The Gas-Phase Oxidation Of *n*-Hexadecane

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ABSTRACT: Since *n*-hexadecane or cetane is a reference fuel for the estimation of cetane numbers in diesel engines, a detailed chemical model of its gas-phase oxidation and combustion will help to enhance diesel performance and reduce the emission of pollutants at their outlet. However, until recently the gas-phase reactions of *n*-hexadecane had not been experimentally studied, prohibiting a validation of oxidation models which could be written.

This paper presents a modeling study of the oxidation of *n*-hexadecane based on experiments performed in a jet-stirred reactor, at temperatures ranging from 1000 to 1250 K, 1-atm pressure, a constant mean residence time of 0.07 s, and high degree of nitrogen dilution (0.03 mol% of fuel) for equivalence ratios equal to 0.5, 1, and 1.5. A detailed kinetic mechanism was automatically generated by using the computer package (EXGAS) developed in Nancy. The long linear chain of this alkane necessitates the use of a detailed secondary mechanism for the consumption of the alkenes formed as a result of primary parent fuel decomposition. This high-temperature mechanism includes 1787 reactions and 265 species, featuring satisfactory agreement for both the consumption of reactants and the formation of products. © 2001 John Wiley & Sons, Inc. Int J Chem Kinet 33: 574–586, 2001

INTRODUCTION

Cetane or *n*-hexadecane is a reference fuel for the estimation of cetane numbers, which characterize the ability of Diesel fuels to auto-ignite. The cetane number of *n*-hexadecane is equal, by definition, to 100. Despite the importance of this compound for diesel engines, its gas-phase combustion and oxidation had not been experimentally studied until recently [1]. However, the pyrolysis of *n*-hexadecane and its steamcracking have been investigated [2,3]. Chevalier et al. [4] proposed a mechanism to model the autoignition of a stoichiometric cetane–air mixture at 13.6 bar. However, because of the lack of experimental data for n-hexadecane oxidation, they compared their simulations with experimental results obtained for n-heptane. More generally there are very few studies of the combustion or the oxidation of actual components of Diesel fuel heavier than n-decane [5].

The manual generation of detailed mechanisms for compounds as heavy as *n*-hexadecane becomes difficult, whereas an automatic procedure is a convenient and rigorous way to write such large mechanisms. It is worth noting that the mechanism proposed by Chevalier et al. [4] was also developed by a computational technique based on generic rules of oxidation reactions. However, the mechanism represents only the formation of primary products in low temperature

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conditions and it is just able to predict ignition delays but no product profiles. In this work, we used the computer package (EXGAS) to perform the automatic generation of a detailed kinetic model to reproduce experimental results obtained in a jet-stirred reactor (JSR) [1]. This package and its application to model the oxidation of several alkanes (e.g., n-butane [6], n-heptane and iso-octane [7], *n*-octane [8], and *n*-decane [8,9]) have been described previously [10]. Because of the long linear chain of *n*-hexadecane, it was necessary to update EXGAS in order to improve the secondary mechanism of alkenes which are primary products formed in large amounts. Thus, primary alkenes consumption reactions were detailed and a feedback between primary and secondary mechanisms was introduced for alkyl free radicals formed during the consumption of alkenes. Finally, an analysis of the mechanism permitted to point out the relative importance of the various reaction pathways.

EXPERIMENTAL SETUP

The JSR setup used for studying n-hexadecane oxidation is similar to that described earlier [11,12]. The reactor consisted of a 40-mm diameter (30.5 cm^3) sphere made of fused silica (to prevent wall catalytic reactions), equipped with four nozzles of 1-mm ID for the admission of the gases, which achieve the stirring. A nitrogen flow of 100 l/h was used to dilute the fuel; all the gases were preheated before injection in order to minimize temperature gradients inside the JSR. High-purity reactants were used in these experiments: oxygen was 99.995% pure and *n*-hexadecane >99% pure [1]. The samples (30 Torr, i.e. 4 kPa) were taken at steady temperature and residence time via some probe sampling. They were analyzed on-line by GC-MS (lowvapor pressure species) and off-line after collection in 1-1 Pyrex bulbs (high-vapor pressure species and permanent gases). These experiments were performed at steady state, constant mean residence time of 0.07 s, and high degree of dilution (0.03 mol% of fuel). A carbon balance of $\pm 5\%$ was obtained in the present experiments [1]. Inlet concentrations of $C_{16}H_{34}$ are the same for all equivalence ratios $(3 \times 10^{-4} \text{ in mole})$ fraction) while the inlet concentrations of molecular oxygen are equal to 1.47×10^{-2} at $\Phi = 0.5, 7.35 \times$ 10^{-3} at $\Phi = 1$ and 4.9×10^{-3} at $\Phi = 1.5$.

THE GENERATION OF THE MODEL

The main features of EXGAS has been detailed previously [6–10]; hence only a summary of the main features of EXGAS is provided for completeness. Only the part concerning the secondary mechanism of alkenes, which has been improved during this work, is more thoroughly described. Examples of mechanisms generated by EXGAS (i.e., for the oxidation of *n*butane, *n*-heptane, iso-octane, *n*-octane, and *n*-decane) can be found on the web site:

http://www.ensic.inpl-nancy.fr/ENSIC/ DCPR /cinetique/Chimieinfo/TEXTES/software.htm

Construction of the Mechanism

The system of generation (EXGAS) provides reaction mechanisms made of three parts:

- A C₀-C₆ reaction base, including all the reactions involving radicals or molecules containing less than three carbon atoms (C₀-C₂ reaction base [13]) and the reactions of C₃-C₄ unsaturated hydrocarbons [14], such as propyne, allene, or butadienes, including reactions leading to the formation of benzene. The kinetic data used in these reaction bases were taken from the literature. Values recommended by Baulch et al. [15] and Tsang et al. [16] are mainly used in the C₀-C₂ reaction base; the pressure-dependent rate constants follow the formalism proposed by Troe [17].
- A comprehensive primary mechanism, where the only molecular reactants considered are the initial organic compounds and oxygen. The primary mechanism includes only elementary steps. The generation of this mechanism is performed using an algorithm warranting its comprehensiveness [10]. Above 1000 K, primary mechanisms can be strongly reduced, since the rate of the additions of alkyl radicals to an oxygen molecule becomes negligible compared to that of decompositions and oxidations [18]. The types of reactions that are considered are presented in Table I, along with the corresponding rate constants used.
- A secondary mechanism describes the consumption of the products formed in the primary mechanism that do not react in the reaction base (C₀-C₆).

In the case of the long linear molecule of n-hexadecane, the primary mechanism leads to the formation of 1-alkenes by decomposition of alkyl free radicals. Even if 1-alkenes are very important products and have to be considered in more details than in our previous work [6–9], the significant number of 1-alkenes generated prevents the writing of a secondary mechanism as comprehensive as the primary

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Turner of H.A.L. Arrested	Primary H (i.e. R–CH ₃)			Secondary H (i.e. R_1 -CH ₂ - R_2)				
(per H-atom)	$\log A$	b	Ε	$\log A$	b	E	Reference	
Initiation with O ₂ to form alkyl radicals and ·OOH	12.62	0	205	13.00	0	201	[19]	
Oxidation i.e. the reaction of alkyl radicals with O ₂ to form the conjugated alkene and ·OOH H atom abstraction by	11.37	0	20.9	11.90	0	20.9	Estimated from [20,21]	
	12 22	0	22 8	12 11	0	21.7	[10]	
. О. Ц	6.09	0	32.0 22.2	13.11	2	21.7	[19]	
-11 -11	5.05	2	1.2	6.11	2	20.9	[19]	
CHa	1	4	34.3	11.0	0	-3.20 30.8	[22]	
-OOH	11 30	4	54.5 71.1	11.0	0	64.8	[17]	
CHO	4 53	25	77.3	6.73	19	71.1	[17]	
CHOOH	1.55	2.95	58.5	1 48	2.95	50.2	[23]	
OCH2	10.73	0	30.5	10.68	0	18.8	[23]	
.00CH2	12 30	0	83.6	12.18	0	73.2	[23]	
·C2Hs	11.00	0	56.4	11.00	0	46.0	Estimated	
iC ₂ H ₂	-2.85	42	36.4	-2.85	42	33.4	Estimated	
·Banimony	11.00	0	56.4	11.00	0	46.8	[24]	
·R _{secondary}	11.00	0	60.6	11.00	0	51.0	[24]	
Other reactions								
Beta-scission	to ·CH ₃ +	molecule ^b		13.30	0	130.0	Estimated	
of a free radicals by breaking of a C—C bond	to $\cdot \mathbf{R}$ +	- molecule ^b		13.30	0	120.0	from [19,23,25]	
Isomerizations involving the internal transfer of an hydrogen atom				Calculated by using the software KINGAS according to the method proposed by S.W. Benson [26]		[26,27]		
Unimolecular initiations by breaking of a C—C bond				Calculated by using the software KINGAS using the modifiedm collision theory		[26,27]		

Table I	Quantitative Structure–Reactive Relationships Used for the Estimation of the Rate Constant ^a	Used in the
Primary N	Mechanism for the Oxidation of <i>n</i> -Hexadecane	

^{*a*}Rate constants are assumed to follow the modified Arrhenius law, $k = AT^{b} \exp(-E/RT)$, with the units cm³, mol, s, kJ. ^{*b*}Values given for log *A*, *b*, and *E*.

one. Nevertheless, it is necessary to write for the consumption of 1-alkenes less global reactions than those usually written and to create for secondary free radicals for which that is possible, a feedback with the primary mechanism. By this coupling effect between the two parts of the mechanism, it is possible to better describe the combustion of primary 1-alkenes.

The reactions considered in the secondary mechanism for alkene consumption are unimolecular initiations, additions to the double bond, H-abstractions, retro-ene reactions, and combinations of allylic free radicals. *Unimolecular Initiations.* Because of their relatively low activation energy (approximately 290 kJ/mol), only unimolecular initiations leading to the formation of allyl radical (\cdot C₃H₅) have been considered. The kinetic parameters used have been estimated using the software KINGAS [26].

Additions. Table II presents the secondary reactions proposed for 1-alkenes and the related rate constants used for additions to the double bond. The addition of \cdot H atom and \cdot CH₃ radicals leads to the formation of alkylic radicals which react in the detailed primary

Type of Addition	log A	b	Ε
Addition of an ·H atom			
(A) $\cdot H + CH_2 = CH - C_n H_{2n+1} \leftrightarrow CH_3 - CH \cdot - C_n H_{2n+1}$	12.86	0	2.6
(B) $\cdot H + CH_2 = CH - C_n H_{2n+1} \leftrightarrow CH_2 - CH_2 \cdot - C_n H_{2n+1}$	12.86	0	5.8
Addition of ·CH ₃			
(C) $\cdot CH_3 + CH_2 = CH - C_n H_{2n+1} \leftrightarrow CH_3 - CH_2 - CH \cdot - C_n H_{2n+1}$	11.0	0	14.7
(D) $\cdot CH_3 + CH_2 = CH - C_n H_{2n+1} \leftrightarrow \cdot CH_2 - CH(CH_3) - C_n H_{2n+1}$	11.0	0	16.0
$CH_2 - CH(CH_3) - C_n H_{2n+1} \rightarrow C_3 H_6 + C_n H_{2n+1}$	13.3	0	57.4
Addition of •OH			
(E) $\cdot OH + CH_2 = CH - C_n H_{2n+1} \leftrightarrow HCHO + \cdot CH_2 - C_n H_{2n+1}$	12.10	0	-2.1
(F) \cdot OH + CH ₂ = CH - C _n H _{2n+1} \leftrightarrow C _n H _{2n+1} - CHO + \cdot CH ₃	12.10	0	-2.1
Addition of ·O·-atoms			
(G) $\cdot O \cdot + CH_2 = CH - C_n H_{2n+1} \leftrightarrow \cdot H + \cdot CH_2 CO - C_n H_{2n+1}$	7.53	1.83	1.1
\cdot CH ₂ CO $-$ C _n H _{2n+1} \rightarrow CH ₂ CO $+ \cdot$ C _n H _{2n+1}	13.3	0	57.4
Addition of HO_2 .			
(H) $HO_2 \cdot + CH_2 = CH - C_n H_{2n+1} \leftrightarrow cyclo(C_2H_3O) - C_n H_{2n+1} + OH$	12.0	0	28.8

Table IISecondary Mechanism of Alkenes: Detailed Reaction^a and Rate Constants^b for the Additions of Radicals to
the Double Bond

^{*a*} The reactions of all the free alkyl radicals formed ($\cdot C_n H_{2n+1}$) are included in the primary detailed mechanism.

^bThe rate constants for the additions of \cdot H, \cdot CH₃, \cdot O, and \cdot OH are derived from those proposed by Tsang [28] for propene. In the case of the addition of HO₂, the values of Baldwin et al. [29] are used. Rate constants are assumed to follow the modified Arrhenius law, $k = AT^b \exp(-E/RT)$, with the units cm³, mol, s, kJ.

mechanism (reactions A–C in Table II). A particular point concerns the addition of \cdot CH₃ leading to a branched alkyl free radical. As this last radical does not exist in the primary mechanism, a β -scission is written in order to give propene and a linear alkyl radical which reacts in the detailed primary mechanism (reaction D in Table II).

The additions of $\cdot O \cdot$ atoms, $HO_2 \cdot$, and $\cdot OH$ radicals (reactions E–H in Table II) lead to the formation of alkyl free radicals which decomposed according to steps already written in the primary mechanism, or of stable species (aldehydes and cyclic ethers) which react in the secondary mechanism according to rules previously defined [6].

H-Abstractions. Tables III and IV present the secondary reactions proposed for 1-alkenes reactions and their rate constants for the abstraction of allylic (Table III), vinylic (Table III), and alkylic (Table IV) hydrogen atoms.

1. The abstraction of an allylic H-atom. This leads to the formation of a resonance-stabilized radical. This radical can react by terminations with radicals such as \cdot H, \cdot CH₃, and HO₂ \cdot or by β -scissions to give 1,3-butadiene and an alkyl free radical reacting according to the detailed primary rules of oxidation (reaction A in Table III).

- 2. The abstraction of a vinylic H-atom. This leads to the formation of acetylene or allene and an alkyl free radical (reactions B and C in Table III). These H-abstractions being more difficult than the previous ones, only those involving ·H, ·OH, and ·CH₃ free radicals have been taken into account.
- 3. The abstraction of an alkylic H-atom. It is worth noting that these reactions were never taken into account in our previous studies because the linear chain of alkenes formed were sufficiently small, and so the alkylic H-abstraction were negligible with respect to the allylic metatheses. In the case of long linear alkenes, these H-abstractions play a significant role and explain the formation of specific products observed experimentally, such as diolefins (e.g. C_5H_8). The reactions included in the kinetic scheme are derived from an analysis of the detailed reactions of linear 1-alkenes and are summarized in Table IV.

The abstraction of an alkylic H-atom leads to an alkenyl radical. In the temperature range 1000-1200 K, this alkenyl radical reacts according to two main pathways: isomerization and β -scission (Table IV).

• Alkenyl radical isomerization gives a resonance-stabilized free radical (allylic radical). The fastest isomerizations are those

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Type of Abstraction	·R	$\log A$	b	Ε
Abstraction of an allylic H· atom	·H	4.45	2.5	0.6
	·CH ₃	-0.2	3.5	7.1
(A) $\cdot \mathbf{R} + \mathbf{CH}_2 = \mathbf{CH} - \mathbf{C}_n \mathbf{H}_{2n+1} \rightarrow \mathbf{RH} + \mathbf{C}_4 \mathbf{H}_6 + \cdot \mathbf{C}_{n-2} \mathbf{H}_{2(n-2)+1}$	$\cdot C_2H_5$	-0.15	3.5	8.7
	·OH	6.17	2	3.0
	٠O٠	10.5	0.7	15.3
	HO_2 ·	3.5	2.6	27.8
Abstraction of an vinylic H· atom				
	·Н	5.61	2.5	40.9
(B) $\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \rightarrow \mathbf{R}\mathbf{H} + a\mathbf{C}_3\mathbf{H}_4 + \mathbf{C}_{(n-3)}\mathbf{H}_{2(n-3)+1}$	·OH	6.04	2	6.1
	$\cdot CH_3$	-8.8×10^{-3}	3.5	48.9
	·H	5.91	2.5	51.3
(C) $\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{C}_2 \mathbf{H}_2 + \cdot \mathbf{C}_{(n-2)} \mathbf{H}_{2(n-2)+1}$	·OH	6.34	2	11.6
	·CH3	0.13	3.5	53.9

Table IIISecondary Mechanism of Alkenes: Detailed Reactions^aand Rate Constants^bfor Abstractions of Allylic andVinylic H Atoms

^{*a*} The reactions of all the alkyle free radicals formed ($\cdot C_n H_{2n+1}$) are included in the primary detailed mechanism.

involving a cyclic transition state containing five or six atoms. At 1100 K, the isomerization of an alkenyl radical to give an allylic radical is about 5–10 times faster than β -scission. Consequently, if the alkenyl free radical obtained by H-abstraction can isomerize via a cyclic transition state containing five or six atoms, the formation of an allylic radical is written. This allylic radical is decomposed by β -scission in 1,3butadiene and an alkyl radical which reacts in the primary mechanism (reaction A in

Table IV). In the following example, the alkenyl free radical $\cdot C_7 H_{13}$ can isomerize and gives an allylic radical, which decomposes in 1,3-butadiene and *n*-propyl radical

The reaction written in the secondary mechanism is then

$$C_7H_{14} + R \cdot \longrightarrow RH + 1,3 \cdot C_4H_6 + n \cdot \cdot C_3H_7$$
(2)

Table IV Secondary Mechanism of Alkenes: Detailed Reactions^{*a*} and Rate Constants^{*b*} for Abstractions of alkylic H Atoms

	Abstraction of an Alkylic H. Atom	Examples $(C_{10}H_{20})$
(A)	$\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \rightarrow \mathbf{R}\mathbf{H} + 1, 3 \cdot \mathbf{C}_4 \mathbf{H}_6 + \cdot \mathbf{C}_i \mathbf{H}_{2i+1}$	$\cdot R + C_{10}H_{20} \rightarrow RH + 1,3-C_4H_6 + 1-C_6H_{13}$ (4 secondary H atoms involved)
(B)	$\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{C}_m \mathbf{H}_{2m-2} + \cdot \mathbf{C}_i \mathbf{H}_{2i+1}$	$\begin{split} & \mathbf{R} \cdot + \mathbf{C}_{10}\mathbf{H}_{20} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{C}_5\mathbf{H}_8 + 1 \mathbf{C}_5\mathbf{H}_{11} \\ & \mathbf{R} \cdot + \mathbf{C}_{10}\mathbf{H}_{20} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{C}_6\mathbf{H}_{10} + \cdot \mathbf{C}_4\mathbf{H}_9 \\ & \mathbf{R} \cdot + \mathbf{C}_{10}\mathbf{H}_{20} \rightarrow \mathbf{R}\mathbf{H} + \mathbf{C}_9\mathbf{H}_{16} + \cdot \mathbf{C}\mathbf{H}_3 \end{split}$
(C)	$\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \to \mathbf{R}\mathbf{H} + \mathbf{C}_m \mathbf{H}_{2m} + \begin{cases} \cdot \mathbf{C}_3 \mathbf{H}_5 \\ \cdot \mathbf{C}_3 \mathbf{H}_2 \end{cases}$	$\begin{array}{l} R\cdot + C_{10}H_{20} \rightarrow RH + 1\text{-}C_8H_{16} + \cdot C_2H_3 \\ R\cdot + C_{10}H_{20} \rightarrow RH + 1\text{-}C_7H_{14} + \cdot C_3H_5 \end{array}$
(D)	$\cdot \mathbf{R} + \mathbf{C}_n \mathbf{H}_{2n} \rightarrow \mathbf{R} \mathbf{H} + \mathbf{C}_m \mathbf{H}_{2m} + 1,3 \cdot \mathbf{C}_4 \mathbf{H}_6 + \cdot \mathbf{C}_i \mathbf{H}_{2i+1}$	$\begin{array}{l} R \cdot + C_{10}H_{20} \rightarrow RH + C_{4}H_{8} + 1,3 \cdot C_{4}H_{6} + \cdot C_{2}H_{5} \\ R \cdot + C_{10}H_{20} \rightarrow RH + C_{3}H_{6} + 1,3 \cdot C_{4}H_{6} + 1 \cdot \cdot C_{3}H_{7} \\ R \cdot + C_{10}H_{20} \rightarrow RH + C_{2}H_{4} + 1,3 \cdot C_{4}H_{6} + 1 \cdot \cdot C_{4}H_{9} \\ (3 \ primary \ H \ atoms \ involved) \end{array}$

 $\begin{array}{ll} n \geq 10 \\ (\text{E}) & \cdot \text{R} + \text{C}_n\text{H}_{2n} \rightarrow \ \text{RH} + \text{C}_m\text{H}_{2m} + 1,3\text{-}\text{C}_4\text{H}_6 + \text{C}_2\text{H}_4 + \cdot\text{C}_i\text{H}_{2i+1} \end{array}$

 $^{{}^{}a} \cdot C_{i} H_{2i+1}$ reacts in the primary mechanism; $C_{m} H_{2m}$ reacts in the secondary mechanism as 1-alkene; $C_{m} H_{2m-2}$ reacts in the secondary mechanism. b The rate constants for alkylic metatheses derived from those presented in Table I.

• If an isomerization of the alkenyl radical is not possible, a β -scission of a C–C bond occurs giving an alkyl radical and a diolefin (reaction 3) or an 1-alkene and a smaller alkenyl radical (reaction 4). For instance, the alkenyl radical 3-C₁₁H₂₁ can react as follows:

The reaction of H-abstraction written in the secondary mechanism for reaction (3) is then

$$C_{11}H_{22} + \cdot R \longrightarrow RH + C_{10}H_{18} + \cdot CH_3$$
(5)

This reaction (reaction B in Table III) formed 1-alkene, which in turns reacts in the secondary mechanism according to the rules previously described.

For the reaction 4, the 1-alkenyl radical formed must still undergo specific reactions. In fact, several cases can be viewed:

If the unsaturated radical formed in reaction 4 is small ($\cdot C_3H_5$ and $\cdot C_2H_3$), it cannot undergo isomerization or β -scission of a C–C bond (reaction C in Table IV).

If the alkenyl radical can isomerize, we considered isomerization yielding an allylic radical, followed by a β -scission producing 1,3-butadiene and an alkyl radical (reaction D of Table IV). In the previous example (reaction 4), 1-C₇H₁₃ isomerizes and the reaction written in the secondary mechanism is

$$C_{11}H_{22} + \cdot R \longrightarrow RH + 1,3 \cdot C_4H_6 + 1 \cdot C_4H_8 + 1 \cdot C_3H_7$$
(6)

For larger alkenes (C \geq 10), 1-alkenyl free radical produced by reaction 4 cannot isomerize because of the too large cyclic transition state. In this case, it can only react by successive β -scissions until the new alkenyl free radical produced can isomerize. For instance, the alkenyl free radical 1-·C₁₂H₂₃ reacts according to the following scheme:



This reaction corresponds to reaction E in Table IV.

Retro-ene Reactions. Another new type of reaction considered is retro-ene reaction [30,31]. A retro-ene reaction is a 1,5-hydrogen shift reaction followed by dissociation. The detailed mechanism of these reactions has been discussed and structures of the transition state have been explored [31]. For example in the case of 1-heptene, the transition state can be represented as follows:

$$\longrightarrow \left[\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

In the case of linear 1-alkenes, the products formed are propene and lower 1-alkenes:

$$1 - C_n H_{2n} \leftrightarrow C_3 H_6 + C_{(n-3)} H_{2(n-3)}$$
(9)

A pre-exponential factor of $8 \times 10^{12} \text{ s}^{-1}$ and an activation energy of 236 kJ/mol has been used based on the results presented in Ref. 30. As shown in the following part of this paper, the retro-ene reactions are very important to explain the formation of C₃H₆.

The diolefins formed in the secondary mechanism can react in the same ways as 1-alkenes. We considered unimolecular initiations, additions of free radicals, H-abstractions, and retro-ene reactions. The species formed are smaller 1-alkenes and diolefins, which react again in the secondary mechanism.

Thermochemical data for molecules and radicals are automatically calculated and stored as 14 polynomial coefficients, according to the CHEMKIN II formalism [32]. These data were calculated using the software THERGAS [33], based on the group and bond additivity methods proposed by Benson [27].

COMPARISON BETWEEN COMPUTED AND EXPERIMENTAL RESULTS

Simulations have been performed using the software PSR of CHEMKIN II [32]. In order to keep this

paper reasonably short, the kinetic mechanism used is not presented, but it is available on request. The primary mechanism involves 87 species and includes 346 reactions and the secondary mechanism involves 91 species and includes 815 reactions. Overall, the reaction scheme includes 1787 reactions involving 265 species.

Figures 1-7 present a comparison of the computed profiles and the experimental results [1]. The agreement obtained for the conversions of *n*-hexadecane (Fig. 1a) and oxygen (Fig. 1b) is satisfactory. Computations capture the conversion of n-hexadecane without significant consumption of oxygen below 1100 K. However, above 1050 K, the experiments show a stronger dependence of fuel conversion with increasing temperature than the calculations. A sharp decrease in oxygen is observed at a higher temperature and for equivalence ratios equal to 0.5 or 1. Simulations also show that the temperature at which the concentration of oxygen drops, increases with the equivalence ratio. However, a difference of 20 K is observed between experimental data and modeling results for an equivalence ratio of 1. It is worth noting that we have used the same reaction bases and the same set of kinetic parameters (see Tables I-IV) in the primary and secondary mechanisms generated by EXGAS as in our



Figure 1 Oxidation of n-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms. Evolution of the conversions of alkane (a) and oxygen (b) with temperature. The points refer to experimental observations and the curves come from simulations.



Figure 2 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 0.5$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.

previous studies [6–9]. However, some kinetic parameters of the C_0-C_2 reaction base have been updated and are presented in Table V.

It is worth noting that the rate constant of the reaction

$$\cdot CH_3 + HO_2 \cdot \longrightarrow CH_3O \cdot + \cdot OH \tag{10}$$

is relatively sensitive and the uncertainty factor given by Baulch et al. [15] is about 10.

The formation of alkenes such as 1-pentene, 1-heptene, 1-octene, and 1-nonene (Figs. 2c, 3a, 4c, 5a, 6c, and 7a) are adequately reproduced. Hence, the primary production and the secondary consumption of these products are mostly correct. However, we observe a lack of conversion of these intermediate products between 1050 and 1150 K. This problem is more significant at low equivalence ratios. The formation of other important alkenes such as propene (Figs. 2b, 4b, and 6b) and 1-butene (Figs. 2c, 4c, and 6c) is satisfactory and thus validates the different ways of production and consumption of these species. On the other hand, a problem arises for the formation of ethylene which is always underestimated by a factor up to 2 at high temperature.

Reactions	$\log A$	b	Ε	References
$\cdot CH_3 + HO_2 \cdot \leftrightarrow CH_3O \cdot + \cdot OH$	13.17	0	0.0	[34]
$C_2H_4 + \cdot H \leftrightarrow \cdot C_2H_3 + H_2$	7.7	1.93	54.0	[35]
$C_2H_4 + \cdot CH_3 \leftrightarrow \cdot C_2H_3 + CH_4$	11.8	0	16.0	[36]
$O_2 + \cdot C_2 H_3 \leftrightarrow C_2 H_2 + HO_2 \cdot$	6.1	1.61	-1.7	[37]
$O_2 + \cdot C_2 H_3 \leftrightarrow HCHO + HCO \cdot$	16.6	-1.39	4.2	[37]

Table VUp-dated Reactions of the C_0-C_2 Reaction Base

^aRate constants are assumed to follow the modified Arrhenius law, $k = AT^{b} \exp(-E/RT)$, with the units cm³, mol, s, kJ.

This problem will be discussed in the following part of this paper. The formation of 1,3-butadiene (Figs. 2b, 4b, and 6b) is well predicted, showing that the secondary reactions proposed for its formation are reasonable. The formation of other unsaturated species such as C_5H_8 , acrolein, C_3H_4 (allene and propyne), C_2H_2 , or benzene (Figs. 3(b,c), 5(b,c), and 7(b,c)) are rather well reproduced. The reactions of formation and consumption of these last three species are essentially included in the C_0-C_6 reaction base.

The shape of the oxygenated compounds (i.e., CO, CO₂, and formaldehyde) are correctly reproduced by the simulations (Figs. 2a, 4a, and 6a), even if the yield of final products (i.e., CO and CO₂) is overestimated for equivalence ratios of 1 and 1.5 at high temperatures (T > 1100 K).

ANALYSIS OF THE MECHANISM OF *n*-HEXADECANE OXIDATION

In order to better understand the results obtained and to point out the main reaction pathways, a sensitivity



Figure 3 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 0.5$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.



Figure 4 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 1$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.



Figure 5 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 1$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.

analysis of the mechanism of *n*-hexadecane oxidation was performed at 1100 K in the conditions of Fig. 4 (Fig. 8).

n-Hexadecane

The flow rate analysis shows that the consumption of *n*-hexadecane is essentially due to the reactions of H-abstraction by the free radicals ·H and ·OH. The metathesis by methyl radical is only important at low temperature (11% at 1050 K). An interesting point is related to the role of unimolecular initiations which become significant at high temperature (35% at 1200 K against 14% at 1050 K). In fact, the sensitivity analysis (Fig. 8) shows that the major reactions governing the conversion of reactant are included in the C0-C2 reaction base. The branching step between H. atoms and oxygen molecules to give .O. atoms and OH. radicals is especially important. As the concentrations of the rather unreactive ·CH₃, HO₂·, and ·a-.C₃H₅ radicals are relatively high, the reactions involving these species are also important for the overall rate of reaction.



Figure 6 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 1.5$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.

Alkenes

Primary 1-Alkenes (C > 3). Two flow rate analyses have been carried out for temperatures of 1050 K (Fig. 9) and 1200 K, an equivalence ratio of 1, and a conversion of $C_{16}H_{34}$ of 85% for each case.

The primary alkenes formed are all 1-alkenes and are mainly produced by β -scissions of primary alkyl free radicals. The flux of formation by these reactions can reach 90% of their total production, as shown in Fig. 9. A second way of formation of these species is through retro-ene reactions. As previously described, these reactions yield propene and 1-alkenes. However, the flux of production is relatively small compared to the flux of β -scissions. On the other hand, retroene reactions are also important consumption reaction for 1-alkenes.

Other important reactions of consumption are unimolecular initiations (UI) leading to the formation of the allyl radical ($\cdot C_3H_5$) and alkyl radicals reacting in the primary mechanism. The importance of this channel increases with temperature and decreases with the number of carbon atoms in the molecule, e.g., U.I.



Figure 7 Oxidation of *n*-hexadecane in a jet-stirred reactor at 1 atm and a residence time of 70 ms for $\Phi = 1.5$. Evolution of the concentrations of products with temperature. The points refer to experimental observations and the curves come from simulations.

represent 8% of the total consumption of $C_{12}H_{24}$ at 1050 K against 40% for C_5H_{10} at 1200 K. The variation with the number of carbon atom is due to a competition with H-abstraction reactions for which the number increases with the size of alkene. In fact



Figure 8 Sensitivity analysis for the mole fraction of *n*-hexadecane at 1100 K, in the conditions of Fig. 4.

H-abstraction reactions must be differentiated according to the type of H-atom (allylic or alkylic) which can be abstracted. For large alkenes such as $C_{12}H_{24}$, the allylic H-abstractions, represent about 14% of the total consumption against 35% for alkylic H-abstractions, while for C_5H_{10} , alkylic H-abstractions represent only 8% of its consumption against 17% for allylic metatheses. So, even if the activation energies of alkylic Habstraction are greater than those involved in the allylic metatheses, the high number of alkylic H-atoms in large alkenes do not allow to neglect them.

The last type of reaction playing a role in the consumption of alkenes is addition. The flux of consumption of alkenes by these reactions is relatively small, especially at high temperature. Thus, at 1050 K, the reactions of addition consume approximately 9% of $C_{12}H_{24}$ (addition of \cdot H and \cdot OH) against 5% at 1200 K (addition of \cdot H and \cdot O \cdot).

Propene. Propene is a significant product of the reaction of oxidation of n-hexadecane and its formation differs from that of the other alkenes. Indeed, it is mainly formed by retro-ene reactions according to the following iterative process:

$$C_n H_{2n} \to C_{n-3} H_{2(n-3)} + C_3 H_6$$
 (11)

This result can be explained by the fact that all linear primary alkenes are 1-alkene and can react by retro-ene reactions to give propene and another linear 1-alkene which can react, in its turn, in the same way (iterative process). Therefore, about 50% of propene is formed by this type of reaction at 1050 K; the other way of formation occurs by β -scissions of primary alkyl free radicals.

Propene is mainly consumed by two ways: additions and H-abstractions. At 1050 K, additions of \cdot H, \cdot O \cdot , and \cdot OH free radicals represent about 50% of the global consumption of C₃H₆:

$$\cdot H + C_3 H_6 \rightarrow C_2 H_4 + \cdot C H_3$$
 (17%) (12)

$$\cdot O \cdot + C_3 H_6 \rightarrow \cdot H + \cdot C H_3 + C H_2 C O \qquad (12\%)$$

$$\cdot OH + C_3 H_6 \rightarrow HCHO + \cdot C_2 H_5 \qquad (17\%) \qquad (14)$$

The H-abstraction reactions by \cdot H and \cdot OH free radicals, leading to the formation of allyl radical (\cdot C₃H₅), represent about 43% of the global flux of consumption.

Ethylene. The formation of ethylene is mainly due to β -scissions of primary and secondary alkyl free radicals (85%). These reactions involved C–C and C–H



Figure 9 Rate analysis performed at 1050 K, an equivalence ratio of 1, and a conversion of *n*-hexadecane of 85% for $C_{12}H_{24}$ (a) and C_5H_{10} (b). The numbers represent the percentage of the normalized flux of formation or consumption of the 1-alkene.

bonds and an important reaction is

$$\cdot C_2 H_5 + (M) \rightarrow C_2 H_4 + \cdot H + (M)$$
(15)

This reaction represents more than 30% of the total production of C_2H_4 . All the important reactions of consumption of ethylene are contained in the C_0-C_2 reaction base:

 $\cdot H + C_2 H_4 \rightarrow \cdot C_2 H_3 + H_2$ (12%) (16)

$$O \cdot + C_2 H_4 \rightarrow \cdot CH_3 + \cdot CHO$$
 (22%) (17)

- $\cdot O \cdot + C_2 H_4 \rightarrow C H_2 C H O + \cdot H \qquad (13\%) \qquad (18)$
- $\cdot OH + C_2H_4 \rightarrow \cdot C_2H_3 + H_2O$ (24%) (19)

$$\cdot OH + C_2 H_4 \rightarrow \cdot CH_3 + HCHO \qquad (19\%) \qquad (20)$$

A problem remains for the concentration of C_2H_4 , which is underestimated by the model. In fact, two problems can be pointed out:

A lack of conversion of the reactant or large primary alkenes can lead to a deficit in the production of ethylene. This problem arises in a temperature ranging from 1050 K to 1150 K and can be explained by a lack of reactivity in the primary and secondary mechanisms.

The other problem is closely linked in a too fast consumption of C₂H₄, at high temperature, and it is well connected with the too high concentration of final oxygenated products observed (CO, CO₂) (Figs. 2a, 4b, and 6a). At 1100 K, the flow rate analysis shows clearly that CO is formed especially from formaldehyde via the radical HCO:

 $HCO \cdot + M \rightarrow CO + H \cdot + M$ (41%) (21)

$$O_2 + HCO \rightarrow CO + HO_2 \cdot$$
 (33%) (22)

HCO· is formed by H-abstraction of HCHO (about 50% of its global consumption) but also directly from reactions involving C_2H_4 or $\cdot C_2H_3$:

$$\begin{array}{ll} C_2H_4+\cdot O\cdot \rightarrow \cdot CH_3+HCO\cdot & (14\%) \\ & (23)\\ O_2+\cdot C_2H_3 \rightarrow HCHO+HCO\cdot & (21\%) \\ & (24) \end{array}$$

This last reaction is very important because it forms two species directly related to the formation of CO. Moreover, a significant part of the formaldehyde formed is due to a reaction directly involving C₂H₄:

 $\cdot OH + C_2H_4 \rightarrow \cdot CH_3 + HCHO \qquad (20\%) \quad (25)$

Thus, it seems that the high rate of C₂H₄ consumption observed in the simulations, and leading to a too high formation of final products (CO, CO₂, CH_4, \ldots), is due to a too high reactivity of small species involved in the C_0 - C_2 base. This result is corroborated by the sensitivity analysis; the reactions with the highest sensitivity coefficients for the consumption of ethylene are those involving ·OH radicals, the metathesis giving vinyl radicals (Eq. (19)) and the addition leading to formaldehyde and methyl radicals (Eq. (25)). In order to improve the level of C_2H_4 , we have increased, by a factor 2, the rate of unimolecular initiations of *n*-hexadecane. This factor is reasonable because of the uncertainties in Benson's methods used in the software KINGAS. In addition, rate constants of terminations between H atom and important free radicals such as allyl $(\cdot C_3H_5)$ have been taken to be equal to 2.0×10^{14} cm³/(mol s), according to Ref. 28. These modifications have led to a better agreement between experimental and simulated C₂H₄ concentrations.

Toxic pollutants

Model presented reproduces the reactivity of n-hexadecane as well as the formation of pollutants like CO, CO₂ or formaldehyde. In addition, the model is able to reproduce correctly the formation of some toxic species observed experimentally.

I,3-*C*₄*H*₆. About 50% of the 1,3-butadiene formed is produced by allylic H-abstraction from 1-alkenes against 14% for alkylic metatheses. Another way of production of 1,3-C₄H₆ is the β-scission of the resonance-stabilized free radical \cdot C₄H₇. This radical comes from H-abstraction from 1-butene and produces 20% of the amount of 1,3-C₄H₆ at 1050 K. On the other hand, the consumption of 1,3-C₄H₆ is mainly due to reactions of additions (55%) and metatheses (28%).

Benzene. In our conditions, the formation of benzene is essentially due to the reaction between allyl and propargyl radicals according to the reaction proposed by Marinov et al. [38]

$$\cdot C_3 H_5 + \cdot C_3 H_3 \rightarrow C_6 H_6 + \cdot H + \cdot H \qquad (26)$$

It is worth noting that this reaction has been proposed for flame conditions, i.e. for high temperature, but also allows simulating properly the benzene formation in the temperature range studied, i.e. 1000–1200 K.

Acrolein. CH_2CHCHO is formed mainly by the reaction between allyl radical and HO_2 .

$$\cdot C_{3}H_{5} + HO_{2} \cdot \rightarrow CH_{2}CHCHO + \cdot OH + \cdot H \quad (76\%)$$
(27)

This reaction is rather sensitive (see Fig. 8) because this step acts as a branching step in the mechanism by converting two unreactive free radicals into two reactive ones.

The other way of production is the reaction between 1,3-butadiene and ·OH radicals:

$$1,3-C_4H_6 + \cdot OH \rightarrow CH_2CHCHO + \cdot CH_3 \quad (20\%)$$
(28)

CONCLUSION

A kinetic detailed mechanism was built by automatic generation in order to simulate the oxidation of *n*-hexadecane in a JSR operating at 1 atm and for $0.5 < \Phi < 1.5$. The importance of large alkenes as major primary products required significant refinements of their consumption mechanisms in comparison with our previous studies on alkane oxidation. Generic reactions were added, such as unimolecular initiations, abstractions of alkylic hydrogen atoms, and retro-ene reactions. To our knowledge, it is the first time that retro-ene reactions are considered in a detailed combustion mechanism. A feedback was carried out between the primary and secondary mechanisms, in order to consume the alkyl free radicals formed during the reaction of alkenes. Simulations performed with the software CHEMKIN II reproduced, with a reasonable agreement, experimental profiles for major species (CO, CO₂, CH₄, ...) as well as minor products $(C_3H_6, 1, 3-C_4H_6, \text{ acrolein, benzene, ...})$. However, a too important reactivity of small species involved in the C_0-C_2 reaction base was observed. A large part of this too high reactivity results in a too important consumption of ethylene and in concentrations of CO and CO₂ higher than those observed experimentally.

The analysis of the mechanism showed that cetane reacts mostly by H-abstractions followed by decomposition of alkyl free radicals into 1-alkenes. The importance of the different reaction channels for the consumption of alkenes was studied. Retro-ene reactions represent an important way that permits one to reproduce correctly the formation of propene whereas alkylic H-abstractions are very important consumption paths for larger alkenes. This analysis also pointed out the importance of unimolecular initiations at high temperature (1200 K).

An important point in the modeling of diesel fuel is the low-temperature chemistry and autoignition phenomenon. Further experimental work should focus on these conditions in order to validate low-temperature models.

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