable HO₂ radical. As an example Table 2 reports some values of the rate constant adopted in the mechanism.

Abstraction Reactions

The rate constants for this class of reactions were obtained with a generalized approach using a set of reaction rate rules for the abstracting radicals. These rate constant parameters are corrected taking into account the type of the H atom abstracted. Also in this case, the allylic position plays a fundamental role because of the lower activation energy and pre-exponential factor required for the formation of a resonantly stabilized alkenyl radical. As an example, when considering an abstraction reaction carried out by a H atom. The activation energy for abstraction of a primary H is about 6500 kcal/kmol, about 4000 kcal/kmol higher than for an allylic one. No differences in frequency factor are accounted for. The reduction of the reaction rate due to the higher activation energy becomes less relevant when temperature increases so that the differences in the rate constants are less significant. An extensive description of the methodology here applied can be found in [29]. As a matter of example, Table 5 reports some of the reference rate constant here adopted. The abstraction reactions of hydrogen by alkyl radicals are listed categorized by the radical site and the hydrogen type.

Radical Decompositions

The radicals formed by abstraction can decompose or isomerize, depending on the type and the position of the radical site. Decomposition reactions of allyl radical are

significantly less favored than primary radicals, because of resonance stabilization. Moreover, because of the presence of the double bond, some decompositions are almost negligible at low temperature conditions, because of the high activation energy required by the vinyl radical formation.

Table 3 reports some values adopted in the kinetic mechanism, considering the contributions coming from the starting radical and the decomposition products. These values are deduced by analogous reaction involving similar structures such as pentenyl decomposition [30].

	Methyl	Primary	Allyl
Primary	32500	30000	25000
Secondary	33500	31500	26000
Allyl	37500	35000	30000

Table 3: Adopted values of activation energy (kcal/kmol) for decomposition reactions starting from primary, secondary or allyl radicals.

Radical Isomerization

An alternative pathway to β -decomposition is the isomerization with the migration the radical position and, in specific cases, even of the double bond. Because of the high concentration of the resonant radicals, at high temperature it is possible to have the formation of less stable alkenyl radicals that decompose faster. Also in this case generalized rules have been used for the evaluation of rate constants, as already discussed in previous papers [13-14]. When considering the internal abstractions, all the reactions

are considered to be reversible and reverse reaction rates are calculated using the thermodynamic properties of the species involved.

Figure 2 shows the radicals obtained starting from the different isomers of hexene as well as the isomerization reactions among them.

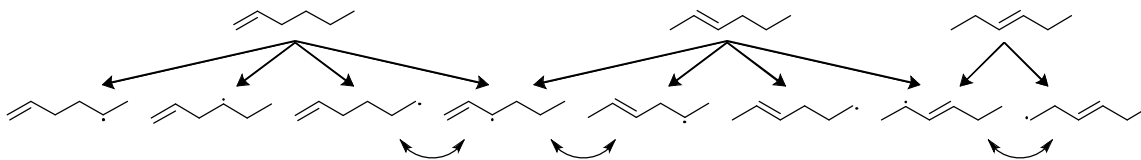


Figure 2: Isomerization reactions among hexenyl radicals

The radical isomerization rates used and their references are given in Table 5.

Low Temperature Mechanism

Even if the main classes of reactions involved in the low temperature oxidation of large alkenes are similar to alkanes, their oxidative behavior can change significantly depending on the length of the saturated portion of the fuels. Addition reactions on the double bond increase the complexity of the typical reaction scheme of unsaturated hydrocarbons, as shown in Fig. 3. Moreover the presence of allylic sites allows preferential reaction pathways to take place. In the next paragraphs the low temperature reaction mechanism will be discussed, focusing the attention on the differences in the chemistry of alkenes compared to alkanes.

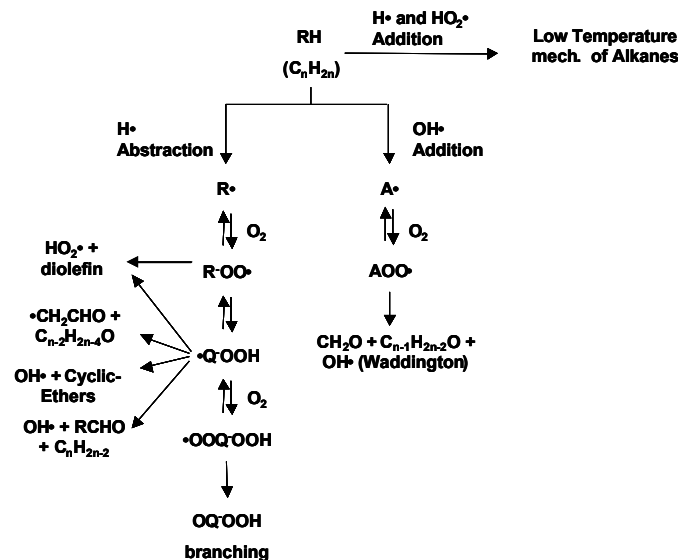


Figure 3: Primary oxidation reactions of olefins

Oxygen Additions

The first step of low temperature oxidation of hydrocarbons is the addition of hydrocarbon radicals ($\text{R}\cdot$) to molecular oxygen (Fig. 3). While this reaction occurs without activation energy on a primary or secondary radical, the allylic site is penalized by a 1000 kcal/kmol barrier and by a lower pre-exponential factor because loss of resonance in the $\text{ROO}\cdot$ adduct. At the same time the decomposition of the alkenylperoxy radicals back to reactants is extremely fast if the O_2 group is located in the allyl position, having an activation energy of about 20000-25000 kcal/kmol when the analogous reaction for an alkylperoxy radical is about 30000 kcal/kmol. These values are in accordance with similar ones proposed by [31] in a recent paper concerning the allyl radical reactivity.

Direct Eliminations ($\text{ROO}\cdot \rightleftharpoons \text{diolefin} + \text{HO}_2$)

An alkylperoxy radicals ($\text{ROO}\cdot$) can form alkene and HO_2 radical through an elimination reaction [32]. In the case of alkenylperoxy radicals, this direct elimination will yield diolefin rather than an alkene (Fig. 3). We are not aware of any studies on HO_2 elimination for this case. We expect that the weakness of the allyl C-H bond compared to a primary or secondary C-H bond will enhance the direct elimination of HO_2 . This aspect is particularly relevant when considering the case of 3-hexene, where the short alkyl chains avoid isomerizations and direct eliminations rule the reactivity of the system. As a result large quantities of 1,3-hexadiene and 2,4-hexadiene are produced during its low temperature oxidation, as experimentally detected by [8].

The rate constant for the direct elimination of HO_2 involving a secondary hydrogen is assumed to be $3 \times 10^{12} e^{-29500/RT}$, when an allylic H is involved, the activation energy is reduced to 26000 kcal/kmol only.

A literature value for the corresponding reaction of the ethylperoxy radical is $7.14 \times 10^4 T^{2.32} e^{-27960/RT}$, as reported by Miller and Klippenstein [33]

Alkenyl peroxy to hydroperoxy alkenyl isomerization ($\text{ROO}\cdot$

$\rightleftharpoons \cdot\text{QOOH}$)

The rate constants for this class of reactions can be influenced by the position of the double bond in four different ways:

- double bonds inside the chain generally is an obstacle to the internal isomerization of the molecules;
- the allyl hydrogen are more easily abstracted than secondary and primary ones;

- the vinyl hydrogen are difficult to abstract
- the presence of weak allyl C-H bonds favors the direct elimination of HO₂.

Double bonds give rigidity to the structure avoiding the formation of the ringed transition state for the internal isomerization, when the alkene has a (E) stereochemistry.

The model assumes that the isomerization between (Z) and (E) geometry can easily occur for allyl radicals. This hypothesis is implemented reducing the frequency factor by a factor 2 for all the isomerization reactions containing a double bond in the ringed transition state.

Since allyl hydrogen requires about 4000 kcal/kmol less than a primary one when it is abstracted, 5 member ring isomerization reactions on allyl H can be competitive or even faster than 6 member isomerizations involving alkyl hydrogens. Table 4 shows the activation energy adopted for the internal isomerization reactions varying the dimension of the involved ring and the type of abstracted hydrogen.

The next three classes of reactions represent alternative pathways to the low temperature branching mechanism and play a fundamental role in the NTC region slowing down the reactivity of the system.

Ring Size	allyl	secondary	primary
5	25200	26800	29100
6	19100	20700	23000
7	19100	20700	23000

Table 4: Adopted values of activation energy [kcal/kmol] for internal isomerization reactions

β -decomposition reactions

This class of reactions involves the decomposition of hydroperoxy-alkenyl radical to smaller fragments and an OH radical. The decomposition is assumed to happen in a single step and the rate parameters as well as the final products are estimated considering the stability of the initial radical site (primary, secondary or allylic) and the bonds that more easily can be broken. Decomposition rates have been then calculated applying the same rules described for alkenyl radicals.

Heterocycle formation

The interaction between the radical site and the hydroperoxy group may result in the elimination of an OH radical and the formation of a heterocycle compound. The model takes into account three possible sizes for the ring formation in the heterocycle compound, 3, 4, and 5 member cycles.

Reaction rates for this class of reaction have to take into account both the entropic and energetic corrections due to the variations in the number of free rotors and the strain due to the ring size. 5 member ring heterocycles are favored in terms of activation energy while 3 member rings have the highest frequency factor.

A more extensive discussion for this set of reactions, typical also of saturated hydrocarbons, is reported in previous papers [13-14].

HO₂ β -decomposition (Q·OOH \rightleftharpoons diolefin + HO₂)

Though isomerizations of ROO· to Q·OOH, it is still possible to obtain a diolefin and HO₂ through the β -scission of Q·OOH structures having a hydroperoxy group adjacent to a radical site. The formation of such Q·OOH structures is characterized by a relatively

high activation energy (nearly 30000 kcal/kmol) because of the 5 member ring transition state. Anyway, since the C-O bond is weaker than C-C, when it is possible, the formation of HO₂ is preferred to breakage of the carbon chain, especially at lower temperature. The corrections due to the different stability of the starting radical are calculated applying the same criteria used for β-decomposition.

Waddington mechanism

At low temperatures, radical additions are easily followed by interactions with oxygen, because of the relative stability of the adduct. Hydroxy-alkyl radicals, the most abundant products of radical additions, can undergo oxygen additions leading to hydroxy-alkyl-peroxyl radicals. This unstable species easily decomposes to aldehydes and propagating OH radicals. This reaction pathway, known as Waddington decomposition, is an important non-branching oxidation route of linear unsaturated compounds. This addition-decomposition process has been recently investigated in a ab initio study by Sun et al. [34].

Similar reaction products are obtained by the direct interaction of O₂ molecules with the double bond of alkenes, through the four center transition state. Although this reaction was included in the mechanism, flux analysis proved it to play a minor role.

Final considerations

The complete mechanism here discussed can be downloaded at [<http://www.chem.polimi.it/CRECKModeling/>]. While this mechanism was developed

for the oxidation of hexenes, most of the considerations presented above can be conveniently generalized to the combustion of other alkenes, C4 and higher.

The rate constant and the corrections due to the presence of double bonds inside the alkyl chain can be summarized in a set of fundamental rate parameters useful to the development of generalized kinetic models for alkanes and alkenes oxidation. Table 5 includes the result of this systematic classification. Similar sets of rate parameters have been successfully used for the automatic generation of reaction mechanisms for higher alkanes oxidation and pyrolysis [35]

This table represents obviously an attempt of identifying and organizing the necessary fundamental kinetic constants for a wide range of non aromatic structures, including alkenes, further investigations will allow to improve the precision and the reliability of these values.

Initiation Reactions: Unimolecular decomposition of C-C bonds				
CH3-Csec	Csec-Csec	Csec-Cter	Csec-Cquat	
$10^{16.7} \exp(-84500/RT)$	$10^{16.7} \exp(-82000/RT)$	$10^{16.7} \exp(-81000/RT)$	$10^{16.7} \exp(-78500/RT)$	
CH3-Call	Csec-Call			
$10^{16.0} \exp(-73000/RT)$	$10^{16.0} \exp(-71000/RT)$			
Initiation Reactions: Unimolecular decomposition of C-H bonds				
Call-Hpri		Call-Hsec		
$10^{15.3} \exp(-84000/RT)$		$10^{15.3} \exp(-82000/RT)$		
Oxygen Addition on radicals				
Alkyl radical		Resonant allyl radical		
$10^{9.5}$		$10^{9.3} \exp(-1000/RT)$		
H-Abstraction Reactions of Alkyl Radicals^a (rate per C-H site)				
	Primary H atom	Secondary H atom	Tertiary H atom	Allyl H atom
Primary radical	$10^8 \exp(-13500/RT)$	$10^8 \exp(-11200/RT)$	$10^8 \exp(-9000/RT)$	$10^8 \exp(-9500/RT)$
Secondary radical	$10^8 \exp(-14500/RT)$	$10^8 \exp(-12200/RT)$	$10^8 \exp(-10000/RT)$	$10^8 \exp(-10500/RT)$
Tertiary radical	$10^8 \exp(-15000/RT)$	$10^8 \exp(-12700/RT)$	$10^8 \exp(-10500/RT)$	$10^8 \exp(-11000/RT)$
Allyl radical	$10^8 \exp(-22500/RT)$	$10^8 \exp(-19200/RT)$	$10^8 \exp(-17500/RT)$	$10^8 \exp(-18000/RT)$

Isomerization Reactions (Transfer of a Primary H-atom ^b , rate per C-H site)				
	1-4 H Transfer	1-5 H Transfer	1-6 H Transfer	
Primary radical	$10^{11.0} \exp(-20600/RT)$	$10^{10.2} \exp(-14500/RT)$	$10^{9.5} \exp(-19500/RT)$	
Secondary radical	$10^{11.0} \exp(-21600/RT)$	$10^{10.2} \exp(-15500/RT)$	$10^{9.5} \exp(-20500/RT)$	
Tertiary radical	$10^{11.0} \exp(-22100/RT)$	$10^{10.2} \exp(-16000/RT)$	$10^{9.5} \exp(-21000/RT)$	
Allyl radical	$10^{11.0} \exp(-26900/RT)$	$10^{10.2} \exp(-20800/RT)$	$10^{9.5} \exp(-25800/RT)$	
Alkyl Radical Decomposition Reactions (to form Primary Radicals)				
Primary radical	Secondary radical	Tertiary radical	Allyl radical	
$10^{14.0} \exp(-30000/RT)$	$10^{14.0} \exp(-31000/RT)$	$10^{14.0} \exp(-31500/RT)$	$10^{13.0} \exp(-35000/RT)$	
Corrections of decomposition rates to form:^c				
Methyl radical	Secondary radical	Tertiary radical	Allyl radical	
$\exp(-2500/RT)$	$\exp(1500/RT)$	$\exp(2500/RT)$	$10^{-5} \exp(5000/RT)$	
H-Abstraction Reactions (per C-H site)				
	Primary H atom	Secondary H atom	Tertiary H atom	Allylic H atom
Peroxy radical	$10^{8.7} \exp(-21500/RT)$	$10^{8.7} \exp(-18800/RT)$	$10^{8.7} \exp(-16500/RT)$	$10^{8.7} \exp(-14500/RT)$
Isomerization Reactions (Transfer of a Primary H-atom ^b , rate per C-H site)				
	1-4 H Transfer	1-5 H Transfer	1-6 H Transfer	
Peroxy radical	$10^{11.8} \exp(-29100/RT)$	$10^{11.0} \exp(-23000.0/RT)$	$10^{10.6} \exp(-23000/RT)$	
Peroxy radical of cycloalkanes	$10^{12.5} \exp(-32600/RT)$	$10^{12.2} \exp(-26500/RT)$	$10^{11.9} \exp(-31500/RT)$	
Hydroperoxy-Alkyl Radical Decomposition Reactions to form:				
HO2• and Conjugate Olefins		Smaller Olefins		
$10^{14.0} \exp(-23000/RT)$		$10^{13.2} \exp(-22500/RT)$		
HO2 group on the allylic C site		HO2 group adjacent to the allylic radical		
$10^{14.0} \exp(-20000/RT)$		$10^{14.0} \exp(-27000/RT)$		
to form Cyclic Ethers				
Oxirans	Oxetans	Furans		
$10^{12.0} \exp(-18000/RT)$	$10^{11.2} \exp(-17000/RT)$	$10^{10.4} \exp(-8500/RT)$		

Table 5 : Kinetic references adopted in this work (kcal-s-kmole-m3 units). Call is an allylic carbon. Cquat is a quaternary carbon.

Footnotes:

a) Usually abstractions have high T^N , in the kinetic mechanism $N=2$ is assumed. For simplicity reasons, in the table the rate constant expression were fitted to the Arrhenius form matching the constant values at 1000K

b) Corrections for secondary and tertiary H-atoms are assumed in analogy to H-abstractions

c) Standard constant should be multiplied by the correction

Results and discussion

The model has been validated on the basis of the available high and low temperature data. The oxidation of 1-hexene has been studied by Yahyaoui et al. [10, 12] in a Shock tube and a Jet Stirred reactor at different conditions ranging from 750K up to about 1800K varying the pressure and the stoichiometry. Unfortunately no information is available for the other two isomers. On the contrary, RCM data are available for all the three isomers at low temperature conditions and different pressures. In the next paragraphs, the comparison of the simulated and experimental data will be presented as well as some comparative calculations for the three isomers.

Shock Tube Data

Shock tube experiments allow investigation of the high temperature reactivity of hydrocarbons. In section, we compare ignition delay times computed from the model with those measured in a shock tube for 1-hexene. The experiments were carried out at CNRS in Orléans for 1-hexene, oxygen and argon mixtures at constant fuel concentration (0.1%) and different equivalence ratio ($\Phi=0.5, 1, 1.5$) [10, 12]. The operating conditions cover a range of temperatures between 1300K and 1900K at 2 and 1.0 MPa. Figure 4 shows the comparison between measurements and calculations. The good agreement with the experiments supports the validity of the model, as it reproduces correctly the influence of pressure and equivalence ratio.

Panel c) of the same figure focuses the attention on the effect of different fuel concentrations, respectively 0.1% and 0.4% [10]. Even if the induction times are over

predicted at higher temperatures (above 1550K), the effect of the fuel concentration is correctly estimated.

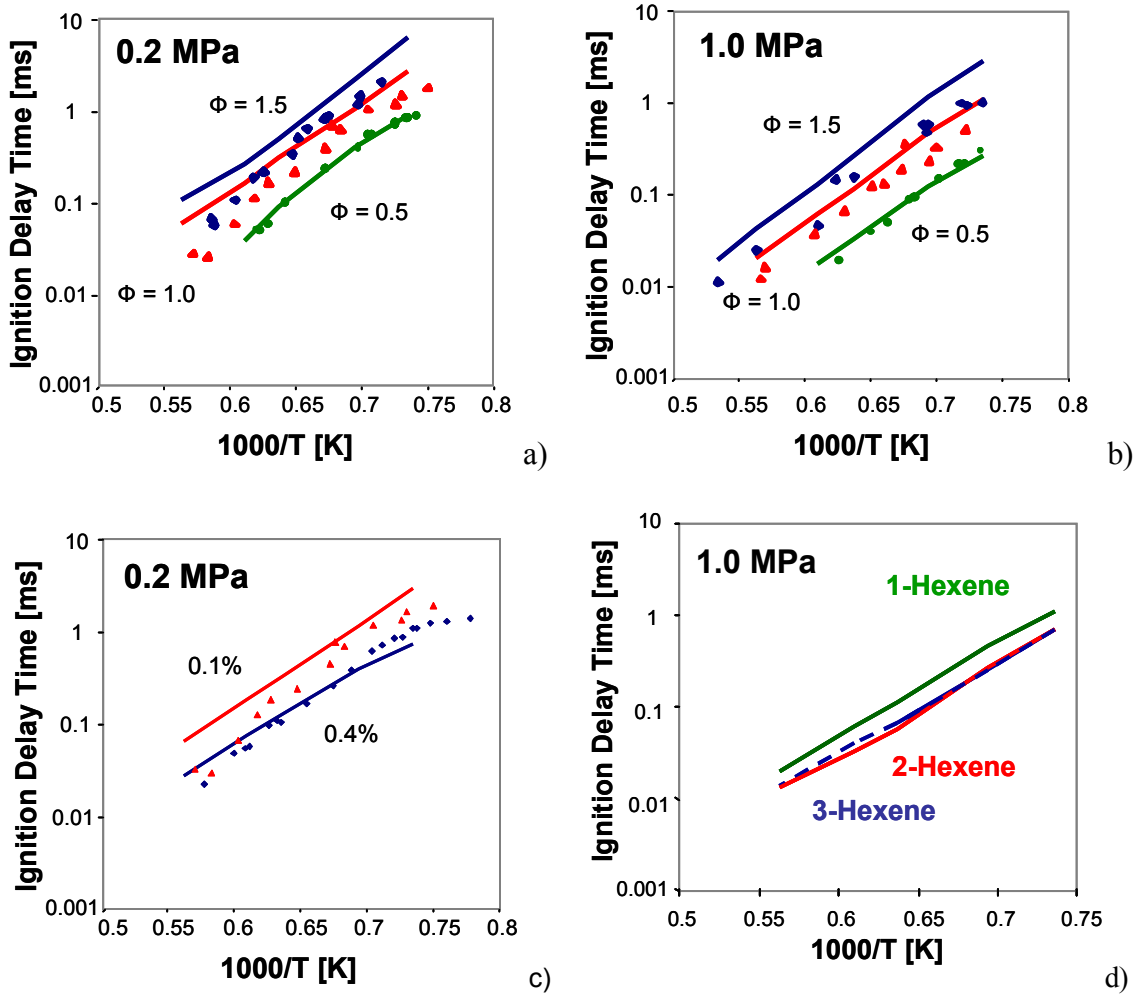


Figure 4: ST experiments (symbols) and simulations (lines): a) ignition delay times of 1-hexene at 0.2 MPa at different stoichiometric conditions; b) ignition delay times of 1-hexene at 1.0 MPa at different stoichiometric conditions [12]; c) ignition delay times of 1-hexene at 0.2 MPa at different fuel concentration conditions [10]; d) ignition delay times of hexene isomers at 1.0 MPa.

After this positive validation of the 1-hexene mechanism, the behavior of the three isomers of the hexene has been then compared in the same conditions. The set of simulations presented in Fig. 4d shows the induction times at 1.0 MPa of 1-hexene, 2-

hexene and 3-hexene in stoichiometric conditions. It's interesting to observe that the mechanism predicts the first isomer have the slowest reactivity.

This behavior can be justified by examining the dominant initiation reactions for each isomer, as discussed later. Future experiments will be necessary to confirm these predicted results.

Jet Stirred Reactor Data

The next sets of comparisons involve Jet Stirred Reactor data obtained in a range of temperature from 750K to 1050K [12]. These data are particularly useful for the validation of the distribution of intermediate and final products. Simulations were performed assuming isothermal, constant pressure conditions, considering a perfect mixing of the reactants and a fixed residence time (0.5 s). Figure 5 shows the oxidation of 1-hexene at two different equivalence ratios. In both the considered conditions the agreement between experiments and calculations can be considered satisfactory. It should be noticed how in the second set of experiments at the lowest temperature, when the fuel is not yet consumed, the amount of measured oxygen is lower than expected based on the reported concentration of oxygen entering the reactor. If the actual inlet concentration of oxygen is lower, the predictions of the model for ethylene are slightly increased and better match experimental values.

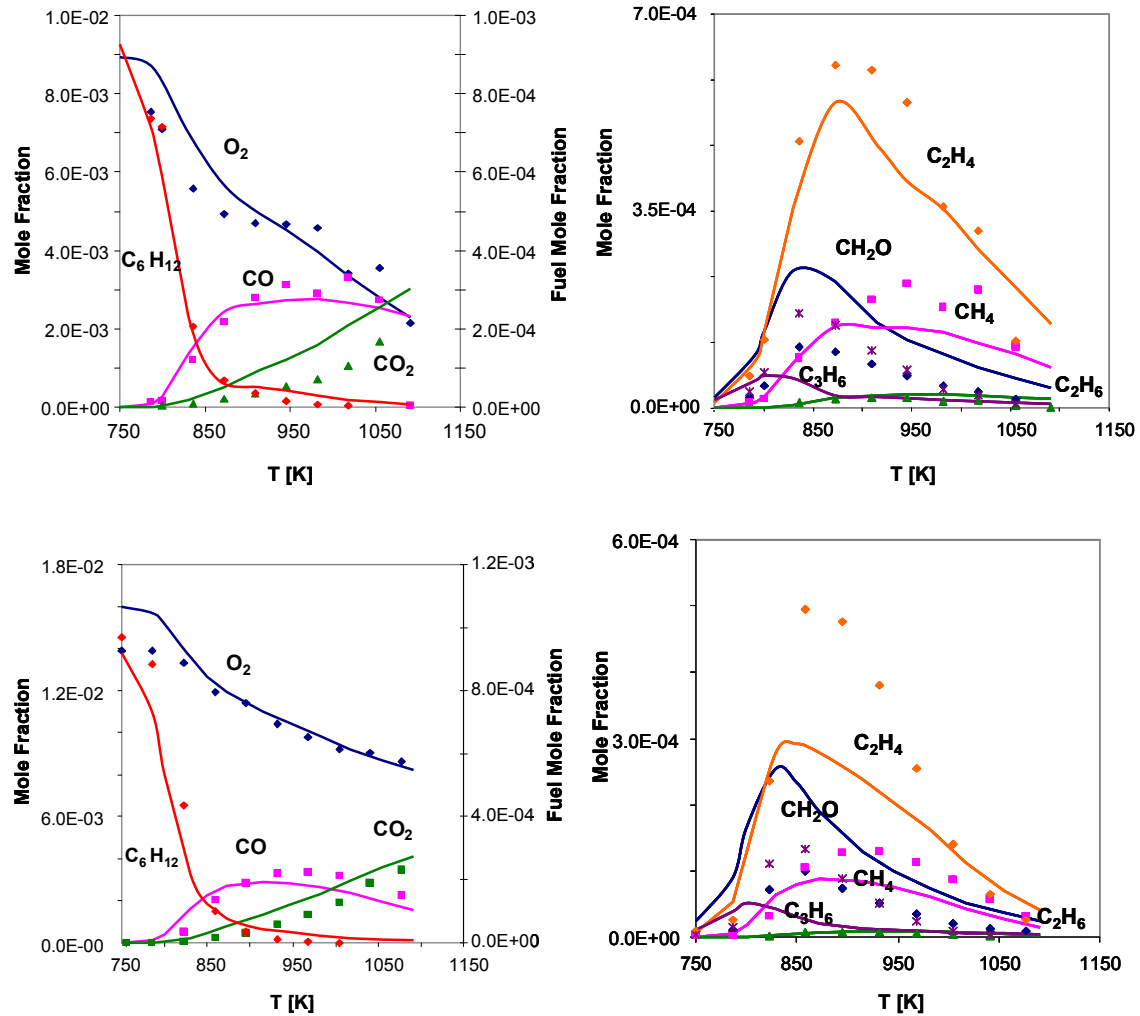


Figure 5: Jet Stirred Reactor experimental measurements (symbols) and calculations (curves) at 1.0 MPa, fixed residence time (0.5 sec) and stoichiometries of 1.0 and 0.5 [12].

Rapid Compression Machine

Vanhove et al. investigated the low temperature reactivity of all the three isomers in a Rapid Compression Machine [8]. They found that the position of the double bond strongly influences the reactivity of the hexene isomers. The presence of long alkyl chains favors low temperature oxidation and yields a prominent NTC region. Short alkyl chains are characterized by lower reactivity in the low temperature region.

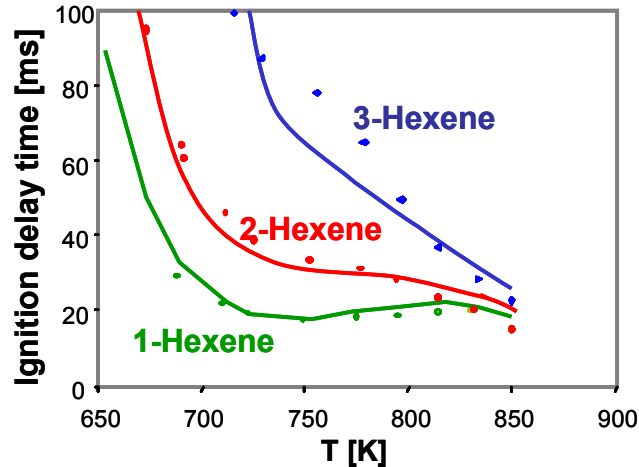


Figure 6: RCM Ignition delay times of hexene isomers(0.86-1.09 MPa, $\Phi=1$): experiments (symbols) and calculations (lines) [8].

The ignition behavior of these isomers have been studied at $\Phi=1$ in simulated “air” considering different pressures and a temperature range between 650 and 850K. The different adiabatic compression temperatures have been obtained substituting a fraction of N_2 with Ar or CO_2 , which have much different heat capacities.

Simulations have been obtained assuming no reaction during the compression phase, so that the RCM is approximated to a batch reactor at TDC conditions. No heat losses are included in the calculations. Figure 6 shows the comparison between experiments and calculations at about 1.0 MPa of pressure for the three isomers. The model reproduces well the differences in the reactivity due to the position of the double bond.

While 1-hexene and 2-hexene show the typical NTC region, 3-hexene reactivity is almost totally governed by high temperature mechanisms.

This behavior can be better evidenced in the next comparison (figure 7) where the three experimental pressure traces are compared with calculated ones. While 1- and 2-hexene present a two step ignition, 3-hexene has a very limited low temperature reactivity.

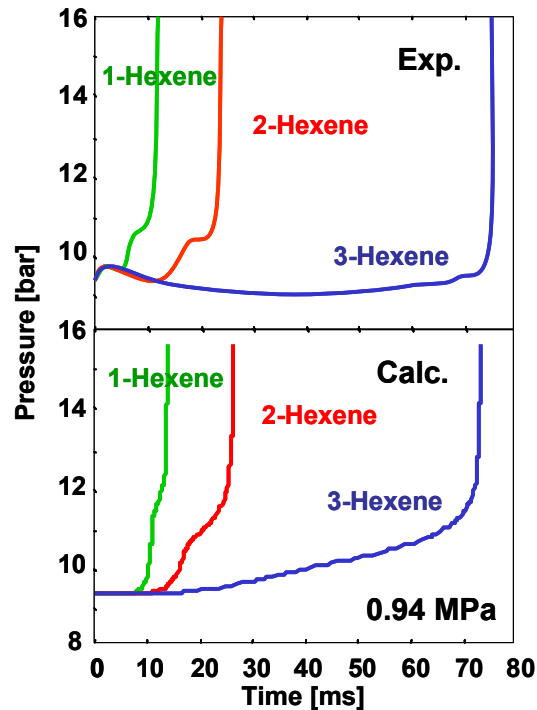


Figure 7: Experimental and Calculated Pressure traces after compression to 725 K and 0.94 MPa for 1-hexene, 2-hexene and 3-hexene. [8].

The validation of the low temperature mechanism has been extended to other pressure conditions. Figure 8 shows the induction times of the three hexene isomers at stoichiometric conditions in a range of pressures between 0.7 and 1.1 MPa. In the case of 1- and 2- hexene the cool flame timing at the central pressure conditions is also shown.

The mechanism is able to predict with a good agreement both the cool flame occurrence and the total ignition times in all the considered conditions.

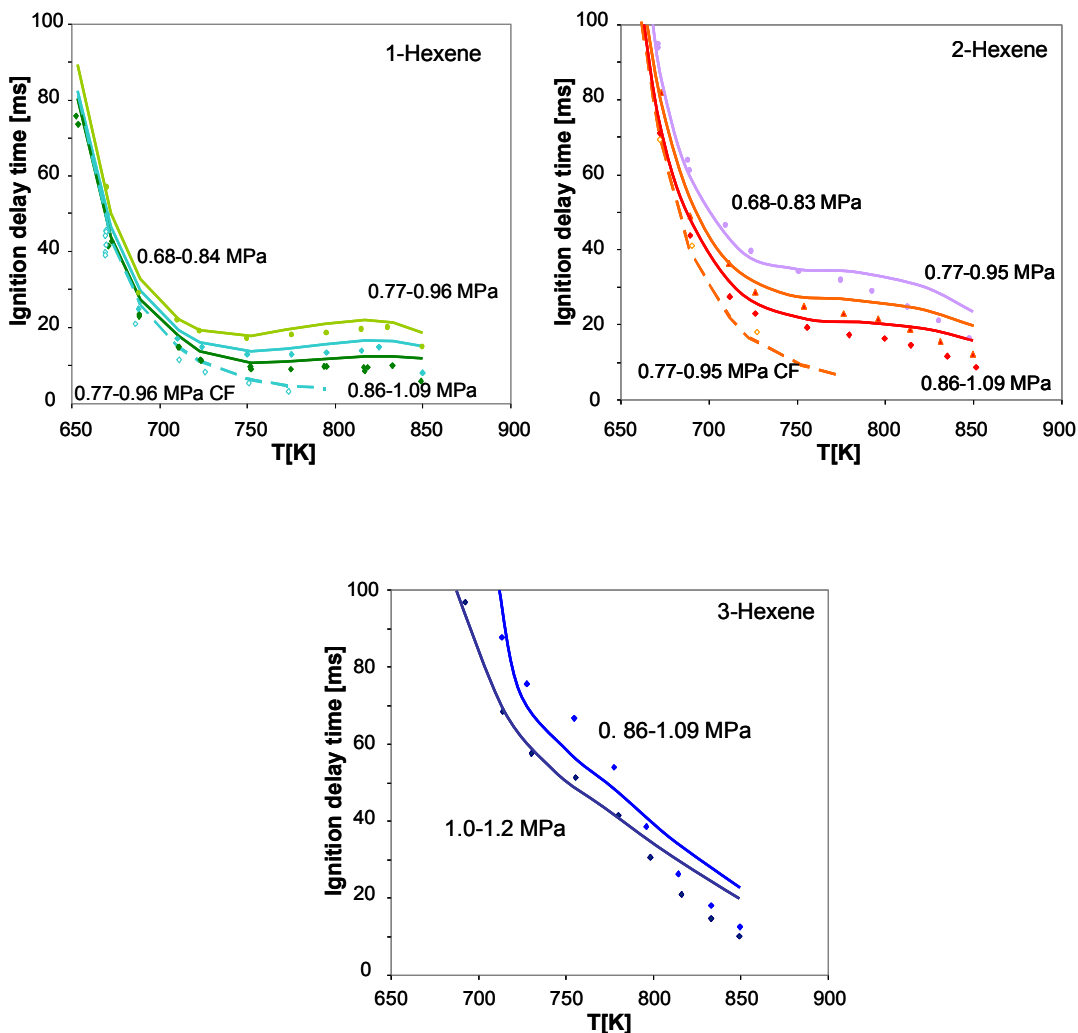


Figure 8: Ignition delay times and cool flames of the three isomers of hexene at different pressures and temperatures: experiments (symbols) and calculations (lines) [8].

Reaction pathway analysis

In order to better understand the role of the structural differences in the three hexene isomers, we performed a reaction pathway analysis each isomer in turn. First, we examine the high temperature behavior of the three isomers. The dominant decomposition path for all three isomers is the breaking of an allylic C-C bond. In the

case of 1-hexene, this leads to allyl and n-propyl radicals. The n-propyl radical decomposes quickly to ethylene and a methyl radical. As a consequence, the initial radical pool is mainly composed of slow reacting radicals (allyl and methyl radicals).

In the case of the decomposition of 2-hexene, the initiation reaction leads preferably to the formation of a resonantly-stabilized butenyl radical and an ethyl one, which rapidly decompose to ethylene and an H radical. This behavior strongly promotes the general reactivity of 2-hexene.

Simulations suggest that the high temperature oxidation of 2-hexene is faster because of the huge amount of H radicals produced by ethyl decomposition. The atomic hydrogen is indeed a powerful branching agent due to its promotion of the $H + O_2 = OH + O$ chain branching reaction.

3-hexene preferably decomposes into methyl and a resonantly-stabilized pentenyl radical. The pentenyl radical leads to the formation of butadiene and another methyl radical. Thus, two relatively unreactive methyl radicals are produced from the decomposition process. Thus, the initial radical pool is less reactive and 3-hexene oxidation rate slightly slower than 2-hexene one at high temperatures.

In the first steps of the oxidation process H addition plays a relevant role, resulting in alkyl radicals that rapidly decompose forming more ethyl and propyl radicals.

Abstractions, internal isomerizations and decompositions are other pathways in the formation of smaller alkyl radicals.

The position of allylic H atoms in the hexene molecule plays a key role in H-atom abstraction reactions since it favors the formation of resonantly stabilized radicals. The

relatively high concentration of hex-1-en-3-yl radical also makes the isomerization to less stable intermediates such as the hex-1-en-6-yl or hex-2-en-5-yl radicals possible.

The situation described above is summarized in Fig. 9, where the main fluxes are represented at 8% of the fuel conversion ($\zeta = 8\%$).

A similar analysis involved the low temperature reactivity of hexenes. The two most representative cases are discussed here. First we discuss the oxidation of 1-hexene (Fig. 10).

The low temperature oxidation of 1-hexene follows the typical pathway eventually leading to ketohydroperoxides formation. First, H-abstraction reactions from hexene primarily lead to the formation of allyl radicals. The high concentration of these radicals favors the oxygen addition while their stability promotes the decomposition back to reactants. The presence of a long saturated alkyl chain aside the hydroperoxy site allows the internal isomerization to the hydroperoxyalkenyl radical. This radical adds to O₂ and undergoes a second internal isomerization reaction. Since the six membered transition state is energetically favored, the pathway leading to 5-hydroperoxy-hex-1-en-3-one and OH radical is the most relevant. Decomposition of 5-hydroperoxy-hex-1-en-3-one leads to a second OH radical and thus chain branching. Another important branching route is the formation of hex-1-en-5-yl radical, radical addition to O₂ and the following isomerization. Also in this case the six membered transition state is favored, moreover, the allyl nature of the C-H bond involved further reduces the energy barrier required.

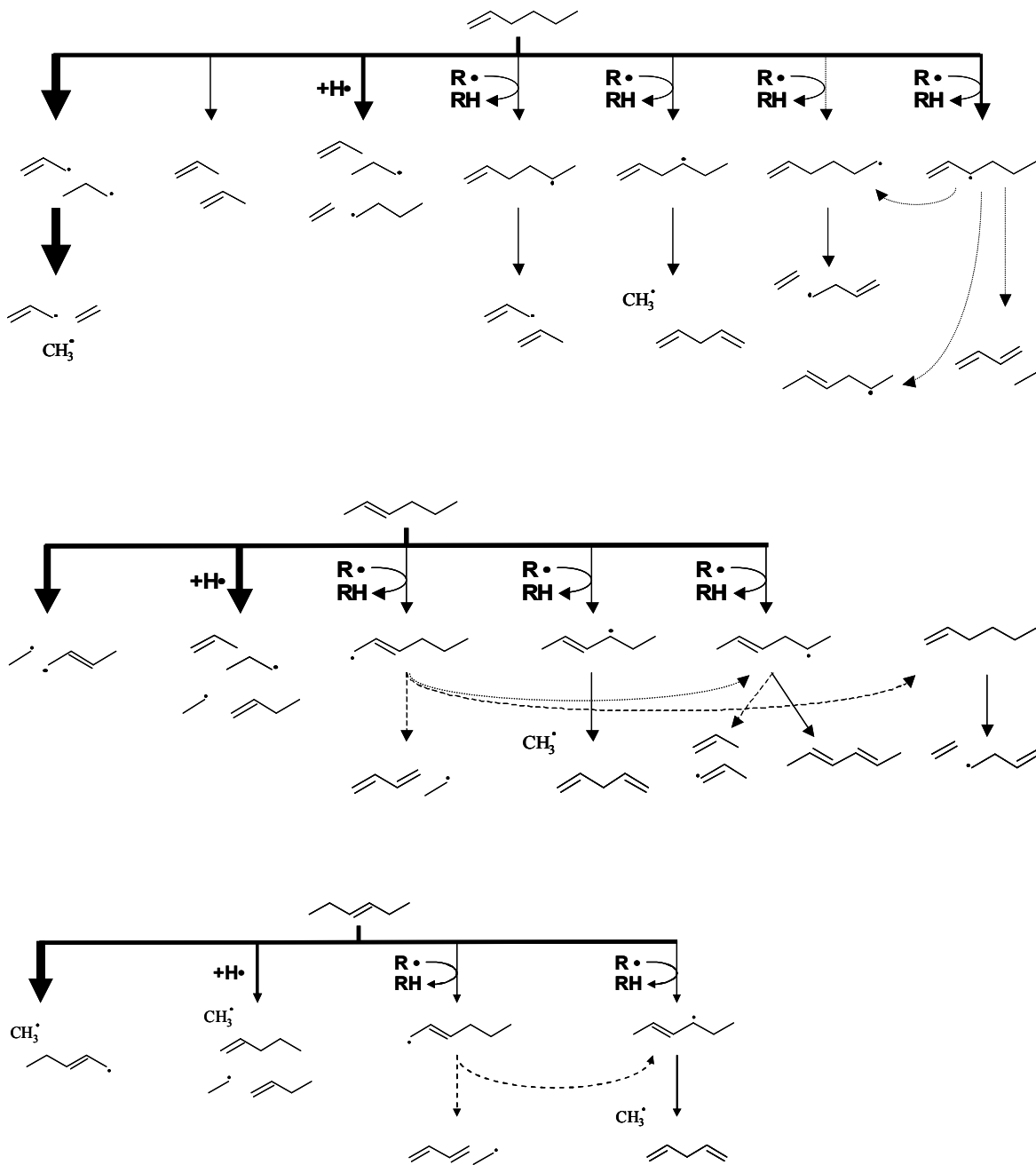


Figure 9: Reaction pathway analysis of the three isomers: ST at 1100K, 0.2 MPa., $\zeta = 8\%$. The width of the arrow indicates the relative flux.

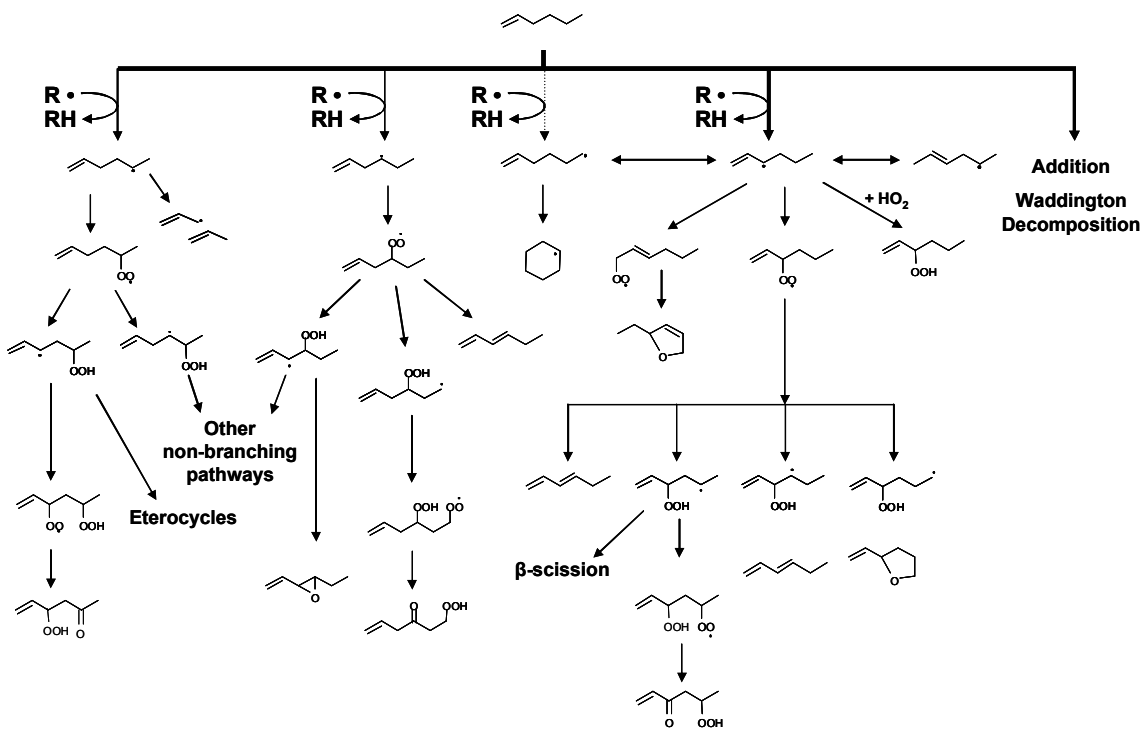


Figure 10: Reaction pathway analysis of 1-hexene at 715K and 1.0 MPa

On the contrary, hex-1-en-4-yl radical is less effective in producing branching intermediates at low temperatures. The weak adjacent C-H allylic bond favors the direct elimination of low-reactive HO₂ radicals and the formation of conjugate dienes, which are strong radical scavengers. Small amounts of 6-hydroperoxy-hex-1-en-4-one are produced via internal isomerization of the resonant 4-hydroperoxy-hex-1-en-3-yl radical followed by the traditional O₂ addition and OH elimination.

Radical additions slow down the reactivity producing substituted intermediates that decompose or form aldehydes and OH via O₂ additions and Waddington decomposition. The low temperature oxidation of 2-hexene has similar feature to 1-hexene and is not discussed.

The low-temperature oxidation of 3-hexene is far slower than 1 and 2-hexene one (Fig. 11). The limited length of the alkyl chains inhibits the classical branching paths and direct eliminations of HO₂ are the prevalent alternatives to internal isomerizations.

Small quantities of two ketohydroperoxides are produced starting from the resonantly stabilized hex-3-en-2-yl. This intermediate radical (which resonates to the hex-2-en-3-yl structure) plays a significant role also in 2-hexene oxidation. The hex-2-en-3-peroxy radical is indeed the precursor of 6-hydroperoxy-hex-2-en-4-one.

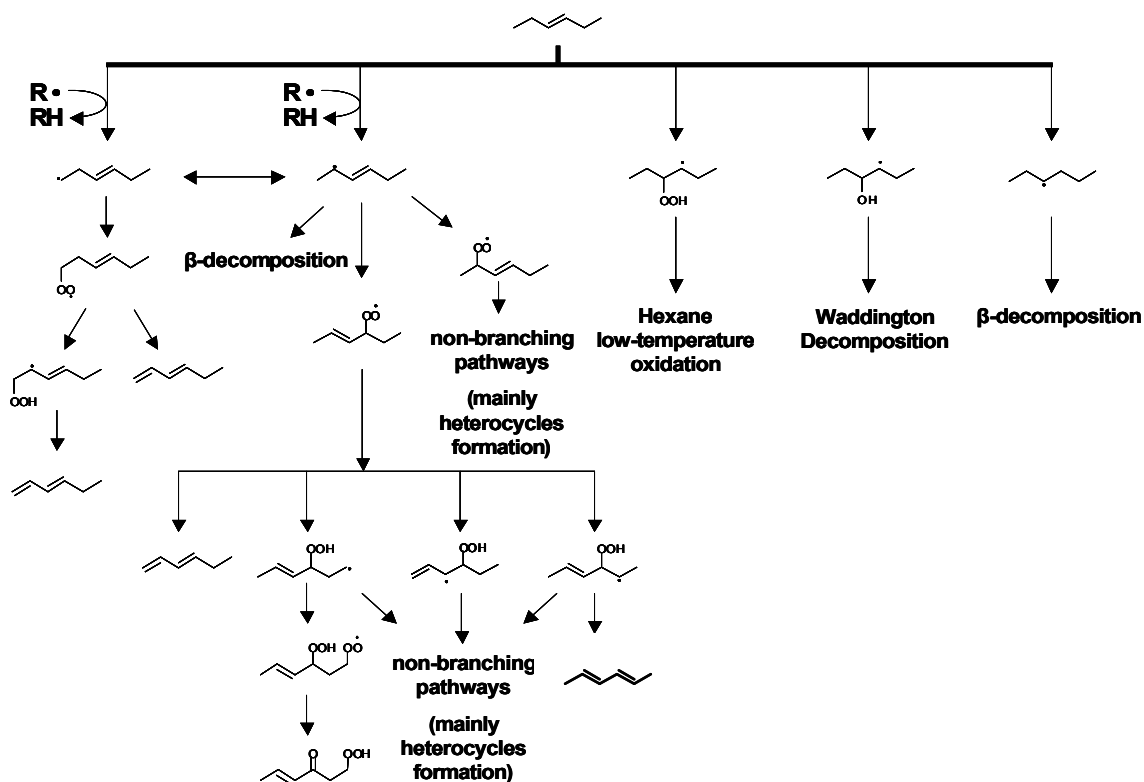


Figure 11: Reaction pathway analysis of 3-hexene at 715K and 1.0 MPa

Sensitivity analysis

Two sensitivity analyses at high and low temperature were carried out to complete the study of 1-hexene oxidation. The sensitivity parameter here referred is the conversion rate of the fuel.

The results at high temperature (1360K, 1.0 MPa, $\Phi=1$), are shown in Fig. 12. A negative sensitivity value (blue color) indicates that an increase in the rate constant of the reaction increases the reactivity of the system, while a positive sensitivity value (red color) indicates a decrease in reactivity. Based on the result in Fig. 12, the reactivity of 1-hexene is strongly promoted by the initiation reaction of 1-hexene to form allyl and n-propyl radicals. Other reactions promoting the conversion of 1-hexene to products are the formation of ethyl and but-1-en-4-yl radicals and the abstraction of the allyl H atom (mainly by H radicals in the very early stages of oxidation, then by OH and H radicals). The rate of molecular decomposition of the fuel is marginal if compared to H-atom abstraction and radical addition pathways at these temperature conditions.

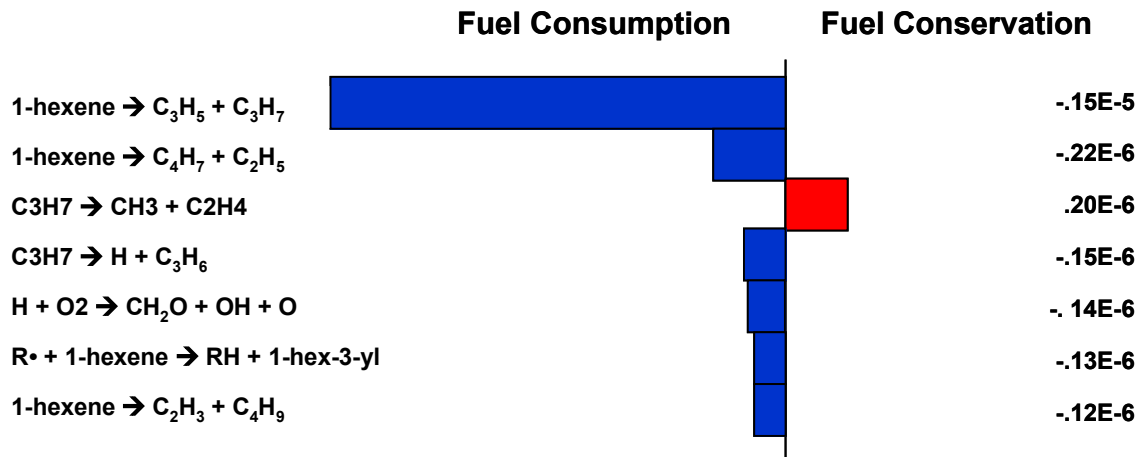


Figure 12: Sensitivity analysis of 1-hexene at 1.0 MPa and 1360K.

The results at low temperature (712K, 1.0 MPa, $\Phi=1$), are shown in Fig. 13. Of the reactions identified as sensitive at high temperature, the only reaction which still remains is the radical abstraction of the allyl H atom which continues to play a promoting effect. In this case the OH radical is the main abstractor rather than an H atom. The abstraction on the 5th position plays a key role too. This can be easily explained considering the important role of the low temperature chain branch path involving 5-hydroperoxy-hex-1-en-3-one and 3-hydroperoxy-hex-1-en-5-one. The chemistry of these radicals involve C-H bonds in the 3 and 5 position that are easily abstractable allylic and secondary H atoms and a low-strain 6-membered ring for RO₂ isomerization. These are characteristics that lead to fast low temperature chemistry. As already highlighted in the previous discussion about flux analysis, hex-1-en-3-yl and hex-1-en-5-yl are the precursors of these two important ketohydroperoxides.

OH additions on the double bond inhibit the general reactivity sequestering reactive radicals and starting the alternative non-branching pathway of Waddington decomposition. On the contrary the decomposition of hydroxyhexenperoxy radicals produces OH radicals which promotes reactivity.

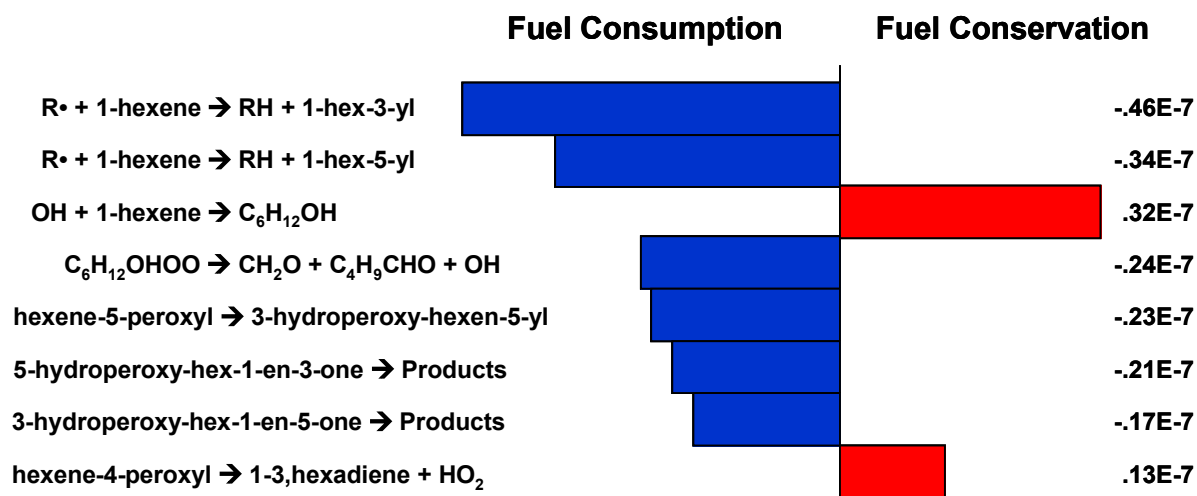


Figure 13: Sensitivity analysis of 1-hexene at 1.0 MPa and 712K.

Conclusion

In this work a kinetic study concerning the oxidation of the three isomers of n-hexene is presented. A kinetic scheme was developed focusing the attention on the effects on the reactivity caused by the alkene hydrocarbon structure. The rate constants of the reactions involving the double bond and the allylic position were discussed. These rate parameters were then summarized and organized in a limited set of reference values which can be applied to the generation of a general oxidation mechanism for saturated and non saturated fuels. The reference values obtained should be considered as an initial attempt in the evaluation of the fundamental rate parameters of alkenes oxidation. Also considering the relatively scarce literature concerning this class of compounds, further studies will be necessary to a more precise definition of this set of values.

The kinetic mechanism proposed here has been validated on the basis of both literature and new data covering a large range of operating conditions. The agreement with

experimental data is generally good in all the considered temperature and pressure ranges.

It is worth emphasizing how the experimental and modeling information concerning different isomers of the same fuel are very valuable for gaining a better comprehension of the fundamental mechanism underlying oxidation processes of n-alkenes. The direct comparison between their behaviors at different operating conditions can be an important source of knowledge regarding their main reaction pathways as well as a solid benchmark for kinetic model validation.

Unfortunately experimental data were not available for all the three isomers at all the considered operating conditions. For this reason future experiments will be necessary to confirm the validity of some assumptions. Despite of this, some shock tube simulations were provided in order to gain insight into the high temperature reactivity of the three isomers.

Summarizing some results of this work the following can be stated:

- at high temperature the oxidation of hexenes is governed in the very early stages by the thermal decomposition of the fuel. The formation of resonantly stabilized radicals is strongly favored. The stability of the radical fragments influences the following stages of oxidation ;
- internal isomerizations strictly connect the oxidation pathways of the three isomers. The presence of resonant radical structure makes it possible to obtain similar intermediates starting from different isomers;
- at low temperature the length of the saturated portion of the fuel strongly influences the oxidative behavior: long chains allow two stages ignition and the

NTC behavior typical of alkanes due to low temperature branching pathways, short chains give single stage ignition and lead more easily to the formation of dienes and aldehydes instead of ketohydroperoxides formation.

- Reactivity at low temperature for alkenes is favored when RO_2 and subsequent O_2QOOH isomerizations can occur involving allylic and secondary C-H bonds and six member ring transition states. 1-hexene and 2-hexene have these paths available and have high reactivity at low temperature, but 3-hexene does not have these paths available and thus has low reactivity.
- Radical additions on the double bond generally decrease the oxidation rate of unsaturated hydrocarbons sequestering reactive radicals and starting an alternative pathway to branching (e.g. Waddington oxidative decomposition).

Acknowledgments

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