# Modeling the Oxidation of Mixtures of Primary Reference Automobile Fuels

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A kinetic model for the oxidation of mixtures of *n*-heptane/iso-octane, the primary reference fuels for octane rating in spark-ignited internal combustion engines, has been written by using the system of automatic generation of mechanisms developed in Nancy. The relevant mechanism involves 647 species and includes 2386 reactions. The concentration profiles predicted by this model have been compared with experimental results obtained in a perfectly jet-stirred reactor in a temperature range from 580 to 1150 K, which includes the negative temperature coefficient region. A good agreement has been obtained for both the conversion of reactants and the distribution of the products formed. Reaction rates analyses have been performed for both compounds at 650 and 1100 K. A sensitivity analysis and a study of the influence of the structure of each molecule on the preferential reaction channels have been carried out and have enabled us to explain the changes in reactivity with the composition of the mixtures studied.

## Introduction

The modeling of the combustion and the oxidation of hydrocarbons, of which gasolines are composed, leads to a better understanding of the auto-ignition phenomena in engines, as well as a prediction of the emission of pollutants. Due to the complexity of the phenomena involved in combustion, detailed chemical models involving elementary steps are required to predict the efficiency of new antiknock additives and to quantify the formation of pollutants (e.g., carbon monoxide, unburned hydrocarbons, nitrogen oxides, soot).

*n*-Heptane and iso-octane are primary reference fuels for octane rating in spark-ignited internal combustion engines; their octane numbers are 0 and 100, respectively. Reference fuels, which have intermediate octane numbers, are obtained from mixtures of these two compounds and are used to measure the octane number of actual gasolines in CFR engines. For a given octane number, the modeling of the reference mixture is important to understand the chemical phenomena which govern the auto-ignition of relevant gasolines. Callahan et al.[1] modeled the results obtained in an adiabatic plug flow reactor and in a rapid compression machine for pure *n*-heptane and iso-octane and for mixtures having high octane numbers. These results

clearly show the nonlinear variation of the auto-ignition characteristics of fuels versus octane number. Griffiths et al.[2] have also studied the spontaneous ignition of a range of mixtures of *n*-heptane and iso-octane in a rapid compression machine.

A system (EXGAS) of computer-aided generation of mechanisms has been developed to provide detailed kinetic models for the oxidation and the combustion of hydrocarbons. This software and its application to the oxidation of alkanes has been previously described for *n*-butane,[3] *n*-heptane,[4,5] iso-octane,[4,5] *n*-octane,[6] *n*-decane,[6,7] and *n*-hexadecane.[8] In the case of the oxidation of pure *n*-heptane and iso-octane, the kinetic models obtained have been validated by using the experimental results obtained by Dagaut et al.[9] in a perfectly stirred reactor at 10 atm, with temperatures ranging from 550 to 1150 K and significant dilution with nitrogen.

This paper presents a detailed kinetic model for the oxidation of *n*-heptane/iso-octane mixtures, as well as

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a comparison between the profiles of species computed using this mechanism and the experimental results of Dagaut et al.[10] obtained for mixtures of different compositions. As this model satisfactorily reproduces the experimental results, an analysis of the mechanism should permit the identification of the important parameters which explain the variations of reactivity of these mixtures.

## Kinetic Model

The kinetic model used in this study has been obtained by means of EXGAS, the system of automatic generation of mechanisms, developed in Nancy for the combustion and the oxidation of hydrocarbons and already extensively described in several papers.[3-8] This model includes a reaction mechanism, the kinetic data of every reaction and the thermochemical data of each species.

The mechanism is divided into three parts:

(i) A $C_0-C_2$ reaction base[11] involves each of the elementary steps which are possible between species including hydrogen, oxygen, and up to two atoms of carbon and for which kinetic data are available in the literature. This data base involves 42 species, which include up to two atoms of carbon in the molecule, and induces 835 reactions; 15 species including 3 or 4 atoms of carbon in the molecule appear as products resulting from addition or recombination reactions, but are not consumed by the reactions included in this base. The relevant kinetic data are taken mainly from the evaluations of Baulch et al.[12] and of Tsang and Hampson.[13] The pressure-dependent rate constants are obtained by using the formalism proposed by Troe.[14] This base has been validated in various conditions, such as the oxidation of methane and ethane in a perfectly stirred reactor between 773 and 1573 K[11] or the combustion of methane and acetylene in a laminar premixed flame.[15]

(ii) A comprehensive primary mechanism includes the reactions of the initial reactants (*n*-heptane, iso-octane, and oxygen) and of the primary radicals derived from them and contains only elementary reactions. The rules of generation represent the chemical steps usually taken into account in the description of the oxidation and the combustion of alkanes.[16-18] According to the choices of the user, the reactant and the primary radicals can be systematically submitted to the different types of following elementary steps:

• unimolecular initiations involving the breaking of a C−C bond,

• bimolecular initiations with oxygen to produce alkyl and •$HO_2$ radicals,

• additions of alkyl (R•) and hydroperoxyalkyl (•QOOH) radicals to an oxygen molecule,

• isomerizations of alkyl and peroxy radicals involving a cyclic transition state.

As previous studies[5,7,18] have shown the important role played by the reactions of peroxy and hydroperoxyalkyl radicals during the oxidation of alkanes at low temperature, a specificity of this system is to consider the isomerizations of hydroperoxy peroxyalkyl radicals (•OOQOOH) with as much detail as those of peroxyalkyl radicals (ROO•):

• decompositions of radicals by $\beta$-scission involving the breaking of C−C or C−O bonds for all types of radicals (for low-temperature modeling, the breaking of C−H bonds is not written);

• decompositions of hydroperoxyalkyl and dihydroperoxyalkyl (•$U(OOH)_2$) radicals to form cyclic ethers and •OH radicals;

• oxidations of alkyl radicals with $O_2$ to form alkenes and $HO_2$• radicals;

• metatheses between radicals and the initial reactants (H-abstractions);

• recombinations of radicals;

• disproportionations of peroxyalkyl radicals with $HO_2$• to produce hydroperoxides and $O_2$ (disproprtionnations between two peroxyalkyl radicals or beween peroxyalkyl and alkyl radicals are not taken into account).

With the purpose of reducing the number of new molecular species thus produced, the molecules which have the same molecular formulae and the same functional groups are lumped into one unique species, without distinguishing the different isomers.

(iii) A secondary mechanism describes the reactions consuming the molecular products formed in the primary mechanism. These reactions are not elementary steps, but *global reactions*, which lead in a limited number of steps to decomposition products, whose reactions are included in the $C_0-C_2$ reaction base. The rate of a global reaction is the rate of the first elementary step involved. The globalization of the secondary mechanism permits the model to keep a limited size allowing computation.

The secondary mechanism includes:

• degenerate branching steps, which consume peroxide species and start by the breaking of a O−OH bond;

• reactions of aldehydes, alkanes, alcohols, and epoxides, occurring first by a metathesis followed by subsequent decompositions;

• metatheses with alkenes yielding resonance stabilized radicals, which lead to the formation of dienes, when a $\beta$-scission involving the breaking of a C−C bond is possible, or are so unreactive that they react mainly by termination steps;

• additions of •H, •OH, •$CH_3$, or $HO_2$• to alkenes and ketones.

• Reactions of Cyclic Ethers. Cyclic ethers react first by a metathesis to give lumped radicals, which can either decompose or react with oxygen. The reactions with oxygen involve the classical sequence of oxygen

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**Table 1. Parameters Used for the Calculation of the Rate Constants of Internal Isomerizations of Free Radicals**

Activation Energy for a H-Atom Abstraction ($E_{abs}$)

| type of H atom | primary | secondary | tertiary |
|---|---|---|---|
| abstraction by ROO$^\bullet$ (kJ mol$^{-1}$) | 84 | 71 | 58 |
| abstraction by R$^\bullet$ (kJ mol$^{-1}$) | 56 | 46 | 38 |

Strain Energy of Cyclic Compounds ($E_{cycle}$)

| size of the ring | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 12 |
|---|---|---|---|---|---|---|---|---|
| rings containing zero or one O atom (kJ mol$^{-1}$) | 109 | 26 | 4.2 | 27 | 41 | 53 | 53 | 18 |
| rings containing two O atoms (kJ mol$^{-1}$) | 96 | 65 | 35 | 21 | 17 | | | |

addition, isomerization, second oxygen addition, second isomerization, and $\beta$-scission to lead to the formation of hydroperoxides, which are degenerate branching agents and decompose to give $^\bullet$OH radical and several molecules or radicals considered as reactants in the $C_0$–$C_2$ reaction base.

The kinetic data for the isomerizations of radicals, the recombinations of free radicals, and the unimolecular decompositions of molecules are calculated by using a software (KINGAS) developed in our department by Bloch-Michel,[19] which is based on the thermochemical kinetics methods proposed by Benson.[20] As the isomerizations of R$^\bullet$, ROO$^\bullet$, and $^\bullet$OOQOOH radicals have an important role to explain the differences of reactivity observed between *n*-heptane and iso-octane, we detail here the method used for the calculation of the relevant rate constants. Pre-exponential factor ($A$) is mainly based on the changes in the number of internal rotations as the reactant moves to the transition state; the equation uses a mean value of 15 J mol$^{-1}$ K$^{-1}$ for each lost rotor:[3,21]

$$A = e \times \frac{k_B T}{h} \times \text{rpd} \times \exp\left[\frac{(\Delta n^{\neq}_{\text{i.rot.}}) \times 15}{R}\right] \text{ s}^{-1}$$

where $\Delta n^{\neq}_{\text{i.rot.}}$ represents the change in the number of internal rotations as reactant moves to the transition state, e = base of natural logarithms, $h$ = Planck constant, $k_B$ = Boltzmann constant, $R$ = gas constant (J mol$^{-1}$ K$^{-1}$), rpd represents the reaction path degeneracy = number of identical abstractable H atoms, and $T$ = temperature.

Activation energy ($E$) is set equal to the sum of the activation energy for H-abstraction from the substrate by analogous radicals ($E_{abs}$) and the strain energy of the cyclic transition state ($E_{cycle}$). The values used for these energies are given in Table 1. The strain energy of the cyclic compounds containing zero or one oxygen atom are those proposed by Benson,[20] while the values for the cyclic compounds containing two oxygen atoms are derived from the work of the teams of R. W. Walker and M. J. Pilling.[17]

For the other types of primary reactions, for which thermochemical kinetics methods are not relevant, and for secondary reactions, kinetic data are obtained by structure–reactivity correlations. These correlations are either proposed in the literature (e.g., the metatheses of $^\bullet$OH radicals with organic compounds[22]) or obtained by analogy with data of the literature. Rate constants depend only on temperature, on the type of elementary step involved, and in some cases on the type of hydrogen atom, which is transferred during the reaction. Thus a limited number of parameters allow one to obtain rate constants for the large number of elementary steps included in the primary and secondary mechanisms. A one-page table previously published[3] summarizes all the parameters used for the correlations related to the primary mechanism.

Thermochemical data of molecular or radical species are automatically calculated and stored as 14 polynomial coefficients, according to the CHEMKIN II formalism.[23] These data are calculated by using a software (THERGAS) developed in our department,[24] which uses the group and bond additivity methods proposed by Benson[20] as a basis.

The mechanism, described here, involves 647 species, among which 485 are radicals, and includes 2386 reactions. It is written in a format to be directly used by the software of the CHEMKIN II library.[23] This mechanism is available on our web site: http://www.ensic.inpl-nancy.fr/ENSIC/DCPR/cinetique/Chimieinfo/Chiminfo.htm.

## Comparisons between Experimental and Computed Results

Dagaut et al.[10] have studied the oxidation of *n*-heptane/iso-octane mixtures in a jet-stirred reactor, at a residence time of 1 s, a pressure of 10 atm, and temperatures ranging from 550 to 1150 K. The mixtures studied corresponded to research octane numbers (RON) 10, 50, 70, and 90, i.e., to *n*-heptane/iso-octane ratios 9/1, 5/5, 3/7, and 1/9, respectively. The mixtures were composed of 0.1% (molar) hydrocarbons diluted in nitrogen with a stoichiometric amount of oxygen. This work followed a study of the two pure compounds in similar experimental conditions and for stoichiometric ratios from 0.3 to 1.5.[9] Temperatures varied from the low to the high temperature ranges for the oxidation of alkanes, including especially the negative temperature coefficient (NTC) region, where the conversion of fuel decreases when temperature increases.

Figure 1 presents the variation of the conversion of *n*-heptane and iso-octane vs temperature for mixtures with RON 10 (Figure 1a), 50 (Figure 1b), and 90 (Figure 1c), respectively. In all the figures of this paper, symbols are related to experiments and lines to simulations. Calculated profiles are in good agreement with the experimental results concerning the reactivity of the mixtures both at low and high temperatures, and especially in the NTC region. Simulations reproduce

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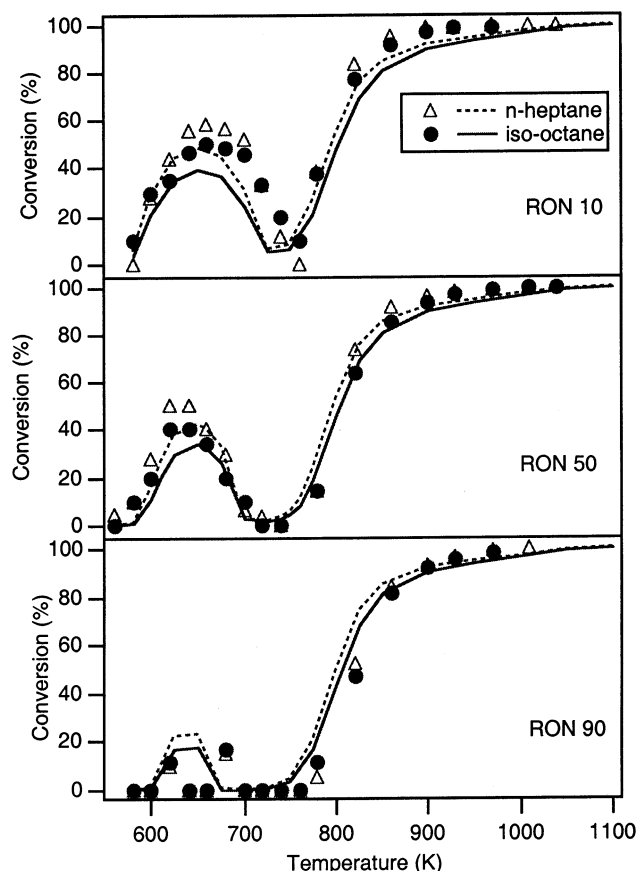(20) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley: New York, 1976.
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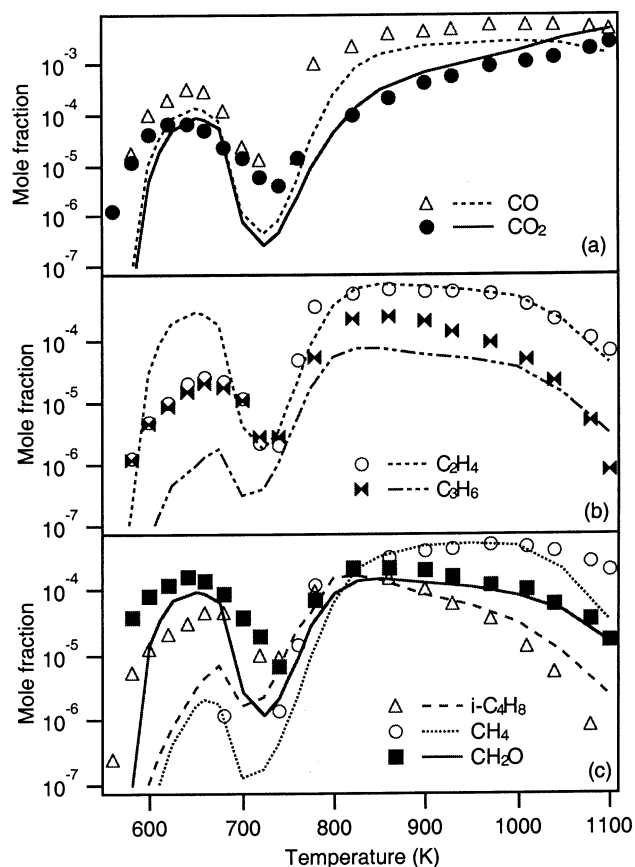
**Figure 1.** Conversion of initial alkanes during the oxidation of mixtures of RON 10, 50, and 90. Symbols are experimental data, curves are simulation results.



**Figure 2.** Products formation during the oxidation of a mixture of RON 50. Symbols are experimental data, curves are simulation results.

well the decrease in conversion at low temperature as the iso-octane ratio increases. For mixtures with a low octane number, conversion is slightly underestimated; a limited adjustment of the kinetic parameters for the oxidations of alkyl radicals or the isomerizations of peroxyalkyl radicals in their uncertainty ranges would enable this problem to be corrected; but to be consistent with the previous validations of the EXGAS system,[3–8] no fitting was performed here.

Figure 2 shows the variations of the mole fractions of the main products vs temperature for the RON 50 mixture. Due to the wide range of reactivity observed, this figure is presented in logarithmic scale. The formation of carbon monoxide and carbon dioxide (Figure 2a) is well reproduced over the whole temperature range. Carbon monoxide is mainly formed by oxidation of formaldehyde, which is obtained from methyl radicals and ethylene (by addition of OH• radicals). At low temperatures, carbon dioxide is produced more by the degradation of oxygenated compounds (such as cyclic ethers[5]), than by oxidation of carbon monoxide. At low temperatures, ethylene (Figure 2b) is overestimated and propene (Figure 2b) and iso-butene (Figure 2c) are underestimated. These three alkenes are obtained from the decomposition reactions of primary molecules, which are written in the secondary mechanism favoring the formation of small species included in the $C_0$–$C_2$ reaction base. At high temperatures, alkenes are more easily formed in the primary mechanism by the $\beta$-scissions of the alkyl radicals derived from initial alkanes. The computed profiles agree then more with the experimen-

tal points, especially in the case of isobutene, which is the main primary product of iso-octane oxidation in these conditions. The experimental and computed profiles are in good agreement in the cases of methane and formaldehyde (Figure 2c).

For each product studied, the mole fraction profile exhibits a maximum around 650 K, which corresponds to the maximum for the reactant conversions at low temperature, below the NTC region. Above the NTC region, the amounts of products increase again with temperature to reach a second maximum. After this maximum, the consumption of these products become more important and only the $CO_2$ mole fraction still increases. Figure 3 presents a comparison between experimental and computed results in the cases of the maximum mole fractions obtained for carbon dioxide in the temperature range below the NTC region and for ethylene in the temperature range above the NTC region. These results have been obtained for *n*-heptane/iso-octane mixtures with RON ranging from 0 to 100 (here, the octane number is just a way to characterize the mixtures).[10] This figure has been completed by the addition of the data observed during the oxidation of *n*-decane (RON 41) in similar experimental conditions;[25] the mechanism used for these simulations has been previously published[6,7] and was based on the same thermochemical and kinetic data as the mechanism presented in this paper. The model predicts that the maximum $CO_2$ mole fraction, in the temperature range

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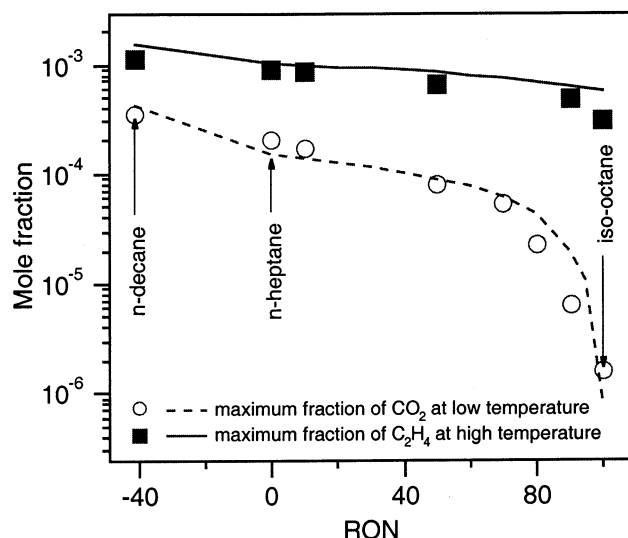
**Figure 3.** Variation of the maximum mole fraction of $CO_2$ at low temperature (~650 K) and of $C_2H_4$ at high temperature (~850 K) versus RON during the oxidation of *n*-decane, *n*-heptane, iso-octane, and mixtures of *n*-heptane and iso-octane in the experimental conditions of Dagaut et al.[9,10,25] Symbols are experimental data, curves are simulation results.

below the NTC region, is reached at 650 K for *n*-heptane; the temperature of this maximum decreases when RON increases and reaches a value of 630 K for iso-octane. The maximum ethylene mole fraction, in the temperature range above the NTC region, is reached at 850 K for *n*-heptane; the temperature of the maximum gets up slightly with RON to reach a value of 870 K for iso-octane. Carbon dioxide and ethylene maximum mole fractions give good indications of the global reactivity of the mixtures in the low and high temperature ranges, respectively, and Figure 3 clearly shows that the higher RON, the lower the reactivity at low temperature. This variation is particularly important for high iso-octane ratios, i.e., from RON 70. The effect of the initial composition of the mixtures on the reactivity at high temperature is weak.

## Analysis of the Mechanism

**Mechanisms for the Oxidation of Pure *n*-Heptane and Iso-octane.** Figure 4 displays a scheme representing the main reaction paths for *n*-heptane and iso-octane for an initial temperature of 650 K. This figure shows that the initial alkanes are consumed primarily by metatheses with •OH radicals to produce heptyl or octyl radicals, which mainly react by addition with oxygen to give peroxyalkyl radicals (ROO•) or by metathesis to form alkenes conjugated to the reactants.

The main reaction of peroxyalkyl radicals is isomerization to give hydroperoxyalkyls radicals (•QOOH), which can decompose to give cyclic ethers, alhehydes, or ketones or react again by addition with oxygen and involve the formation of •OOQOOH radicals. The decomposition of •QOOH to give alkenes and HO$_2$• radicals is only a very minor channel. The isomerizations of •OOQOOH radicals lead to •U(OOH)$_2$ radicals which can decompose to form hydroperoxy cyclic ethers or ketohydroperoxides (these last species have been detected experimentally by Sahetchian et al.[26] in the case of *n*-dodecane). Hydroperoxides are degenerate branching
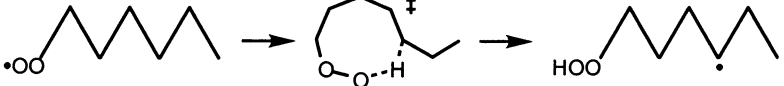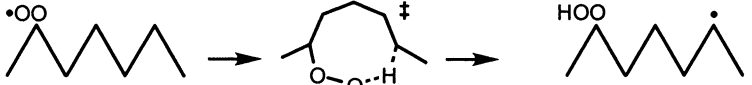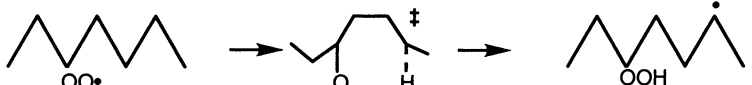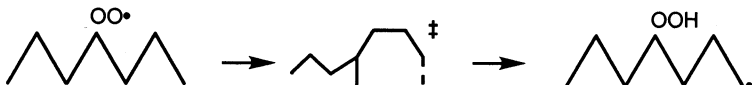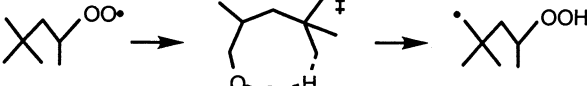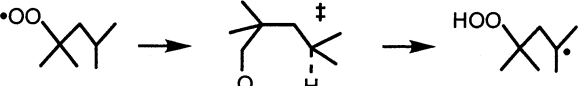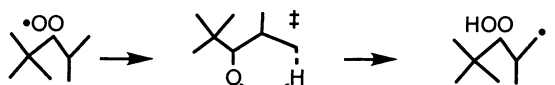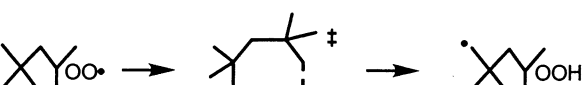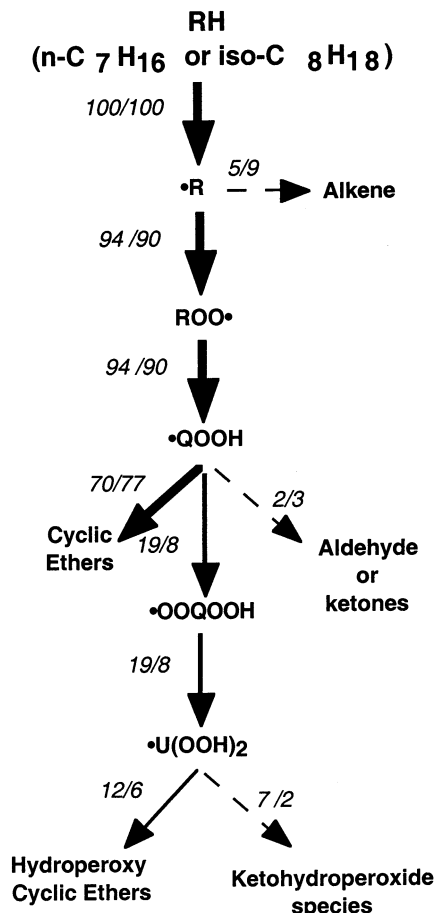


**Figure 4.** Flow rate analysis for the oxidation of *n*-heptane and iso-octane at 650 K in the experimental conditions of Dagaut et al.[9] The thickness of the arrows is roughly proportional to the rate of the channel considered (for the reversible steps, the net rate of the overall channel was taken into account) and the number near the arrow is the ratio (%*n*-heptane/%iso-octane) between the related rate and the global rate of consumption of the alkane.

agents, which can easily decompose by breaking an O–O bond and induce an increase of the amounts of •OH radicals, which ensure the propagation of the reaction.

In this temperature range, the reactivity of the mixture is directly related to the amounts of peroxides formed from the reactant, and the primary initiations have no kinetic effect. The difference in reactivity between *n*-heptane and iso-octane can then be explained mainly by the difference in the amounts of peroxides produced. Unlike *n*-heptane, the branched structure of the molecule of iso-octane leads to an increase of the number of primary hydrogen atoms, which react more slowly by metatheses and internal isomerizations. Table 2 presents the activation energy of the easiest isomerization for each peroxyalkyl radical formed during the oxidation of *n*-heptane and iso-octane. Except the second isomer in the second part of Table 2, all the isomerizations related to iso-octane have a larger activation energy than those related to *n*-heptane. The flux of formation of the fourth isomer in the second part of Table 2 represents around 50% of the global flux of

(26) Sahetchian, K.; Champoussin, J. C.; Brun, M.; Levy, N.; Blin-Simiand, N.; Aligrot, C.; Jorand, F.; Socoliuc, M.; Heiss, A.; Guerassi, N. *Combust. Flame* **1995**, *103*, 3, 207–220.

**Table 2. Activation Energy of the Easiest Isomerization for Each Peroxyalkyl Radical Formed during the Oxidation of *n*-Heptane and Iso-octane ($E = E_{abs} + E_{cycle}$) in kJ mol$^{-1}$**
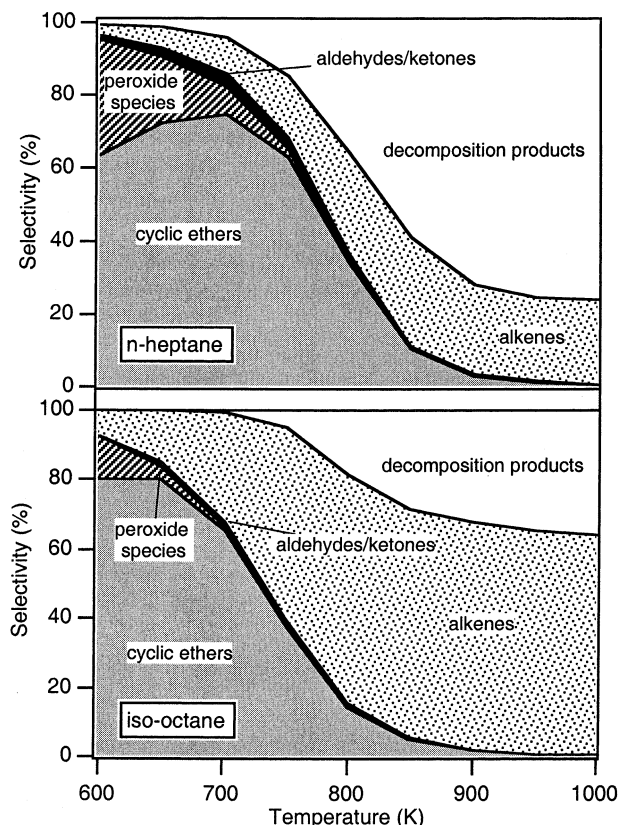
### *n*-heptane

| Reaction | Description |
|---|---|
| (structure) | 8 member ring / secondary H abstracted / E = 71 + 17 = 88 |
| (structure) | 8 member ring / secondary H abstracted / E = 71 + 17 = 88 |
| (structure) | 7 member ring / secondary H abstracted / E = 71 + 21 = 92 |
| (structure) | 7 member ring / primary H abstracted / E = 84 + 21 = 105 |

### *iso-octane*

| Reaction | Description |
|---|---|
| (structure) | 8 member ring / primary H abstracted / E = 84 + 17 = 101 |
| (structure) | 7 member ring / tertiary H abstracted / E = 58 + 21 = 79 |
| (structure) | 5 member ring / primary H abstracted / E = 84 + 35 = 119 |
| (structure) | 7 member ring / primary H abstracted / E = 84 + 21 = 105 |

production of peroxyalkyl radicals during the oxidation of iso-octane and the activation energy of its easiest isomerization is equal to 105 kJ mol$^{-1}$. The second isomer of the first part of Table 2 is the most abundant peroxyalkyl radical formed during the oxidation of *n*-heptane and the activation energy of its easiest isomerization is equal to 88 kJ mol$^{-1}$. This difference of 17 kJ mol$^{-1}$ represents a factor 30 at 650 K and 15 at 750 K for the rate constants. These remarks are still true for the isomerizations of peroxy hydroperoxide radicals formed by the second addition to oxygen.

The fact that isomerizations are slower in the case of iso-octane favors reactions, which compete with the additions of oxygen. These reactions are oxidations (i.e.,

the reaction between alkyl radicals and oxygen to give conjugated alkenes and HO$_2$• radicals) and formations of cyclic ethers (competing with the second addition to oxygen). Figure 5 displays the evolution of the initial selectivity (at 10$^{-3}$ s to avoid secondary reactions) in carbon-containing products with temperature. It clearly shows that, in all the temperature range studied, the initial selectivity of alkenes is larger in the case of iso-octane, while that of peroxide species (degenerate branching agents) is much smaller.

Oxidations have a strong inhibiting effect because of the production of the very stable HO$_2$• radicals. These most abundant HO$_2$• radicals can almost only react by termination, mainly to give H$_2$O$_2$ molecules, which

**Figure 5.** Initial selectiviy (at $10^{-3}$ s) in carbon-containing products vs temperature during the oxidation of *n*-heptane and iso-octane in the experimental conditions of Dagaut et al.[9] "Decomposition products" include secondary products and products of the $C_0$–$C_2$ reaction base, among those are ethylene and formaldehyde, which have primary and secondary production channels.

decompose slowly below 800 K:

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2$$
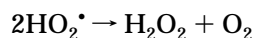
Consequently, the structure of the molecule of iso-octane, which promotes the formation of $HO_2^{\bullet}$ radicals instead of that of degenerate branching agents, leads to a much lower reactivity of this compound with oxygen than in the case of *n*-heptane.

When temperature increases, the reversible additions to oxygen are no longer favored and the importance of oxidation (the elementary reaction of alkyl radicals giving alkenes and $HO_2^{\bullet}$ radicals) increases. The reactivity of mixtures decreases then to reach a minimum around 750 K. If the temperature rises above 850 K, the rates of $\beta$-scission reactions become important and the alkyl radicals, derived from the reactants, decompose to alkenes and smaller alkyl radicals. A very sensitive reaction of this high-temperature mechanism is then the decomposition of $H_2O_2$ molecules to give the very reactive $^{\bullet}OH$ radicals.
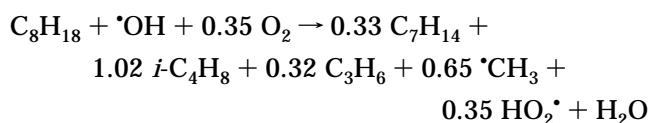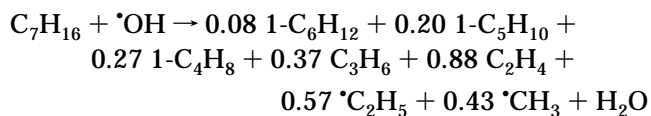
$$H_2O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$$
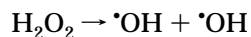
Above 950 K, the branching step

$${}^{\bullet}H + O_2 \rightarrow {}^{\bullet}OH + {}^{\bullet}O^{\bullet}$$
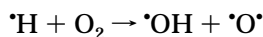
greatly speeds up the overall reaction rate.

Figure 6 displays a scheme representing the main reaction paths for *n*-heptane and iso-octane at an initial temperature of 1100 K. As at 650 K, the initial alkanes are mainly consumed by metatheses, with $^{\bullet}OH$ radicals and $H^{\bullet}$ atoms, to produce heptyl or octyl radicals. The larger number of primary hydrogen atoms in iso-octane, compared to *n*-heptane, induces a slower reaction rate for metatheses.

At 1100 K, alkyl radicals react mainly by $\beta$-scission reactions to give alkenes and smaller alkyl radicals. The primary reactions can be summarized by the following global steps:

$$C_7H_{16} + {}^{\bullet}OH \rightarrow 0.08 \; 1\text{-}C_6H_{12} + 0.20 \; 1\text{-}C_5H_{10} +$$
$$0.27 \; 1\text{-}C_4H_8 + 0.37 \; C_3H_6 + 0.88 \; C_2H_4 +$$
$$0.57 \; {}^{\bullet}C_2H_5 + 0.43 \; {}^{\bullet}CH_3 + H_2O$$

$$C_8H_{18} + {}^{\bullet}OH + 0.35 \; O_2 \rightarrow 0.33 \; C_7H_{14} +$$
$$1.02 \; i\text{-}C_4H_8 + 0.32 \; C_3H_6 + 0.65 \; {}^{\bullet}CH_3 +$$
$$0.35 \; HO_2^{\bullet} + H_2O$$

During the oxidation of iso-octane, molecular oxygen is involved in the oxidation of $t$-$C_4H_9^{\bullet}$ radicals, which cannot decompose easily by $\beta$-scission reactions.

It is worth noting that the major primary product of the oxidation of iso-octane at 1100 K is isobutene, with the production of the rather unreactive $^{\bullet}CH_3$ radicals. Secondary metatheses from isobutene produce resonance-stabilized $i$-$C_4H_7^{\bullet}$ radicals, which react mainly by termination steps and induce then an inhibiting effect. In the case of *n*-heptane, the yield of formation of propene, which can lead to resonance-stabilized $C_3H_5^{\bullet}$ allyl radicals, is lower and the main radicals obtained are $^{\bullet}C_2H_5$, which can easily decompose to produce $^{\bullet}H$ atoms and favor then the branching step.

The slower rate of metathesis of iso-octane, as well as the important formation of isobutene and $^{\bullet}CH_3$ radicals, explains also why this branched alkane is less reactive than *n*-heptane toward oxygen even at high temperature.

**Explanation of the Reactivity of the Mixtures.** Figure 7 presents a sensitivity analysis performed for the production of $CO_2$ in the case of a RON 50 mixture at 650 K. The primary coefficients obtained for the reactions of the primary mechanism of the mixture are in agreement with what was discussed previously for each alkane. Metatheses between $^{\bullet}OH$ radicals and *n*-heptane and the isomerizations of peroxyoctyl radicals have strong positive sensitivity coefficients, while the oxidations of octyl radicals have negative sensitivity coefficients.

It is worth noting that the secondary reactions of the substituted furans obtained from both alkanes accelerate strongly the production of $CO_2$. That is due to secondary reactions of cyclic ethers which have been considered in detail. Cyclic ethers react first by metatheses to give lumped radicals, which can either decompose or react with oxygen. The reactions with oxygen involve the classical sequence of oxygen addition, isomerization, second oxygen addition, second isomer-
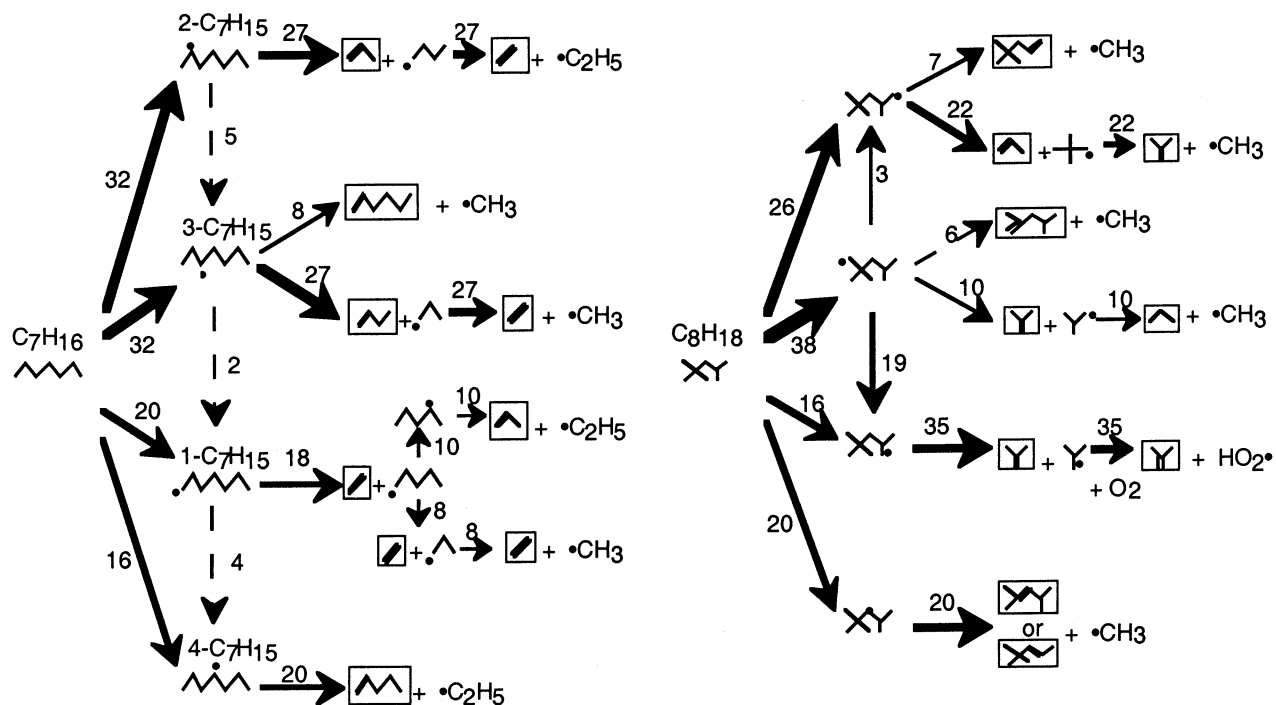
**Figure 6.** Flow rates analysis for the oxidation of *n*-heptane and iso-octane at 1100 K in the experimental conditions of Dagaut et al.[9] As in Figure 4, the thickness of the arrows is roughly proportional to the rate of the channel considered and the number near the arrow is the ratio between the related rate and the global rate of consumption of the alkane.
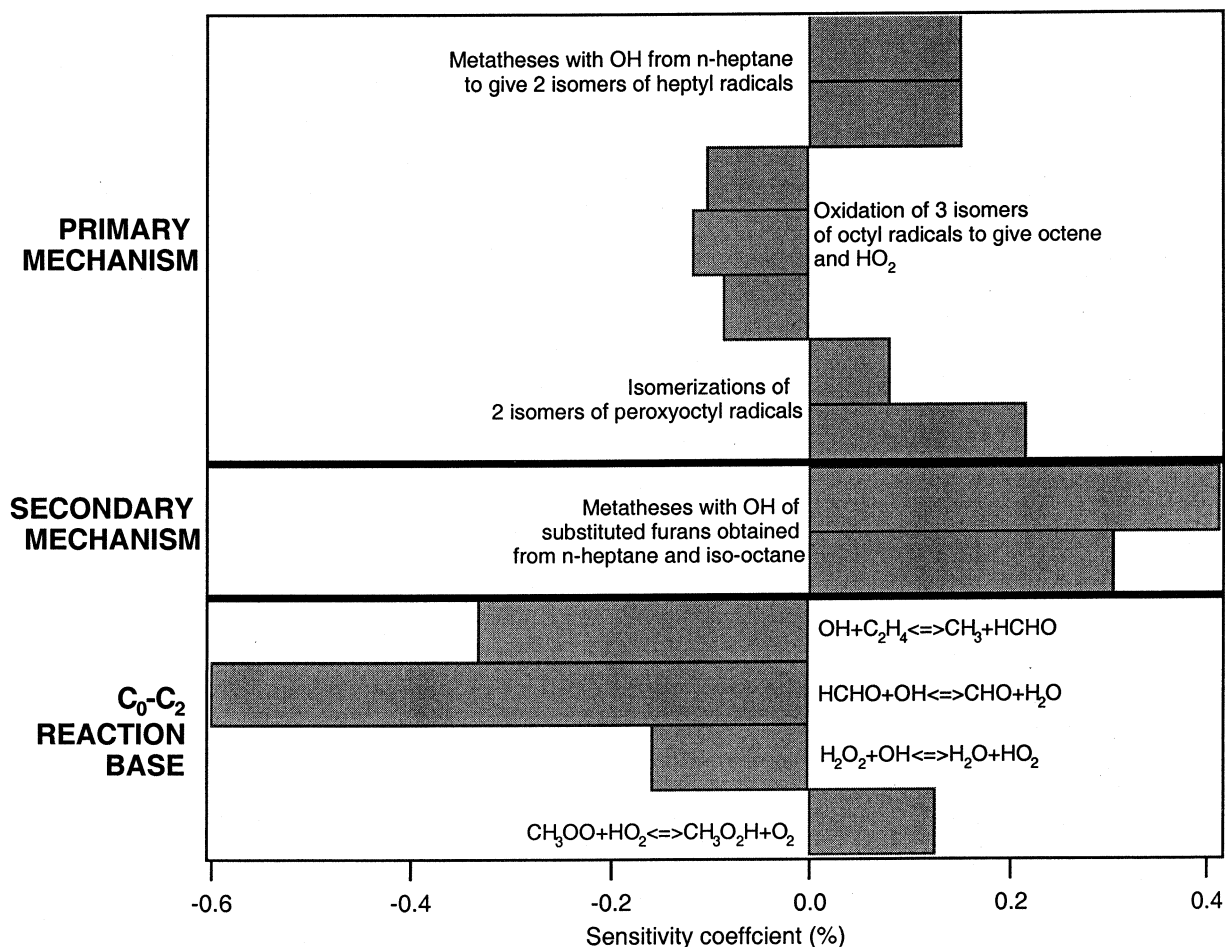


**Figure 7.** Sensitivity analysis for the production of $CO_2$ during the oxidation of a mixture of *n*-heptane and iso-octane for RON 50 at 650 K in the experimental conditions of Figure 3. Only the reactions with an absolute value of sensitivity coefficient above 0.1% are presented.

ization, and $\beta$-scission to lead to the formation of hydroperoxides, degenerate branching agents, which decompose to give •OH radicals and several molecules or radicals involving the $C_0-C_2$ reaction base, including $CO_2$.

The other important reactions are included in the $C_0-C_2$ reaction base. Reactions of methathesis with •OH radicals to give unreactive radicals have an inhibiting effect. That is especially the case for the metathesis with formaldehyde to give •HCO radicals. At 650 K, •HCO radicals can only react with oxygen to give •$HO_2$ radicals and CO. The reaction between •$HO_2$ and •$CH_3O_2$ radicals to give the branching agent $CH_3OOH$ has a positive sensitivity coefficient, as the decomposition of $CH_3OOH$ ($E_a = 175$ kJ/mol) is easier than that of $H_2O_2$ ($E_a = 201$ kJ/mol).

Figure 3 indicates that the reactivity of the mixtures at low temperature (shown by the $CO_2$ maximum mole fraction) strongly decreases as RON increases, i.e., with decreasing $n$-heptane concentration, while the reactivity at high temperature (shown by the $C_2H_4$ maximum mole fraction) shows less variation. At high temperature, the most sensitive reactions are not directly related to the reactants and the differences of reactivity are moderate, as explained above.

At low temperature, the reactivity of the mixtures does not vary linearly with composition, but decreases very strongly above RON 70. Figure 8 shows the variations of the ratios of alkenes and degenerate branching agents among the carbon-containing primary products versus RON, at 650 K and for a very low conversion. When RON increases, the amount of hydroperoxides decreases while the amount of alkenes increases; these variations are almost linear. Above RON 60, the ratio of alkenes is higher than the ratio of degenerate branching agents. At 650 K, alkenes are almost only produced by the oxidation of alkyl radicals. This reaction also produces the very unreactive $HO_2$• radicals and act then almost as a termination step.

Because of the degenerate branching steps, the successive addition of an alkyl radical on two oxygen molecules, to form hydroperoxide species, induces the production of three radicals, among which two of them are •OH chain carriers:

$$•U(OOH)_2 \rightarrow •OH + X(OOH)$$

$$X(OOH) \rightarrow •OH + XO•$$
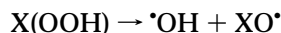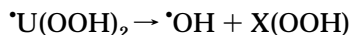
When oxidation reactions (the elementary reactions of alkyl radicals giving alkenes and $HO_2$• radicals) overcome the formations of peroxides, •OH radicals are no longer regenerated and the fuel conversion drops.

Figure 9 shows the variations of the percentage of •OH and $HO_2$• radicals among the other radicals present in the mixture with RON, at 650 K and for a very low conversion. The percentage of $HO_2$• radicals rises strongly above RON 70, while the percentage of •OH radicals drops. Thus from RON 100 to 80, a slight increase of the concentration of $n$-heptane, a compound which favors the formation of degenerate branching agents, leads to a strong rise in the concentration of •OH radicals and then to a relatively important increase of the fuel conversion.
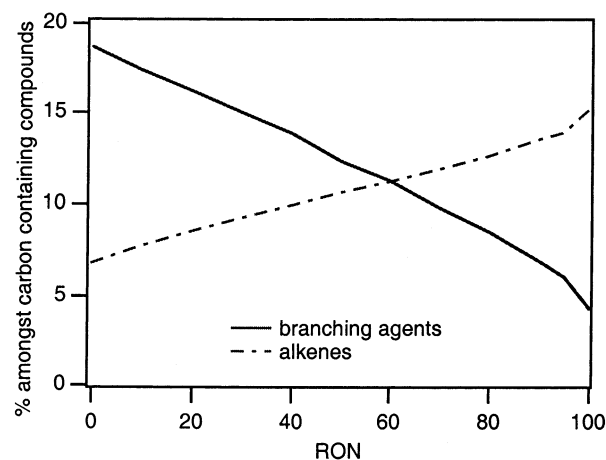


**Figure 8.** Ratios of branching agents and alkenes among the carbon-containing products, calculated at a very low conversion in the conditions of Figure 3 (~650 K), versus the octane number of the relevant mixture.
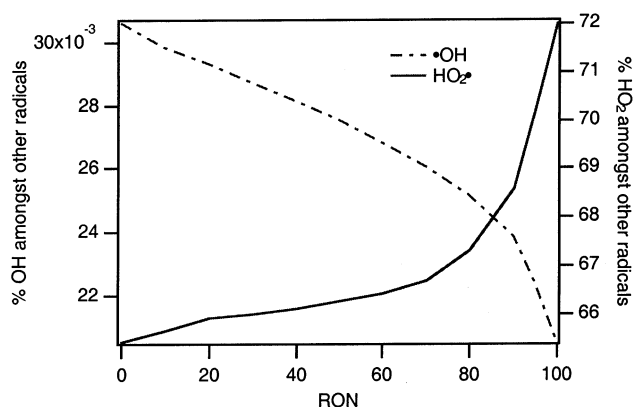


**Figure 9.** Ratios of •OH and $HO_2$• radicals among other radicals, calculated in the conditions of Figure 3, versus the octane number of the relevant mixture.

## Conclusion and Perspectives

This paper describes the first modeling of the oxidation of $n$-heptane/iso-octane mixtures in a jet-stirred reactor in a temperature range from 580 to 1150 K, which includes the negative temperature coefficient region. It presents simulations which agree well with experimental results, especially if one considers that no fitting of the rate constant has been performed. The formation of pollutants, such as carbon monoxide, carbon dioxide, ethylene, propene, isobutene, or formaldehyde, is correctly reproduced in most cases. Reaction rate analyses allow us to explain the changes in reactivity observed when the mixture composition varies and to link that to the differences of structure between branched and linear alkanes.

With the aim of modeling real fuels, work in progress in our laboratory includes the development of mechanisms for ethers,[27] alkenes,[28] naphthenes, and aromatics, as well as the reduction of the detailed mechanisms obtained.[29]

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(28) Heyberger, B.; Battin-Leclerc, F.; Warth, V.; Fournet, R.; Scacchi, G.; Côme, G. M. *Combust. Flame* **2001**, *126*, 1780−1802.
(29) Fournet, R.; Warth, V.; Glaude, P. A.; Battin-Leclerc, F.; Scacchi, G.; Côme, G. M. *Int. J. Chem. Kinet.* **2000**, *32*, 36−51.

**Supporting Information Available:** The mechanism, described here, involves 647 species, among which 485 are radicals, and includes 2387 reactions. It is written in a format to be directly used by the software of the CHEMKIN II library.[23] This material is available free of charge via the Internet at http://pubs.acs.org.

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