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## High Pressure Oxidation of Liquid Fuels from Low to High Temperature. 2. Mixtures of *n*-Heptane and iso-Octane

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**ABSTRACT**—The oxidation of mixtures of *n*-heptane and iso-octane in a high-pressure jet-stirred reactor has been investigated experimentally in a wide range of conditions covering the low and high temperature oxidation regimes (550–1150 K, 10 atm,  $\phi = 1$ ). The cool flame and negative temperature coefficient regimes were observed below 750 K. Above 750 K, the normal high temperature oxidation of both fuels was observed. Reactants, intermediates and final products have been measured providing a useful picture of *n*-heptane-iso-octane mixtures oxidation. Cyclic ethers resulting from the low-temperature oxidation chemistry of *n*-heptane and iso-octane were identified. The evolution of their concentration as a function of RON have been measured. These results are interpreted in terms of reaction mechanism. Tentative correlations between RON and CO, CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the cool flame region and for the high temperature oxidation (normal combustion) are presented.

**Key Words:**

**Subject Index:** Combustion, oxidation, engine-knock, hydrocarbon, kinetics, GC-MS

**Compound Index:** *n*-heptane, iso-octane, 2,2,4-trimethylpentane

### INTRODUCTION

In a recent study from this laboratory, the oxidation of neat *n*-heptane and neat iso-octane, primary reference fuels for the determination of gasoline knock ratings, was investigated from low to high temperature (550 to 1150 K) at high pressure (10 atm) and for equivalence ratios of 0.3 to 1.5, in a jet stirred reactor (Dagaut *et al.*, 1994a). This study covered the cool flame region, the negative temperature coefficient regime (NTC) and the high temperature oxidation domain, in contrast with previous studies restricted to either low or high temperature oxidation regime. An important reactivity of *n*-heptane was observed in the low temperature region (below 750 K), contrasting with the results obtained in the same conditions for iso-octane oxidation. Relevant previous work was reviewed in that paper where literature references can be found and are not repeated here. More recently, Ciezki and Adomeit (1993) have reported shock-tube ignition delays of *n*-heptane-air mixtures between 3.2 and 42 bars from 660 to 1350 K and Griffiths *et al.* (1993) have studied the ignition of *n*-heptane mixtures in a rapid compression machine (600–950 K, up to 9 atm).

The chemical kinetic study of the oxidation of mixtures of *n*-heptane and iso-octane had received very little attention since recently. Brezinsky and Dyer (1987) studied the oxidation of several *n*-heptane-iso-octane mixtures (RON = 0, 25, 50, 75, and 100) at atmospheric pressure and from 1100 to 1300 K in a turbulent flow reactor. Wilk *et al.* (1989) measured CO mole fraction for a series of *n*-heptane-iso-octane mixtures at atmospheric pressure and at 570 to 920 K in a flow reactor. Park and Keck (1990)

measured the ignition delays of several *n*-heptane-iso-octane mixtures in a rapid compression machine and stable species concentration profiles have been obtained from the combustion of such mixtures in research engines (Filipe *et al.*, 1992 and Leppard, 1992). However, no data have been reported at high pressure in conventional reactors.

In the present study, the oxidation of mixtures of *n*-heptane and iso-octane of various compositions has been investigated at 10 atm. The study was restricted to stoichiometric mixtures since as shown previously (Dagaut *et al.*, 1994a) no unusual behavior was observed from equivalence ratios of 0.3 to 1.5. A fused silica jet-stirred reactor operating at 10 atm and 550 to 1150 K was used. GC and GC/MS were used to obtain concentration profiles of over fifty compounds present during the oxidation of *n*-heptane-iso-octane oxidation.

## EXPERIMENTAL DETAILS

A new experimental setup was used, derived from previous JSR experiments presented in details in previous publications (Dagaut *et al.*, 1986; Chakir *et al.*, 1991). The JSR is a 4 cm diameter fused-silica sphere. The inside volume is 35 cm<sup>3</sup>. The reactor is equipped of 4 nozzles of 2 mm diameter admitting the gases which achieve the stirring. It is surrounded by two independent insulated heating wires and located inside a stainless steel pressure resistant jacket filled with insulating material. It can operate at pressures as high as 40 atm. A regulated nitrogen flow in the outer part of the reactor balances the pressure inside the reaction cell.

Previous residence time distribution studies, using pulse injection of a tracer, have demonstrated that this type of reactor is well-stirred for residence times of 10 ms to several seconds, depending on the total pressure in the range 1–10 atm (Dagaut *et al.*, 1986).

All the gases are delivered by mass flow controllers. The liquid fuel is delivered by an HPLC pump to an home-made vaporizer providing an homogeneous nitrogen-fuel mixture flowing through a capillary, up to the mixing point at the top of the reactor, to prevent reactions before the entrance of the reactor. The mixtures of *n*-heptane and iso-octane were prepared volumetrically before use. A nitrogen flow of 100 L/h was used to dilute the fuel. All the gases are preheated before injection in order to reduce temperature gradients in the JSR. A 12.5 kW induction heating system is used. Two regulated heating wires of 1 kW each are used to maintain the temperature of the upper and lower part of the reaction cell to the desired temperature. The upper part of the capillary is also temperature-regulated in order to avoid condensation of the fuel.

The good homogeneity of the reactor in temperature and concentration was checked by moving a thermocouple (uncoated chromel-alumel wires of 0.16 mm of diameter) and a sonic quartz probe along the whole vertical axis of the JSR. In these experiments, no temperature gradients higher than 10 K (typically 2–5 K) were allowed and no concentration gradients were observed. The sampling procedure, using a low pressure sonic quartz probe ( $\leq 30$  Torr), has been discussed previously (Cathonnet *et al.*, 1981). The samples were taken at steady temperature.

In this study, in order to follow the fuel oxidation from low to high conversion, the experiments have been performed varying the temperature of the gases inside the

reactor stepwise from 550 to 1150 K, and keeping the mean residence time constant. The reactants were flowed continually in the reactor. A high degree of dilution was used (0.1% of fuel) in order to reduce temperature gradients and heat release in the reaction cell, thus operating at steady state was possible. It should be noted that no flame occurs in the JSR, due to dilution. Mixtures of iso-octane and *n*-heptane in the proportions 90:10, 80:20, 70:30, 50:50, and 90:10 (RON 90, 80, 70, 50, and 10) were studied.

In this work, several gas chromatographs operating with capillary columns were used for molecular species analyses. Oxygen and CO were separated on a PLOT molecular sieve 5 A column connected to a TCD. CO<sub>2</sub> at low concentration ( $\leq 0.1\%$  mole) was separated on a Poraplot U column and methanized before FID detection. At higher concentration, CO<sub>2</sub> was measured by a TCD. The C<sub>1</sub> to C<sub>8</sub> hydrocarbons were analyzed on a PLOT Al<sub>2</sub>O<sub>3</sub>/KCl column. Formaldehyde, ethylene oxide, methanol, acetaldehyde, propylene oxide, propionaldehyde and acetone were analyzed on a Poraplot U column (methanizer and FID). Cyclic ethers were analyzed on a CPSil 5B column mounted in series with a DB5 column, connected to an FID. Helium was used as carrier gas in these analyses. For hydrogen analyses, we used nitrogen as carrier gas, a CarboPLOT P7 column and a TCD. In all the analyses, the low pressure samples were pressurized to 500–800 Torr before injection in order to improve the detection. Identification and quantification of species was accomplished using standard gas mixtures. GC/MS analyses were carried out to identify initially unknown peaks. A CPSil 5B column mounted in series with a DB5 column were connected to a mass spectrometer (Ion Trap Detector) equipped with electron ionization and methane chemical ionization.

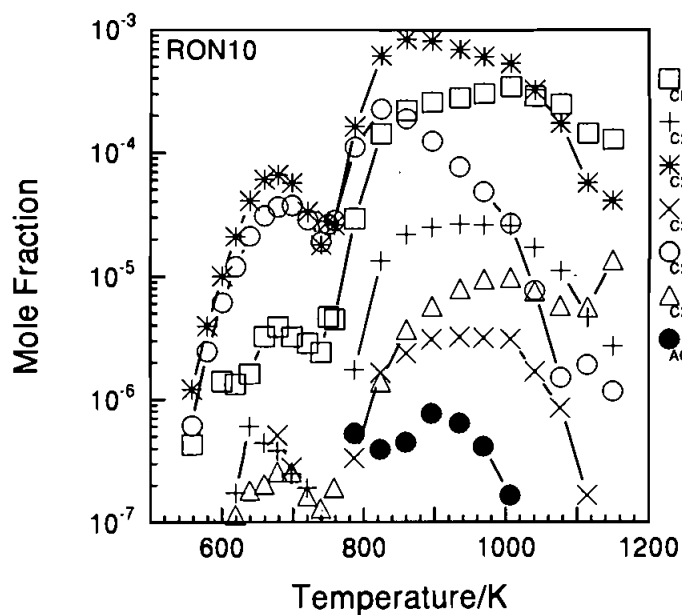
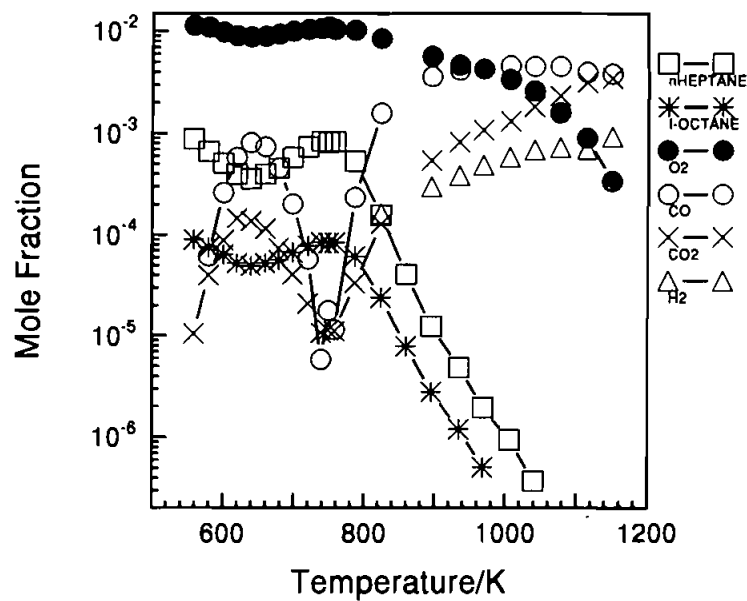
The carbon balance for this series of experiments was within less than 10 percent or better of the initial carbon level.

## RESULTS

The high pressure *n*-heptane-iso-octane oxidation experiments were carried out at a mean residence time of 1 second, at temperatures of 550–1150 K, at 10 atm, for an equivalence ratios of 1.0 and an initial fuel mole fraction of 0.001. Experimental mole fraction profiles as a function of temperature were obtained for H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>4</sub>, ethane, ethylene, acetylene, CH<sub>3</sub>CHO, ethylene oxide, propane, propene, propadiene, propyne, acetone, C<sub>2</sub>H<sub>5</sub>CHO, iso-butene, 1-butene, 2-butene (cis and trans), 1,3-butadiene, 1-pentene, 2-pentene (cis and trans), 1,3-pentadiene, 2-methyl-1-butene, 2-methyl-2-butene, isoprene (2-methyl-1,3-butadiene), 1-hexene, benzene, 1-heptene, 2-heptene (cis and trans), 3-heptene (cis and trans), *n*-heptane, 4,4-dimethyl-2-pentene (cis and trans), 2,4-dimethyl-2-pentene, 4,4-dimethyl-1-pentene, 2,4-dimethyl-1-pentene, iso-octane, 2,4,4-trimethyl-1-pentene, 2-heptanone, 2-methyl-5-ethyl-tetrahydrofuran (cis and trans), 2-methyl-4-propyl-oxetan (cis and trans), 2-ethyl-3-propyl-oxiran, 2-methyl-3-butyl-oxiran (cis), 2-propyl-tetrahydrofuran, 2-ethyl-tetrahydropyran, 2,2,4,4-tetramethyl-tetrahydrofuran, 2-iso-propyl-3,3-dimethyl-oxetan, and 2-terbutyl-3-methyl-oxetan. 2-methyl-tetrahydrofuran, 2-butyl-oxiran, 2,4-diethyl-oxetan, 2-methyl-3-butyl-oxiran (trans), 3-heptanone and heptanal were also detected.

Figures 1 to 4 show the present results. From these figures, it is clear that below 750 K, a low temperature oxidation of *n*-heptane and iso-octane takes place with the formation of CO, CO<sub>2</sub>, and oxygenated compounds. These results also show that a large fraction of hydrocarbon (up to 60% of initial fuel in low RON mixtures) is

### RON10-O<sub>2</sub>-N<sub>2</sub>, $\Phi=1.0$ , 10atm, $\tau=1s$



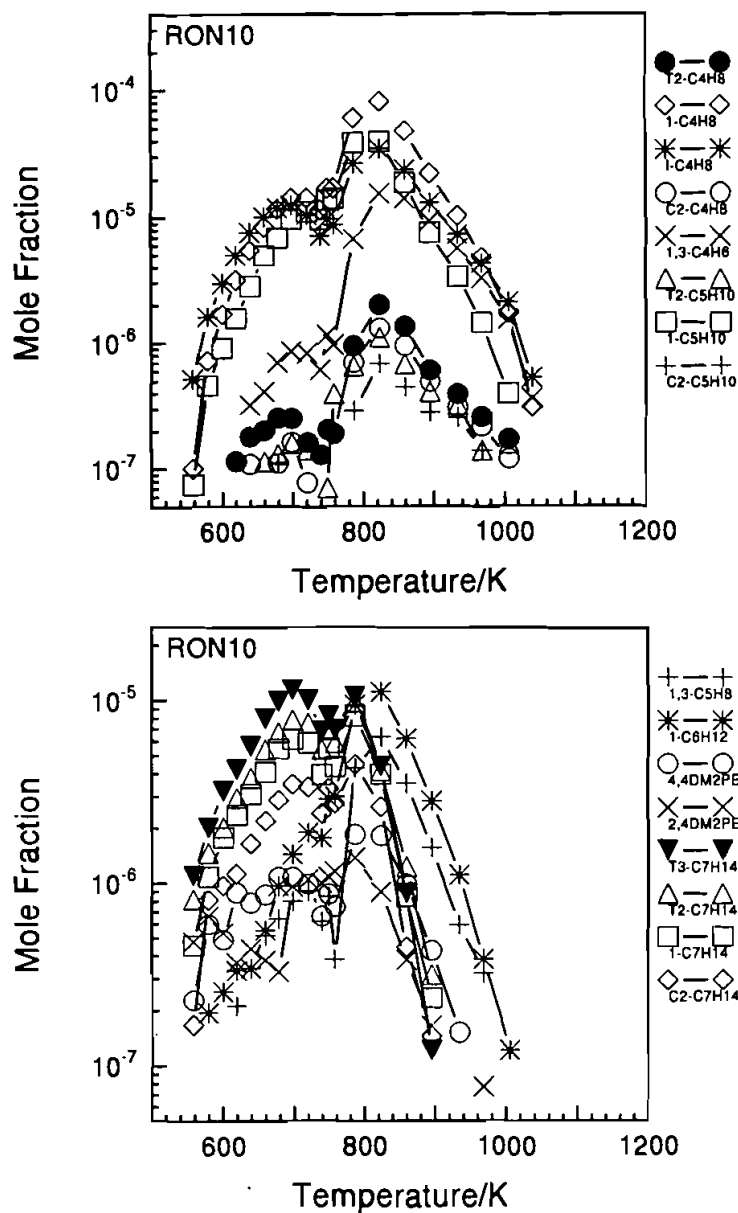


FIGURE 1 Molecular species profiles obtained from the oxidation of 0.1% of *n*-heptane-iso-octane (90:10) in a jet-stirred reactor ( $\tau = 1s$ ,  $\Phi = 1$ ,  $P = 10\text{atm}$ ). In the legends of Figures 1 to 4, AC3H4, T2C4H8, 1C4H8, C2C4H8, 1,3C4H6, T2-C5H10, 1-C5H10, C2-C5H10, 1,3-C5H8, 1-C6H12, 4,4DM2PE, T3-C7H14, T2-C7H14, 1-C7H14, C2-C7H14, C2H4O, C3H6O, PC3H4, 2M1BUTEN, 2M2BUTEN, 2M5ETHFI, 2,2,4,4-tetramethyl-tetrahydrofuran, cis 2-methyl-5-ethyl-tetrahydrofuran, 2-isopropyl, 3,3-dimethyl-oxetan, 2-methyl-3-terbutyl-oxetan, and 2-propyl-tetrahydrofuran.

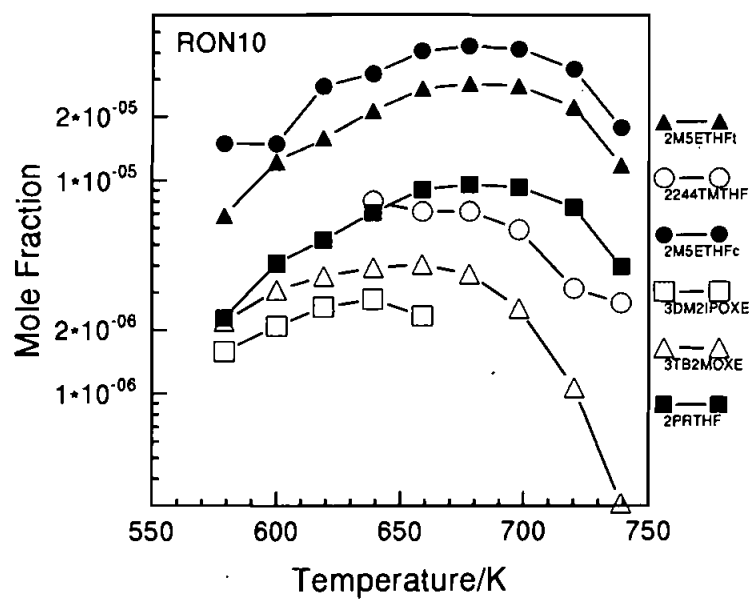
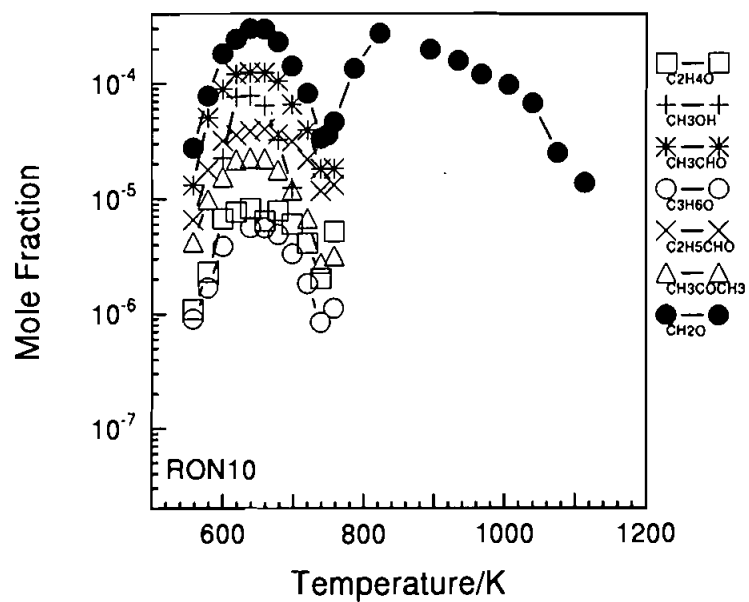


FIGURE 1 (Continued.)

RON50-O<sub>2</sub>-N<sub>2</sub>,  $\Phi=1.0$ , 10atm,  $\tau=1$ s

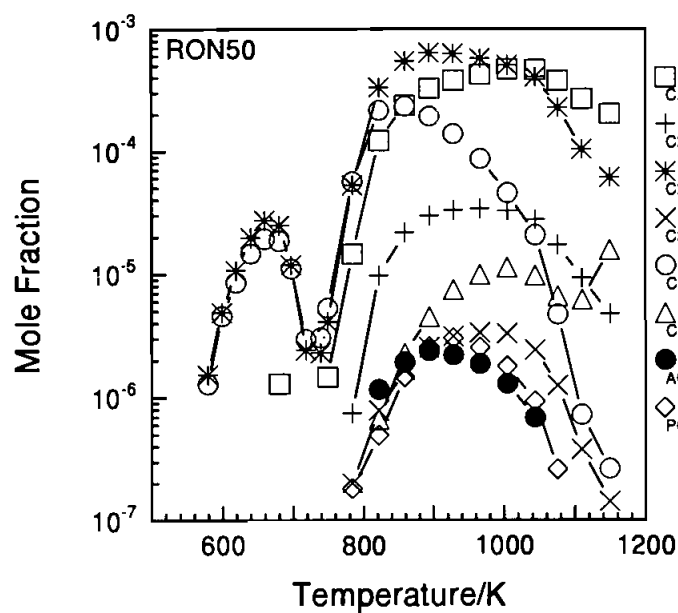
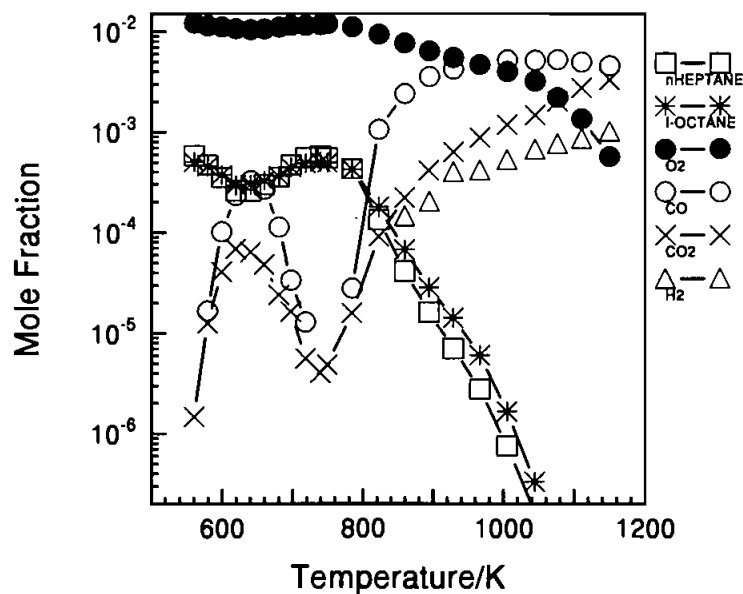


FIGURE 2 Molecular species profiles obtained from the oxidation of 0.1% of *n*-heptane-iso-octane (50:50) in a jet-stirred reactor ( $\tau = 1$  s,  $\Phi = 1$ ,  $P = 10$  atm).



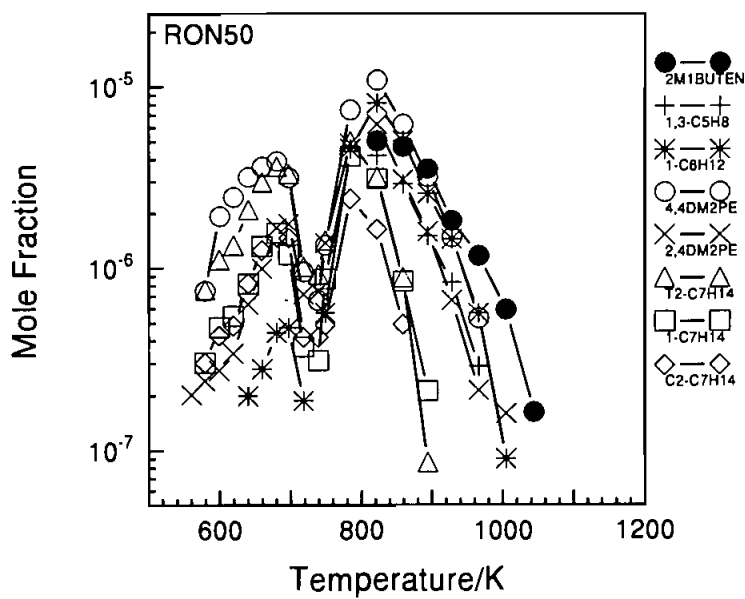
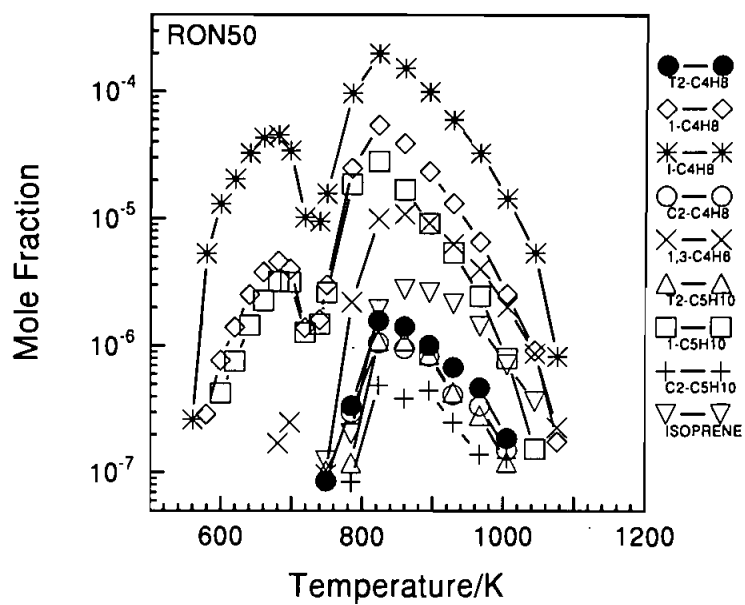


FIGURE 2 (Continued.)

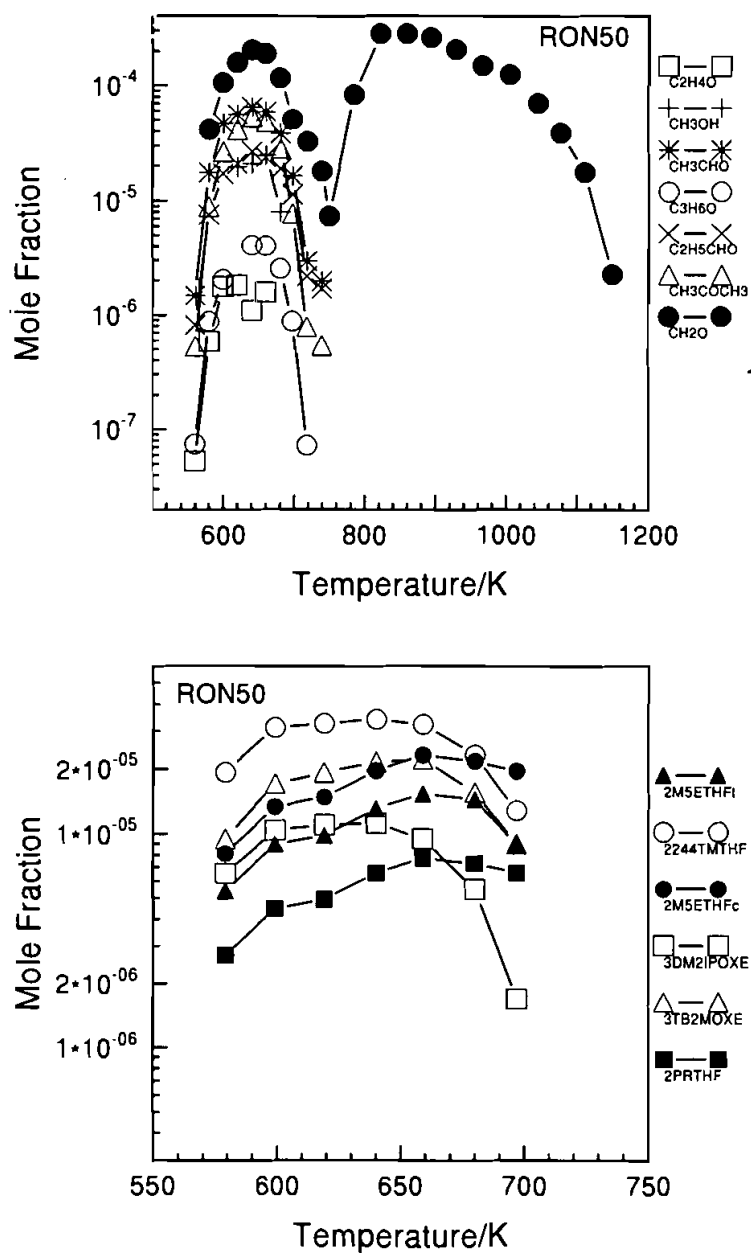


FIGURE 2 (Continued)

converted to products. At very high RON (RON = 90), a much lower reactivity is observed (see Fig. 4) but still higher than for pure iso-octane oxidation in the same conditions (Dagaut *et al.*, 1994a). This low temperature reaction corresponds to the so-called cool-flame region. From 640 to 750 K, a negative temperature coefficient is

RON70-O<sub>2</sub>-N<sub>2</sub>,  $\Phi=1.0$ , 10atm,  $\tau=1s$

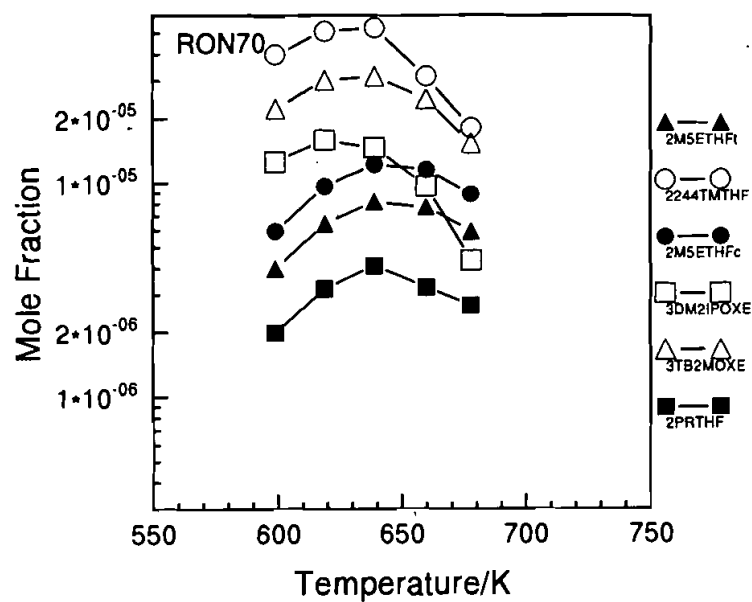
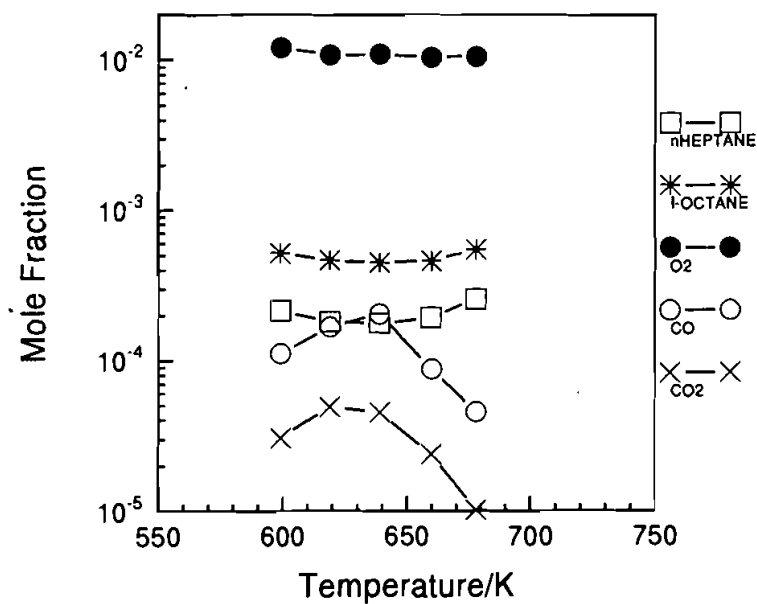


FIGURE 3 Molecular species profiles obtained from the oxidation of 0.1% of *n*-heptane-iso-octane (30:70) in a jet-stirred reactor ( $\tau = 1s$ ,  $\Phi = 1$ ,  $P = 10atm$ ).

RON90-O<sub>2</sub>-N<sub>2</sub>,  $\Phi=1.0$ , 10atm,  $\tau=1s$

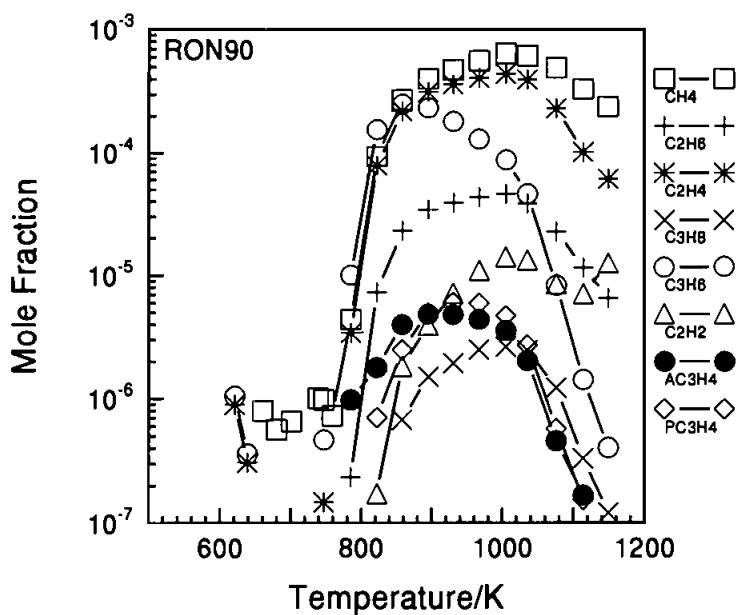
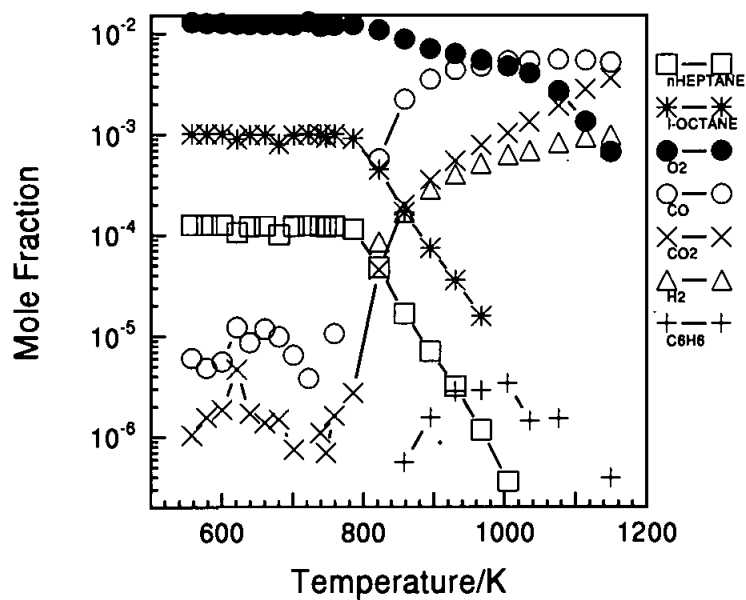


FIGURE 4 Molecular species profiles obtained from the oxidation of 0.1% of *n*-heptane-iso-octane(10:90) in a jet-stirred reactor ( $\tau = 1s$ ,  $\Phi = 1$ ,  $P = 10atm$ ).

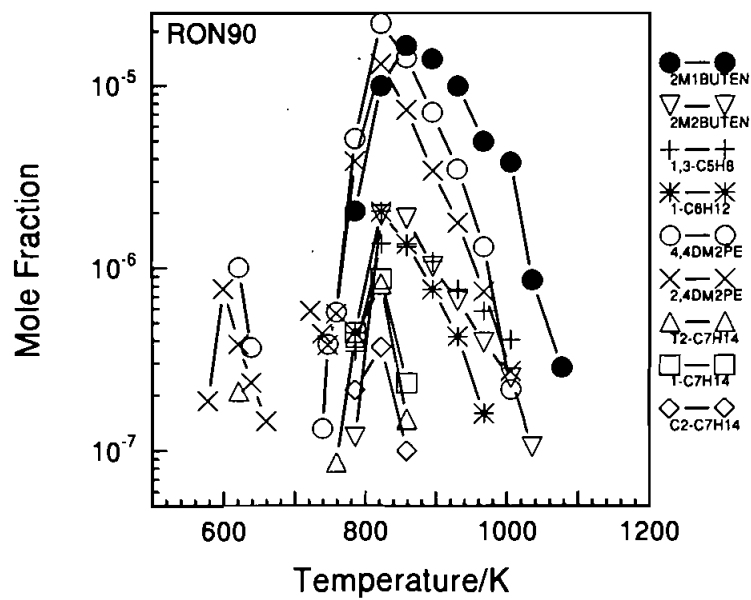
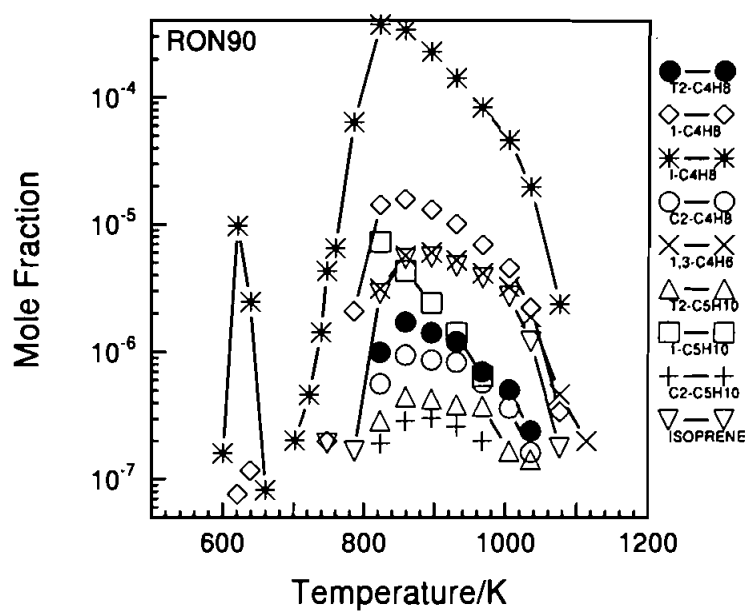


FIGURE 4 (Continued.)

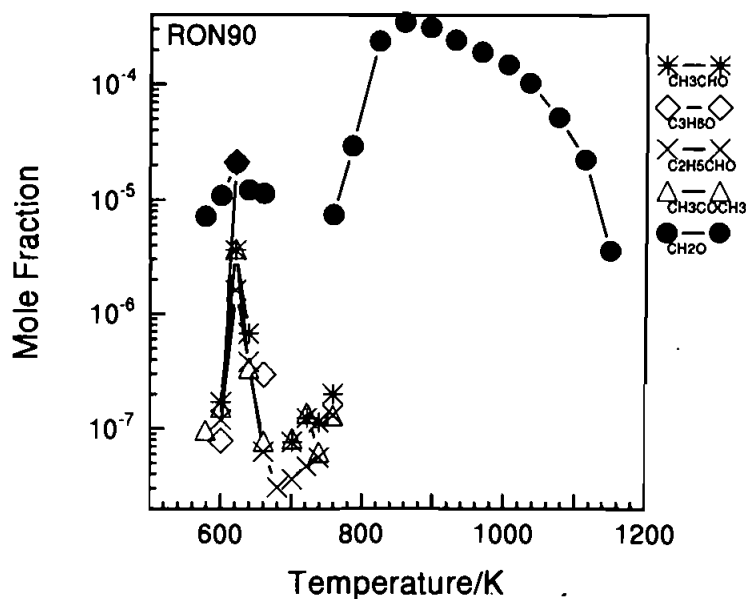


FIGURE 4 (Continued.)

observed. Above 750 K, the high temperature oxidation of *n*-heptane and iso-octane starts with the rapid production of CO, CO<sub>2</sub>, CH<sub>2</sub>O and saturated and unsaturated hydrocarbons. The reaction is followed until complete initial fuel consumption. The importance of the intermediates varies as the ratio *n*-heptane/iso-octane is varied. Ethylene is the major intermediate hydrocarbon in low RON experiments. In high RON experiments, iso-butene, methane and ethylene are the major intermediate hydrocarbons. Formaldehyde is the major oxygenated intermediate after carbon monoxide in all the conditions from cool flame to high temperature oxidation. In the low temperature range, several cyclic ethers are formed, the importance of which varies as a function of RON. In low RON experiments, the cyclic ether formed from *n*-heptane dominate (cis and trans 2-methyl-5-ethyl-tetrahydrofuran, 2-propyl-tetrahydrofuran) while in high RON experiments, those of iso-octane are the most important (2,2,4,4-tetramethyl-tetrahydrofuran, 2-terbutyl-3-methyl-oxetan and 2-isopropyl-3,3-dimethyl-oxetan).

## DISCUSSION

### *Iso-Octane oxidation enhanced by n-heptane*

From the present study, it is very clear that *n*-heptane has a strong activating effect upon the oxidation of iso-octane in the low temperature regime, where an important portion of iso-octane is converted into intermediate species, as can be seen from Figure 1–3 in contrast with what is observed for pure iso-octane oxidation in the same conditions (Dagaut *et al.*, 1994a). Among iso-octane specific intermediates, we found

isobutylene, 2,4-dimethyl-2-pentene, 4,4-dimethyl-2-pentene, and cyclic ethers. It is particularly interesting to note that in a previous work on pure iso-octane oxidation, almost no reactivity was observed, in the same conditions of the present experiments. This demonstrates that iso-octane oxidation is triggered by *n*-heptane products. *N*-heptane reacts first, producing radicals which subsequently reacts with iso-octane. Then, iso-octane oxidation is 'initiated' by a propagation reaction:



In the high temperature regime, the present data also show an activating effect of *n*-heptane, in agreement with Brezinsky and Dryer (1987). An analogy can be made between the observed activating effect of *n*-heptane on iso-octane oxidation and the increased reactivity of natural gas compared to that of methane (Tan *et al.*, 1994c). A mechanism based on detailed kinetic modeling was proposed to explain the high reactivity of natural gas compared to that of methane showing that in that case, H-atoms are rapidly produced by higher hydrocarbons fragments initiating methane consumption. A similar mechanism is expected to operate here.

It is also interesting to compare directly the reactivity of *n*-heptane and iso-octane in the different mixtures studied here. As expected, even if iso-octane oxidation is boosted by *n*-heptane products, iso-octane is still less reactive than *n*-heptane, due essentially to the lower reactivity of the predominant methyl groups in iso-octane. This is depicted in Figure 5 where iso-octane mole fractions are plotted as a function of *n*-heptane mole

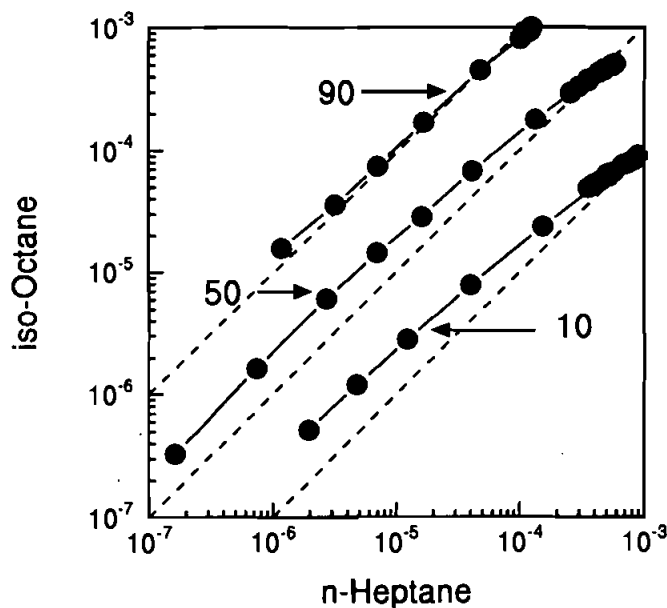


FIGURE 5 Iso-octane versus *n*-heptane oxidation in JSR at  $\tau = 1s$ ,  $\phi = 1$ , and 10atm.

fraction for three mixtures of RON 10, 50, and 90. From this figure, one can see that iso-octane mole fractions lie above the dotted line corresponding to a same reactivity for both hydrocarbons.

#### Chemical Correlation with RON

In previous publications, Brezinsky and Dryer (1987) and Wilk *et al.* (1989) proposed correlations between RON and experimental combustion parameters such as CO or CO<sub>2</sub> mole fractions. The data obtained in the present study and in recent work (Dagaut *et al.*, 1994a,b) were used to test such correlations. Figure 6 presents the evolution of CO and CO<sub>2</sub> maximum mole fractions, in the low temperature oxidation region, as a function of RON. As can be seen from this figure, a good correlation is obtained from a RON of -41 to 70. Above, another correlation is obtained up to a RON of 100. These results are in fair agreement with Wilk *et al.* (1989) findings, although their correlation was limited to RON < 20. In the high temperature regime, due to a broader CO maximum of concentration, it was difficult to draw a correlation between CO concentration and RON. Other products can be used for this purpose. Ethylene, a major ubiquitous intermediate was selected. Figure 7 presents the low and high temperature correlations between ethylene maximum mole fraction and RON from -41 to 100. As can be seen from this figure, a much stronger dependence of ethylene mole fraction with RON is observed at low temperature. This phenomenon is also observed for CO. This result could well support the idea that the knock tendencies of fuels is mainly tight to

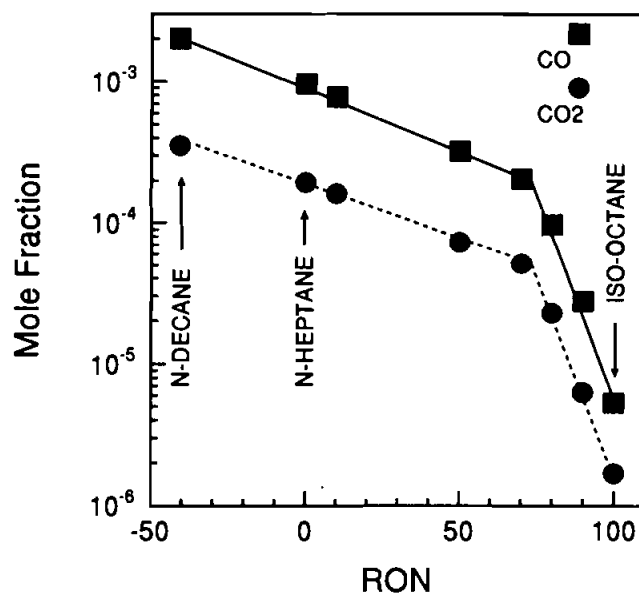


FIGURE 6 Carbon monoxide and carbon dioxide maximum mole fraction at low temperature, as a function of RON.



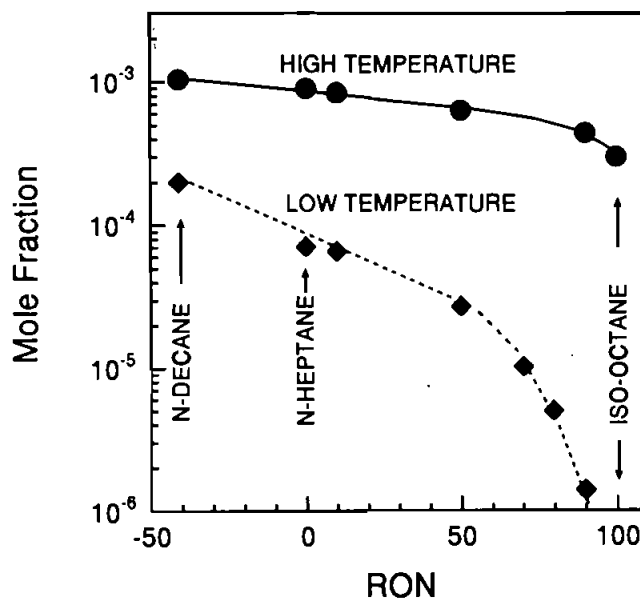


FIGURE 7 Ethylene maximum mole fraction at low and high temperature, as a function of RON.

the low temperature oxidation of the fuel, involving addition of  $O_2$  to alkyl radicals and the further reactions of peroxy radicals.

Engine data obtained by Rifkin *et al.* (1952) Filipe *et al.* (1992), and Leppard (1992) and rapid compression machine measurements for the combustion of *n*-heptane and iso-octane and mixtures of these fuels are interesting to compare to the presents results. Figure 8 present the evolution of several parameters as a function of RON in these conditions. From this plot, it is clear that a transition occurs at about  $RON = 70$ . For low RON mixtures, the different combustion parameters plotted on Figure 8 show a mild evolution while above  $RON \approx 70$ , a much stronger evolution is observed: ignition delay times and minimal ignition compression ratio increase strongly, pre-combustion heat release and CO concentration decrease dramatically. This change has received not firm explanation yet. It could be explained by the fact that the addition of *n*-heptane, a relatively very reactive fuel, to iso-octane, a relatively unreactive fuel, at low concentration level has a strong effect on iso-octane ignition but cannot make any mixture more reactive than neat *n*-heptane. Another potential additional effect can come from iso-octane which produces radical sinks able to slow down the mixture ignition. When a threshold amount of these radical sinks is reached, the reactivity of the mixture would decrease sharply. Detailed kinetic modeling of these experiments are expected to be helpful identifying the mechanism responsible of this phenomenon. Unfortunately available mechanisms can only represent ignition delays (Chevalier *et al.*, 1992). More work is needed in this area to properly represent experimental concentration profiles and assess the mechanisms responsible of the present observations.

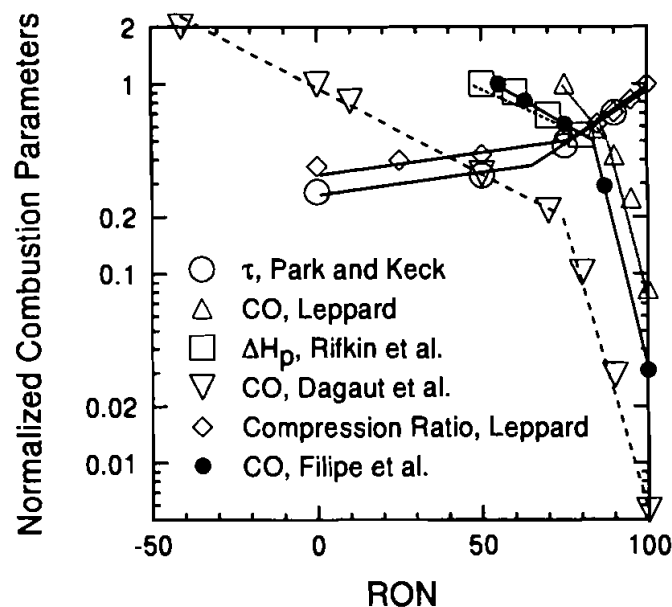
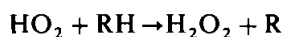
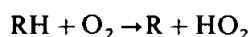


FIGURE 8 Evolution of combustion parameters as a function of RON for *n*-heptane and iso-octane and their mixtures. For simplicity, normalized values are used.

#### Low Temperature oxidation products

In the present study, particular attention was directed towards the identification and analyses of cyclic ethers formed in the low temperature oxidation region. Table I reports the relative importance of these species formed from iso-octane or *n*-heptane.

It is now interesting to relate the relative amounts of ethers to the chemical kinetic mechanism involved. At low temperature, the oxidation of the fuel is initiated by its reaction with  $O_2$  producing an alkyl radical and  $HO_2$  which in turn reacts with the fuel.



The initiation reaction ( $RH + O_2$ ) is quite slow. Hence, the reactions of the fuel with radicals,



represent the main alkyl radical production route in the system.

*N*-heptane can produce four different heptyl radicals: 1-heptyl ( $R^1$ ), 2-heptyl ( $R^2$ ), 3-heptyl ( $R^3$ ), and 4-heptyl ( $R^4$ ). Iso-octane can produce four different radicals:

TABLE I

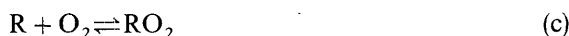
Relative amount of cyclic ethers formed from the low temperature oxidation of *n*-heptane and iso-octane

Cyclic ether	Relative amount		
	(a)	(b)	(c)
cis 2-methyl-5-ethyl-tetrahydrofuran	1	1	1
trans 2-methyl-5-ethyl-tetrahydrofuran	0.66	0.59	0.73
trans 2-methyl-4-propyl-oxetan	0.16	0.15	0.20
cis 2-methyl-4-propyl-oxetan	0.16	0.41	0.55
2-ethyl-3-propyl-oxiran	0.04	0.07	0.12
cis 2-methyl-3-butyl-oxiran	0.01	0.11	0.06
trans 2-methyl-3-butyl-oxiran	0.04		
2-propyl-tetrahydrofuran	0.33	0.21	0.49
2,4-diethyl-oxetan	0.09		
2-ethyl-tetrahydropyran	0.03		
	(a)	(d)	
2,2,4,4-tetramethyl-tetrahydrofuran	1	1	
2-isopropyl-3,3-dimethyl-oxetan	0.6	0.5	
2-terbutyl-3-methyl-oxetan	0.3		

(a), This work; (b), Luck *et al.* (1973): Cool flame in static system, O<sub>2</sub>: *n*-heptane, 1:1; (c) Luck *et al.* (1973): Cool flame in flow system, O<sub>2</sub>: *n*-heptane, 4:1; (d) Leppard (1992) CFR engine iso-octane-air at equivalence ratio of 1.

2,2,4-trimethyl-1-pentyl (R<sup>1</sup>), 2,2,4-trimethyl-3-pentyl(R<sup>2</sup>), 2,2,4-trimethyl-4-pentyl (R<sup>3</sup>), and 2,4,4-trimethyl-1-pentyl (R<sup>4</sup>).

The alkyl radicals can (a) decompose by C—C bond scission to produce an olefin and an alkyl radical, (b) isomerize to another alkyl radical, (c) react with O<sub>2</sub> to produce a peroxy radical,



(d) react with O<sub>2</sub> through H-abstraction,



The rate constant of channel (c) depends on the structure of R. For *n*-heptane, a value of about  $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is expected at 500 K. For channel (d), a rate constant of  $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is expected at 500 K. R<sup>1</sup> reacts through (d) to produce 1-heptene, the reaction of R<sup>2</sup> yields 1-heptene and 2-heptene, R<sup>3</sup> produces 2-heptene and 3-heptene, and R<sup>4</sup> produces 3-heptene. For branched alkyl radicals, the rate constant is significantly smaller and a value of about  $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is expected at 500 K for iso-octane. For channel (d), a rate constant of  $\geq 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is expected at 500 K. R<sup>1</sup> cannot react through (d), R<sup>2</sup> and R<sup>3</sup> produce 2,4,4-trimethyl-2-pentene and R<sup>4</sup> produces 2,4,4-trimethyl-1-pentene.

The peroxy radicals can react with the fuel to produce the corresponding alkylhydroperoxy radical,



It can react with another peroxy radical to mainly produce two alkoxy radicals and O<sub>2</sub> at combustion temperatures, according to recent experimental kinetic studies

(Wallington *et al.*, 1992),



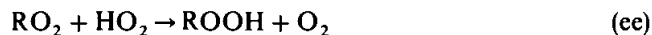
It can also decompose back to  $\text{R} + \text{O}_2$  at temperatures above about 700–800 K,



or isomerize to an alkylhydroperoxy radical QOOH through internal H-atom abstraction.



Alkyl peroxy radicals reaction with  $\text{HO}_2$  also leads to the formation of ROOH and can compete with route (aa):



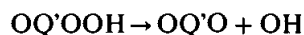
Subsequently, the alkylhydroperoxy radicals can (aaa) eliminate OH and produce a cyclic ether by concerted ring closure,



(bbb) decompose to OH, an olefin and an aldehyde through a  $\beta$ -scission (this path is more energetic, requiring a C—C bond breaking, and (ccc) react with  $\text{O}_2$ :



Finally, this last species reacting through internal H-atom abstraction and OH elimination followed by a second OH elimination becomes a branching agent.



#### *Cyclic ethers formed from the low temperature oxidation of N-heptane*

$\text{R}^1\text{O}_2$  isomerizes and can yield the corresponding ethers: 2-pentyl-oxiran (1,4s), 2-butyl-oxetan (1,5s), 2-propyl-tetrahydrofuran (1,6s), 2-ethyl-tetrahydropyran (1,7s), 2-methyl-oxepan (1,8s), oxocane (1,9p).  $\text{R}^2\text{O}_2$  isomerizes and can produce the corresponding ethers: 2-methyl-3-butyl-oxiran (1,4s), 2-pentyl-oxiran (1,4p), 2-methyl-4-propyl-oxetan (1,5s), 2-methyl-5-ethyl-tetrahydrofuran (1,6s), 2,6-dimethyl-tetrahydropyran (1,7p), 2-methyl-oxepan (1,8s).  $\text{R}^3\text{O}_2$  isomerizes and can form the corresponding ethers: 2-methyl-3-butyl-oxiran (1,4s), 2-butyl-oxetan (1,5p), 2-ethyl-3-propyl-oxiran (1,4s), 2,4-diethyl-oxetan (1,5s), 2-methyl-5-ethyl-tetrahydrofuran (1,6s), 2-ethyl-tetrahydropyran.  $\text{R}^4\text{O}_2$  isomerizes and can yield the corresponding ethers: 2-ethyl-3-propyl-oxiran (1,4s), 2-methyl-4-propyl-oxetan (1,5s), 2-propyl-tetrahydrofuran (1,6p). Based on cyclization barriers (Pollard, 1977) and available abstraction sites, the (aaa) channel is expected to mainly produce 2-methyl-5-ethyl-tetrahydrofuran. The present results as well as those of Luck *et al.* (1973) confirm this mechanism. The initial alkyl radicals involved in the formation of 2-methyl-5-ethyl-tetrahydrofuran are 2-heptyl ( $\text{R}^2$ ) and 3-heptyl ( $\text{R}^3$ ) resulting from a secondary H-abstraction from 4 equivalent sites. The (aaa) type reactions involve a secondary H-atom abstraction (two sites) in both cases.

The next most important cyclic ether is 2-propyl-tetrahydrofuran. The initial most expected alkyl radical involved is 4-heptyl ( $R^4$ ) resulting from a secondary H-abstraction from 4 equivalent sites. The (aaa) type reaction involves a secondary H-atom abstraction (two sites).

*Cyclic ethers formed from the low temperature oxidation of iso-octane*

$R^1O_2$  isomerizes to form the corresponding cyclic ethers: 3-methyl-3-isobutyl-oxetan (1,5p), 2-isopropyl-3,3-dimethyl-oxetan (1,5s), 2,2,4,4-tetramethyl-tetrahydrofuran (1,6t), 3,3,5-trimethyl-tetrahydropyran (1,7p).  $R^2O_2$  isomerizes and can form the corresponding ethers: 2-isopropyl-3,3-dimethyl-oxetan (1,5p), 2,2-dimethyl-3-tert-butyl-oxiran (1,4t), 3-methyl-2-tert-butyl-oxetan (1,5p).  $R^3O_2$  isomerizes and can form the corresponding ethers: 2-methyl-2-neopentyl-oxiran (1,4p), 2,2-dimethyl-3-tert-butyloxiran (1,4s), 2,2,4,4-tetramethyl-tetrahydrofuran (1,6p).  $R^4O_2$  isomerizes and can form the corresponding ethers: 3,3,5-trimethyl-tetrahydropyran (1,7p), 2-methyl-2-neopentyl-oxiran (1,4t), 3-neopentyl-oxetan (1,5p), 3-methyl-2-tert-butyl-oxetan (1,5s).

Considering the available abstraction sites and estimated cyclization barriers (Pollard, 1977), the (aaa) channel is expected to mainly produce 2,2,4,4-tetramethyl-tetrahydrofuran. This was the major cyclic ether resulting from iso-octane oxidation detected in the present work. The initial alkyl radicals involved are 2,2,4-trimethyl-1-pentyl ( $R^1$ ) and 2,2,4-trimethyl-4-pentyl ( $R^3$ ).  $R^1$  results from a primary H-abstraction from 9 equivalent sites while  $R^3$  results from the H-abstraction from a unique site. The (aaa) type reactions involve a tertiary H-atom abstraction (single site) in the case of  $R^1$  and a primary H-atom abstraction (9 equivalent sites) in the case of  $R^4$ .

The next most important cyclic ether resulting from iso-octane oxidation is 2-isopropyl-3,3-dimethyl-oxetan followed by 2-methyl-3-terbutyl-oxetan. 2,2-dimethyl-3-isopropyl-oxetan is formed from 2,2,4-trimethyl-1-pentyl ( $R^1$ ) resulting from a primary H-atom abstraction (9 equivalent sites). The corresponding  $R^1O_2$  is subsequently formed. Follows a 1,5, cyclization and secondary H-atom abstraction (2 equivalent sites). An other channel forms this ether: it involves  $R^2$  resulting from secondary H-atom abstraction (2 equivalent sites) which forms  $R^2O_2$  by reaction with  $O_2$ . Subsequent 1,5 cyclization and primary H-atom abstraction (9 equivalent sites) yield 2-isopropyl-3,3-dimethyl-oxetan.

2-terbutyl-3-methyl-oxetan is formed from 2,2,4-trimethyl-1-pentyl ( $R^4$ ) resulting from a primary H-abstraction from 6 equivalent sites. The following (aaa) type reaction involves a secondary H-atom abstraction (2 equivalent sites). Another channel forms this ether: it involves  $R^2O_2$  reacting through 1,5 cyclization and primary H-atom abstraction (6 equivalent sites) yielding 2-terbutyl-3-methyl-oxetan.

*Comparison with engine results*

Cyclic ethers have been measured for the combustion of *n*-heptane and iso-octane (neat or mixed) in research engines. Comparison with Luck *et al.* (1973) results for *n*-heptane combustion shows a good agreement with the present data (Table I). It is also

interesting to note that engine data obtained by Luck *et al.* (1973) for *n*-heptane combustion and Bradow and Alperstein (1967) and Leppard (1992) for iso-octane combustion, are in reasonable agreement with the present results.

## CONCLUSION

The oxidation of mixtures of *n*-heptane and iso-octane has been investigated in well-defined conditions at 10 atm in a wide temperature range covering the cool flame region, the NTC regime and the high temperature oxidation domain, in contrast with previous studies restricted to either low or high temperature oxidation range and to atmospheric pressure. The present results clearly show an important reactivity of the *n*-heptane-iso-octane mixtures in the low temperature region (below 750 K), in contrast with the results obtained in the same conditions for pure iso-octane oxidation. This reactivity increases non linearly with the amount of *n*-heptane in the mixture. The main low temperature products of *n*-heptane and iso-octane oxidation at low temperature are cyclic ethers. These compounds have been identified and concentration profiles have been measured. They are related to a low-temperature reaction mechanism.

The present results are compared to previous data obtained in research engine and rapid compression machine through a tentative chemical correlation with RON. It shows that CO, CO<sub>2</sub> and ethylene evolution in the cool flame regime as a function of RON correlates well with ignition delays and the lowest compression ratio at which autoignition occurs.

The present results will be particularly useful for testing literature reaction mechanisms in a pressure range for which no such data were available. The comparison, through kinetic modeling, of the present results and of those obtained for the two reference fuels oxidation in the same conditions (Dagaut *et al.*, 1994a) will be very helpful assessing the pro-knock processes.

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## REFERENCES

- Bradow, R. L. and Alperstein, M. (1967). Analytical investigations of iso-octane and diisobutylene slow combustion in an Otto-cycle engine, *Comb. Flame*, **11**, 26.
- Brezinsky, K. and Dryer, F. L. (1987). Molecular structure and component blending effects on knock related chemistry, *SAE* 872109.
- Cathonnet, M., Boettner, J.-C. and James, H. (1981). Experimental study and numerical modeling of high temperature oxidation of propane and *n*-butane, *18th Symposium (International) on Combustion*, The Combustion Institute, 903.
- Chakir, A., Bellimam, M., Boettner, J.-C. and Cathonnet, M. (1991). Kinetic study of *n*-pentane oxidation, *Combust. Sci. and Tech.*, **77**, 239.
- Chevalier, C., Pitz, W. J., Warnatz, J., Westbrook, C. K. and Melenk, H. (1992). Hydrocarbon ignition: Automatic generation of reaction mechanisms and applications to modeling of engine knock, *24th Symposium (International) on Combustion*, The Combustion Institute, 93.
- Ciezki, H. K. and Adomeit, G. (1993). Shock-tube investigation of self-ignition of *n*-heptane-air mixtures under engine relevant conditions, *Comb. Flame*, **93**, 421.

- Dagaut, P., Cathonnet, M., Rouan, J.-P., Foulatier, R., Quilgars, A., Boettner, J.-C., Gaillard, F. and James, H. (1986). A jet-stirred reactor for kinetic studies of homogeneous gas-phase reactions at pressures up to ten atmospheres ( $\approx 1$  MPa), *J. Phys. E: Sci. Instrum.*, **19**, 207.
- Dagaut, P., Reuillon, M. and Cathonnet, M. (1994a). High pressure oxidation of liquid fuels from low to high temperature. 1. *n*-heptane and iso-octane, *Combust. Sci. and Tech.*, **95**, 233.
- Dagaut, P., Reuillon, M. and Cathonnet, M. (1994b). High pressure oxidation of liquid fuels from low to high temperature. 3. *n*-decane, *combust. Sci. and Tech.*, in press.
- Filipe, D. J., Li, H., Miller, D. L. and Cernansky, N. P. (1992). The reactivity behavior of *n*-heptane and iso-octane blends in a motored knock research engine, *SAE Paper No.922325*.
- Griffiths, J. F., Halford-Maw, P. A. and Rose, D. J. (1993). Fundamental features of hydrocarbon autoignition in a rapid compression machine, *Comb. Flame*, **95**, 291.
- Leppard, W. R. (1992). The autoignition chemistry of primary reference fuels, olefin/paraffin binary mixtures, and non-linear octane blending, *SAE Paper No.922325*.
- Luck, C. J., Burgess, A. R., Desty, D. H., Whitehead, D. M. and Prately, G. (1973). A study of the combustion of *n*-heptane in an engine using a novel high-speed sampling technique, *14th Symposium (International) on Combustion*, The Combustion Institute, 501.
- Pollard, R. T. (1977). *Comprehensive Chemical Kinetics*, Vol. 17, *Gas-phase combustion*, (C. H. Bamford and C. F. H. Tipper, Eds.), Elsevier, N.Y.
- Park, P. and Keck, J. C. (1990). Rapid compression machine measurements of ignition delays for primary reference fuels, *SAE Paper No. 900027*.
- Rifkin, E. B., Walcutt, C., Betker, G. W., Jr. (1952). Early combustion reactions in engine operation, *SAE Quarterly Trans.*, **6**, 473.
- Tan, Y., Dagaut, P., Cathonnet, M., Boettner, J.-C., Bachman, J.-C. and Carlier, P. (1994). Natural gas and blends oxidation and ignition: experiments and modeling, *25th Symposium (International) on combustion*, The combustion Institute, in press.
- Wallington, T. J., Dagaut, P. and Kurylo, M. J. (1992). Ultraviolet absorption cross sections and reaction kinetics and mechanisms for peroxy radicals in the gas phase, *Chem. Rev.*, **92**, 667.
- Wilk, R. D., Koert, D. N. and Cernansky, N. P. (1989). Low-temperature carbon monoxide formation as a means of assessing the autoignition tendency of hydrocarbons and hydrocarbon blends, *Energy and Fuels*, **3**, 292.