CONF-9504163--3

UCRL-JC-120938
PREPRINT

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This paper was prepared for submittal to the
Western States Combustion Conference
San Antonio, TX
April 23–26, 1995

April 13, 1995

Lawrence Livermore National Laboratory

A Modelling Study of the Combustion of n-Heptane and iso-Octane in a High Pressure Turbulent Flow Reactor

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Introduction

The primary reference fuels n-heptane and iso-octane, and their mixtures, are used as a measure of the tendency of a given automotive fuel to cause knocking or pre-ignition in an internal combustion engine. Consequently, many experimental studies have been performed on these hydrocarbons in an attempt to better understand their oxidation. Shock tube studies at high temperature and pressure have been performed [1, 2, 3]. Low temperature studies, in which species concentration profiles of primary, intermediate and final products, have been carried out using jet stirred flow reactors [4, 5, 6, 7]. In addition, experiments have been performed in CFR engines [8, 9] and fundamental features of n-heptane autoignition have been observed using a rapid compression machine [10, 11]. A detailed chemical kinetic reaction mechanism is employed here to study the oxidation of both fuels. Computed results are compared with experimental data obtained in the High Pressure Turbulent Flow Reactor at Princeton University.

Experimental

Experiments, carried out in the adiabatic flow reactor, provide a well-characterized environment that is designed to minimize mixing and diffusion effects. The details of the experimental apparatus are provided elsewhere [12], and so only a brief summary is given here. Preheated nitrogen carrier gas is mixed with dilute quantities of reactants in a 10 cm diameter quartz reactor tube, and convected over a distance of 40–125 cm, variable by the movement of the injection port relative to the sampling location. In these experiments, the distance is adjusted to maintain a fixed residence time while varying the initial temperature and/or reactant composition. Both fuels were studied under stoichiometric conditions, the initial concentration of n-heptane was approximately 0.14% and that of iso-octane was 0.125%. Experiments were performed over a temperature range of 550–850 K, and at a pressure of 12.5 atm. The residence time was fixed at 1.8 seconds. Sample gases were extracted by a water-cooled stainless-steel probe, which rapidly quenches the reaction. Sample composition is determined by a Fourier-Transform Infrared spectrometer (FTIR), non-dispersive infrared detectors for CO and CO_2, and a electrochemical O_2 analyser.

Model Formulation

The present detailed reaction mechanism was constructed based on the hierarchical nature of hydrocarbon–oxygen systems and on previous work by the authors [13, 14, 15], but has required extensive refinements. One substantial addition to the mechanism is in the treatment of alkyldihydroperoxide compounds; formation and consumption reaction paths for isomeric forms of ketohydroperoxide species are newly added to the reaction mechanism, with this modification having a significant impact on the magnitude of a region of *negative temperature coefficient* (NTC). Other model improvements include the consideration of a β-decomposition path for selected alkylhydroperoxide (QOOH) species, leading to aldehyde and olefin products, in addition to existing paths leading to other product distributions. Rates of existing reaction paths have also been modified extensively to include improved thermochemical data.

This study analyses the low temperature regime and so initiation occurs *via* H-atom abstraction primarily by OH and to a lesser extent by H, HO_2, O, CH_3, CH_3O_2 and O_2. Alkyl radicals so produced, add with molecular oxygen to produce alkylperoxy radicals, RO_2. Following Benson [16], additions involving large alkyl radicals (i.e. C_7 and C_8) with O_2 were assumed to have the same bimolecular rate of 2×10^{12} cm^3/mol-sec.

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Reactions of RO_2 Species

At low temperatures, reactions of RO_2 species and the equilibrium of the $R + O_2 \rightleftharpoons RO_2$ reaction are of great importance in determining both the product species distributions and the overall rate of fuel oxidation. There are three major types of reactions of the RO_2 radicals.

1. Decomposition to $R+O_2$. This rate is calculated from the equilibrium constant for the $R+O_2 \rightleftharpoons RO_2$ reaction and from thermochemistry.

2. **Abstraction of H atoms from hydrocarbon species to produce alkylhydroperoxides (ROOH), which then decompose to RO + OH, followed by reaction of the RO radicals. This sequence of reactions is of relatively minor importance in this study.**

3. The most important step involves isomerization of the RO_2 radicals *via* internal H atom transfer. A more in-depth description of this type of reaction has been given previously [13, 14]. Rates for the isomerization of the alkylperoxy radical to alkylhydroperoxide, presented in Table 1, are calculated considering recommendations in the literature [18]. The activation energy, $\mathcal{E}_a$, was estimated using the expression,

$$\mathcal{E}_a = \text{ring strain} + E_{\text{abstraction}} + \Delta H_{\text{reaction}}$$

where $\Delta H_{reaction}$ is taken to be the enthalpy of reaction. The activation energy for abstraction, $E_{\text{abstraction}}$ depends on the type (i.e. primary, secondary, or tertiary) of H atom being abstracted and was estimated based on the recommendations of Bozzelli and Pitz [18] using the expression,

$$E_{\text{abstraction}} = 12 - \Delta H_{\text{exothermic}} \times 0.3$$

It was found that, in order to predict correctly relative concentrations of heterocyclic products reported in the literature [7, 11], it was necessary to lower the ring-strain energy for the change in going from a six, (1,5p), to a seven, (1,6p), T.S. ring by 2.8 kcal mol^{-1} and not 4.8 kcal mol^{-1} as recommended by Baldwin et al. [19]. We arrive at a lower activation energy for the seven membered ring as do Baldwin et al. and not a higher value as is assumed for a hydrocarbon species, because there is an oxygen atom in the T.S. ring. In keeping with alkyl radical isomerization analogy we do increase the ring strain energy in going from a (1,6) to a (1.7) T.S. ring choosing a value of 2.8 kcal mol^{-1}. The ring strain is taken as follows:

Number of ring members	Ring strain kcal mol^{-1}
5	8.6
6	2.8
7	0.0
8	2.8

Thus for example, the activation energy for the five membered, primary (1,4p) T.S. ring was calculated to be 29.2 kcal mol^{-1} and is similar to a value given in a paper by Wagner et al. [17] in which an activation energy of 30.0 kcal mol^{-1} is recommended for the internal H atom abstraction of the ethylperoxy radical leading to the formation of ethylhydroperoxide. We chose a value of 29.7 kcal mol^{-1} a number which lies between both of the above values.

The pre-exponential $\mathcal{A}$-factor is assumed to change with increasing ring size due to the loss of internal rotors. This consideration is the main contributor to the decrease in entropy of the molecule [18] and is also dependent on the number of equivalent H atoms being abstracted. The $\mathcal{A}$-factor for the (1,4p) T.S. ring was chosen to be 8.9×10^{12}, a value approximately the same as that recommended by Baldwin et al. [19]. This value is reduced for the (1,5p) T.S. ring by a multiple of 12, assuming a change in entropy, ΔS, of ≈ 5.0 cal mol^{-1} K^{-1}, and in increments of 12 for all singular changes in T.S. ring size thereafter.

Reactions of QOOH Species.

In addition to the 4 RO_2 species formed by O_2 reacting with the heptyl radicals, there are 18 QOOH isomers produced by internal H atom abstraction of these RO_2 radicals, considering intermediate ring structures as large as 8 members. For i-C_8H_{18}, there are 4 RO_2 radicals and 14 QOOH isomers. These QOOH species react *via* four major pathways.

1. Following Pollard [20], these species can react *via* O-O homolysis, producing OH radicals and a cyclic ether, involving a number of C atoms and the remaining O atom. We have altered the rates of these reactions from those published previously [13, 14, 15]. Taking into account loss in entropy as described earlier, we again lower the pre-exponential factor by a multiple of 12 as we tie up one extra rotor in going from a 3 to 4 and progressively larger ring heterocycles. The activation energies have also been altered in order to model correctly cyclic ether distributions measured experimentally. The six-membered ring tetrahydropyran species were assumed to have the lowest ring-strain energy, while the oxirane species were assumed to have the greatest strain energy. The rate parameters for these reactions are given in Table 1.
2. QOOH species that have a radical site alpha to the hydroperoxy group can decompose to yield a conjugate olefin and HO_2 radical. The rate constant for this reaction was considered in the reverse direction (i.e. the attack of a radical at an olefinic site) as the energy barrier for this type of reaction is better known than is the decomposition of the alkylhydroperoxide to products. Thus, following analogy rules for addition of a radical to a double bond, a rate of $1.0 \times 10^{11} \exp(-7800/RT)$ was chosen for olefin + HO_2 and that in the forward direction is calculated from thermochemistry. Wagner et al. [17] recommend the heat of formation for the transition state $C_2H_4 \cdots O_2H$ to be 5–7 kcal mol^{-1}. This reaction has proven to be quite sensitive, and is responsible for a large part of the NTC behaviour in n-heptane.
3. QOOH species that have an intermediate ring structure of 6 atoms can undergo β-scission. These type of reactions were not included in the previous papers by the authors. Similar to Pollard [20], a rate of $5.9 \times 10^{12} \exp(-21000/RT)$ was chosen.
4. In addition, QOOH can react with molecular oxygen to form peroxyalkylhydroperoxide, O_2QOOH, species. The rates are 2×10^{12} cm^3/mol-sec. as given earlier for alkyl plus O_2.

One of the main additions to the current mechanism is the treatment of the decomposition of the O_2QOOH species formed. In recognition of experimental observations by Sahetchian et al. [8], in which heptylketohydroperoxides are observed, we no longer generate radical and carbonyl products in the decomposition of O_2QOOH but have instead included an intermediate step in which the O_2QOOH isomerizes releasing OH and forming different ketohydroperoxide species (dependent on the O_2QOOH involved). The rates for this isomerization *via* an internal H atom transfer, presented in Table 1, are analogous to those for $RO_2 \rightleftharpoons QOOH$ isomerization. However, the activation energy has been reduced by 3 kcal mol^{-1} as the H atom being abstracted is bound to a C atom which is bound to a hydroperoxy group and should be more easily removed. In addition, the $\mathcal{A}$-factor has also been reduced by a factor of 0.5 considering steric hinderance due to the OOH group. These reactions also help in the modelling of two-step ignition phenomena observed in shock tubes [3], CFR engines [8, 9] and rapid compression machines [10, 11].

Finally, the decomposition of ketohydroperoxide molecules which leads to the formation of two radicals, a carbonyl radical and OH, is considered a chain branching reaction. A global rate of $1 \times 10^{16} \exp(-43000/RT)$ was chosen for each molecule even though the ketohydroperoxide species have slightly different thermodynamics. The pre-exponential factor is based on the value for the unimolecular decomposition of a molecule [21], and the activation energy is based on ($\Delta H - RT$) for the reaction. This set of reactions is especially important at low temperatures as the high activation energy ensures an induction period in which large quantities of ketohydroperoxides build up and on reaching a critical concentration, decompose leading to chain branching.

Results

This updated model was first validated using the experiments described above in addition to the results given in the presentation by Gaffuri [22] which models n-heptane only. Both the experimental results and the model predictions indicate quite clearly the totally different behaviour of the two primary reference fuels, Figure 1. Oxidation of n-heptane increases rapidly at temperatures greater than 550 K, conversion reaching a maximum at approximately 600 K, Figure 1a. (It is assumed that fuel conversion is directly proportional to the conversion of O_2). Thereafter, the system exhibits a region of NTC up to a temperature of 700 K, above which there is a rapid consumption of fuel. In contrast, iso-octane is essentially unreactive up to a temperature of about 750 K after which there is a pronounced increase in reactivity with almost complete conversion of fuel by 850 K. One remaining problem is that the model predicts the initial stages of iso-octane oxidation at temperatures approximately 50 K lower than those observed experimentally. We are currently addressing this problem.

In addition, initial modelling attempts greatly underpredicted CO_2 production observed in the n-heptane experiments but on addition of the following sequence of reactions CO_2 production was markedly increased, with current predictions for CO_2 formation given in Figure 1b.

$$\begin{aligned}
\mathrm{HCO} + \mathrm{O_2} &= \mathrm{HCO_3} \\
\mathrm{FUEL} + \mathrm{HCO_3} &= \mathrm{ALKYL\ RADICAL} + \mathrm{HCO_3H} \\
\mathrm{CH_2O} + \mathrm{HCO_3} &= \mathrm{HCO} + \mathrm{HCO_3H} \\
\mathrm{HCO_3H} &= \mathrm{HCO_2} + \mathrm{OH} \\
\mathrm{HCO_2} &= \mathrm{H} + \mathrm{CO_2}
\end{aligned}$$

Finally, Figure 1c shows a comparison of the rise in temperature *versus* initial inlet temperature of the reactor. Again, we can see that the NTC behaviour observed for n-heptane oxidation is reproduced by the model and that the contrasting behaviour of iso-octane oxidation is also reproduced.

In conclusion, we have attempted to improve the reaction mechanism published previously [13, 14], including as an additional propagation pathway, the β-decomposition of alkylhydroperoxide species. The inclusion of ketohydroperoxide species and their subsequent decomposition led to a more pronounced region of NTC for n-heptane oxidation. We have also added an additional route leading to the formation of significant quantities of CO_2. The model, using essentially the same rate constant expressions for the primary oxidation pathways can predict the NTC behaviour in the oxidation of n-heptane while at the same time it also reproduces the contrasting behaviour of iso-octane combustion.

	Rate expression per H atom		
Ring Size	Primary	Secondary	Tertiary
	Alkylperoxy radical isomerization		
5	2.97×10^{12} exp(−29700/RT)	2.97×10^{12} exp(−27900/RT)	2.59×10^{12} exp(−25400/RT)
6	2.47×10^{11} exp(−23900/RT)	2.47×10^{11} exp(−22150/RT)	2.16×10^{11} exp(−19700/RT)
7	2.06×10^{10} exp(−21100/RT)	2.06×10^{10} exp(−19350/RT)	2.06×10^{10} exp(−16400/RT)
8	1.72×10^{09} exp(−23900/RT)	1.72×10^{09} exp(−22150/RT)	1.72×10^{09} exp(−19700/RT)
	Peroxyalkylhydroperoxy radical isomerization		
5	1.49×10^{12} exp(−26700/RT)	1.49×10^{12} exp(−24900/RT)	—
6	1.24×10^{11} exp(−20900/RT)	1.24×10^{11} exp(−19150/RT)	—
7	1.04×10^{10} exp(−18100/RT)	1.04×10^{10} exp(−16350/RT)	—
8	8.64×10^{08} exp(−20900/RT)	8.64×10^{08} exp(−19150/RT)	—
Heterocycle	Rate expression		
oxirane	3.00×10^{11} exp(−22000/RT)	—	—
oxetane	2.50×10^{10} exp(−15250/RT)	—	—
furan	2.08×10^{9} exp (−6500/RT)	—	—
pyran	1.74×10^{8} exp (−1800/RT)	—	—

Table 1: Reaction rate expressions, cm^3–mol–sec–cal units

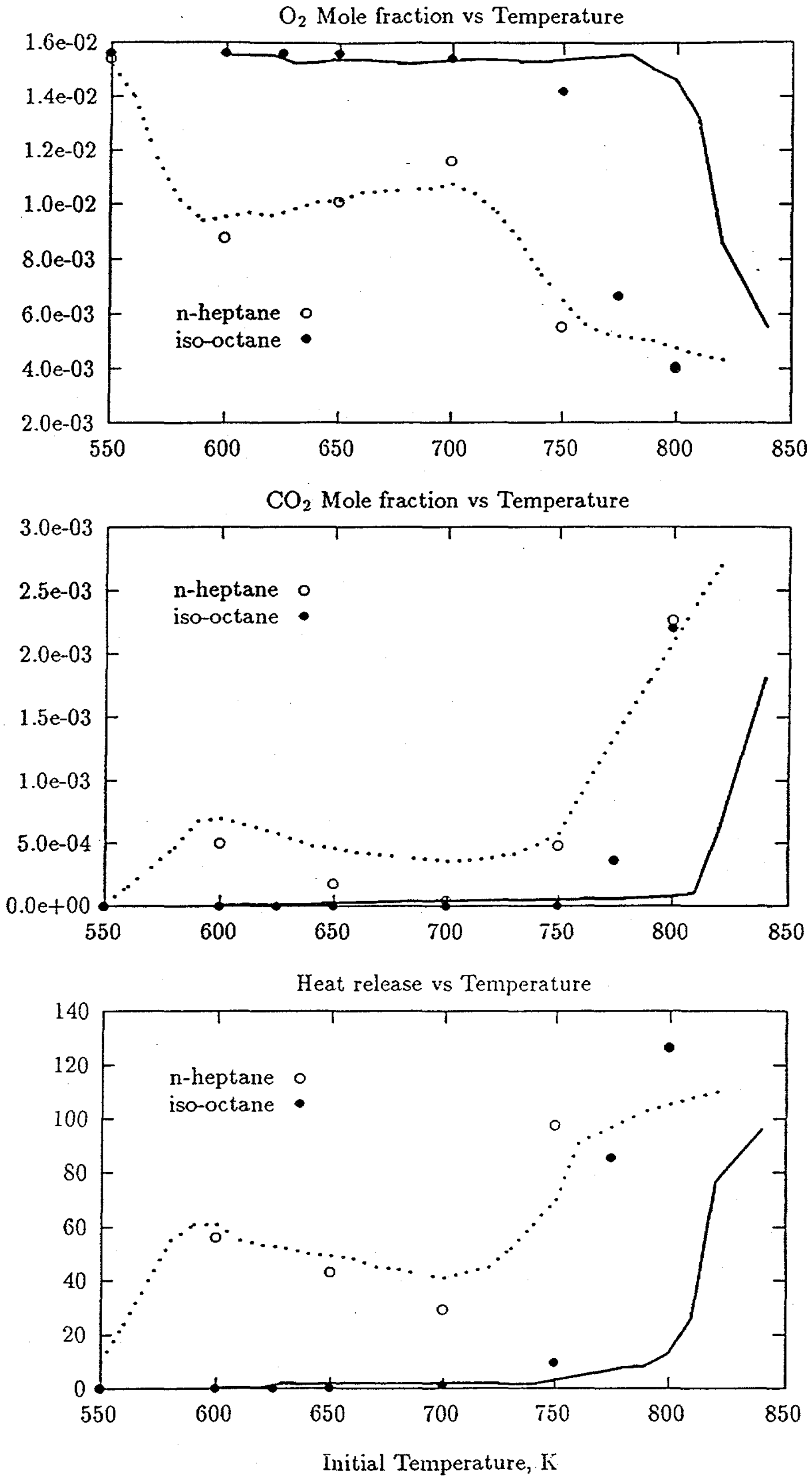

Figure 1: Experimental results (lines) vs model predictions (points) for n-heptane and iso-octane oxidation

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*This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.