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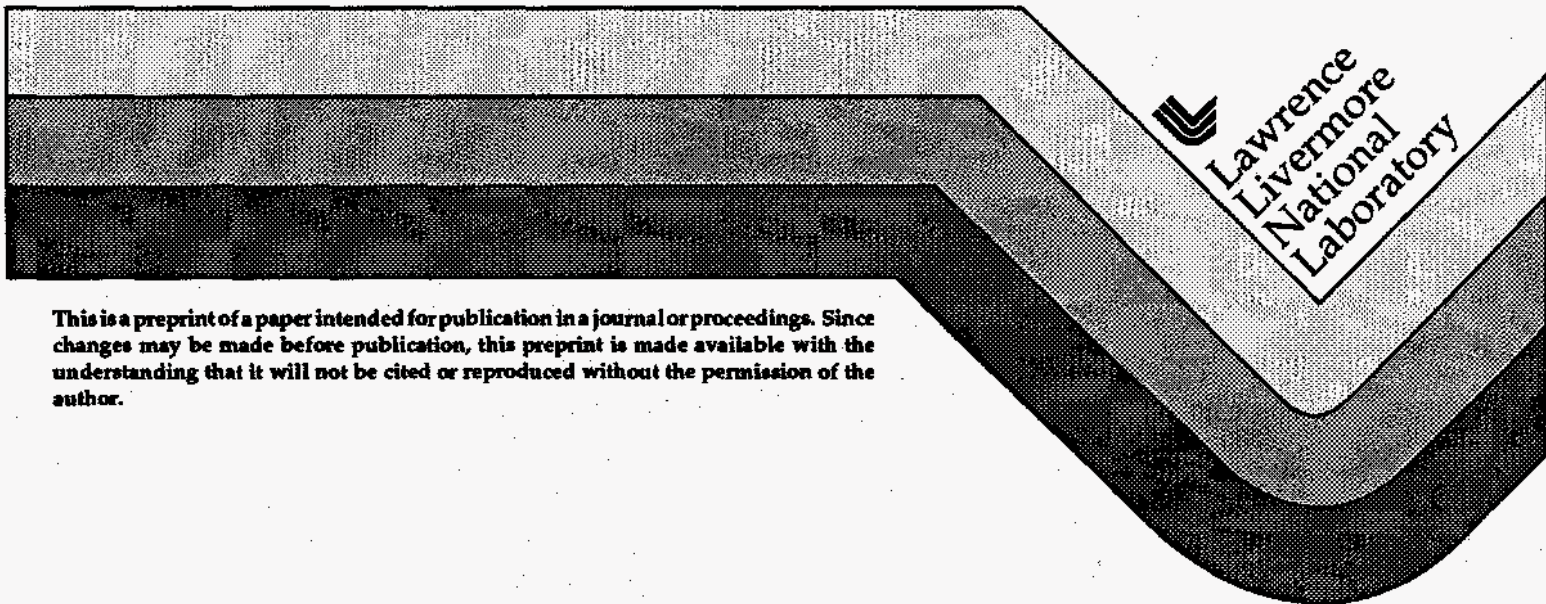
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A Detailed Kinetic Modeling Study**

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Combustion of n-Heptane in a Shock Tube and in a Stirred Reactor: A Detailed Kinetic Modeling Study

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Abstract

A detailed chemical kinetic reaction mechanism is used to study the oxidation of n-heptane under several classes of conditions. Experimental results from ignition behind reflected shock waves and in a rapid compression machine were used to develop and validate the reaction mechanism at relatively high temperatures, while data from a continuously stirred tank reactor (cstr) were used to refine the low temperature portions of the reaction mechanism. In addition to the detailed kinetic modeling, a global or lumped kinetic mechanism was used to study the same experimental results. The lumped model was able to identify key reactions and reaction paths that were most sensitive in each experimental regime and provide important guidance for the detailed modeling effort. In each set of experiments, a region of negative temperature coefficient (NTC) was observed. Variation in pressure from 5 to 40 bars were found to change the temperature range over which the NTC region occurred. Both the lumped and detailed kinetic models reproduced the measured results in each type of experiments, including the features of the NTC region, and the specific elementary reactions and reaction paths responsible for this behavior were identified and rate expressions for these reactions were determined.

Introduction

There is a continuing interest in developing a better understanding of the oxidation of large hydrocarbon fuels over wide ranges of operating conditions, particularly in order to improve the efficiency and performance of practical combustors and reduce pollutant species emissions. In addition, n-heptane is a primary reference fuel (PRF) for octane ratings in internal combustion engines, so a better understanding of its kinetics is also useful in studies of engine knock and autoignition. Recent studies of n-heptane oxidation have focussed on shock tubes [1, 2, 3], jet stirred reactors [4, 5, 6] rapid compression machines [7]-[9], engines [10]-[15], plug flow reactors [16], and jet-stirred flow reactors [17, 18]. All of these systems exhibit phenomena including self ignition, cool flame, and NTC behavior.

Mechanism Consideration

The semi-detailed kinetic scheme used was developed by Ranzi et al. [19, 20]. Both the low and the high temperature reaction submechanisms are reduced to a lumped kinetic model involving a limited number of intermediate steps. This mechanism is capable of predicting accurately the concentration of intermediate components, heat release and ignition delay times. A detailed chemical kinetic mechanism was developed previously [21]- [23] to describe n-heptane oxidation, but the applications of the mechanism to additional classes of experimental data discussed in this and an accompanying study [16], covering a wider range of experimental conditions, have led to significant improvements in the mechanism. The lumped reaction model was found to be extremely valuable in identifying portions of the detailed mechanism which were especially sensitive and which required modification and improvement.

The reaction mechanism for n-heptane was assembled based on a previous C_1 - C_6 reaction mechanism which was not modified further during this computational study. To cover the complete range of temperature and pressure typical of n-heptane oxidation it was important to include both the low and the

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high temperature mechanism. At higher temperatures, unimolecular fuel and alkyl radical species decomposition reactions are especially important, while at low temperatures H atom abstraction from the fuel molecule and addition of molecular oxygen to the alkyl radicals, followed by reactions of the alkylperoxy radicals dominate the oxidation mechanism.

The low temperature submechanism for n-heptane was similar to that used in previous studies [21, 22, 24], but several improvements were made. A β -decomposition reaction path for hydroperoxyalkyl radicals was included, leading to smaller olefins and aldehydes, explaining the selectivity for lower alkenes [4, 5, 9], and increasing the number of chain propagation pathways which compete with chain branching paths in the NTC region. In addition, formation paths of ketohydroperoxide compounds were included as the products of isomerization reactions of O_2QOOH radicals, which had a strong influence on reproducing the observed NTC behavior and two stage ignition. These compounds had also been identified during the oxidation of n-heptane in a motored CFR engine [10]. The lumped reaction model was particularly important in identifying this reaction path as one that had been omitted from previous detailed mechanism. Finally, the THERM program [25] of Ritter and Bozzelli, which uses group additivity rules developed by Benson [26], was used to evaluate thermochemical quantities for all the chemical species. In addition to improving the specific heats and heats of formation for many C_7 compounds, it was found that reverse rates of many reactions in the low temperature regime were quite important, and improved equilibrium constants for these species provided better reverse reaction rates.

The overall flux diagram for n-heptane oxidation can be shown in a particularly simple way as seen in Fig. 1. At high temperatures, the path is quite simple, with the β -scission of the alkyl radicals R proceeding rapidly to small olefin and other species, and chain branching due primarily to the reaction $H + O_2 \rightleftharpoons O + OH$. However, at low temperatures, chain branching is due primarily to the reaction path leading through the ketohydroperoxide species. As the temperature increases, the chain propagation reactions of $QOOH$ species also increase, leading to the formation of heterocyclic species, conjugate olefins, and β -decomposition products. The increasing importance of these propagation channels leads to a lower reactivity of the system which is observed as the NTC region.

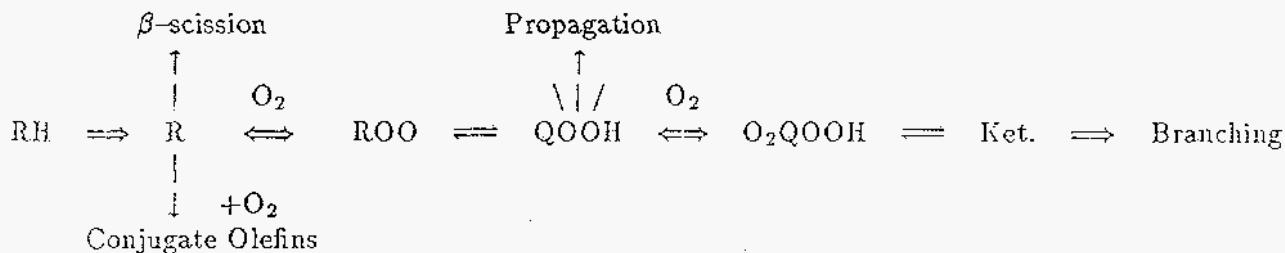


Figure 1: Lumped kinetic scheme of the primary oxidation reactions

Jet-Strirred Reactor

Recently Dagaut et al. [4, 5] reported experimental results on the oxidation of n-heptane in a jet-stirred reactor at 10 and 40 atm covering the low and the high temperature regimes (550–1150 K) with equivalence ratios from 0.3 to 1.5. These experimental results are especially valuable since the reactant concentrations as well as intermediate and final product concentrations were measured. A series of comparisons between computed and experimental results is shown in Fig. 2 for stoichiometric mixtures of 0.1% n-heptane/oxygen/nitrogen at 10 atm and a residence time of 1 second. From the model results, it is clear that below 750 K, oxidation takes place through a low temperature mechanism leading to the formation of CO , CO_2 , CH_2O , CH_3CHO , C_2H_5CHO , and major intermediates including heptenes and cyclic ethers as shown in Fig. 2. All of these species concentrations are reproduced quite well by the model. The accurate

prediction of these species levels relies heavily on the relative rates of alkylperoxy radical isomerization reactions, ultimately leading to the formation of the different heptenes and cyclic ethers. The distinct NTC region between 640 and 750 K is also reproduced well by the model. In the low temperature regime, the model shows a lower overall reactivity than the experiments, which is possibly due the lower reactivity of the intermediates in the model. In the reaction mechanism, products species distribution for the thermal decomposition reactions of the ketohydroperoxide species were postulated, since experimental evidence for these product distributions were unavailable, and additional refinements in this area of the mechanism could improve the model results at the low temperatures.

Above 750 K the oxidation takes place with a high temperature mechanism and the most important branching reaction is the decomposition of hydrogen peroxide $\text{H}_2\text{O}_2 \rightleftharpoons \text{OH} + \text{OH}$. We have used Troe parameter for the falloff expression for this reaction [27], and the model description of this system could not be accurately reproduced without including falloff corrections for this reaction rate. Variations in equivalence ratio at constant pressure were found to change the overall reactivity of this system but did not change the temperature range of the NTC region. Model calculations at higher pressure (40 atm) and residence time of 2 s showed an apparent reduction of the NTC (Fig. 3), due to the higher reactivity of the system under these conditions.

Shock tube and rapid compression machine experiments

The autoignition of n-heptane can be studied conveniently at high temperatures in shock tubes and at lower temperatures in rapid compression machines. We have used the model to examine high temperature shock tube experiments by Vermeer et al. [2] and by Coats and Williams [3], with generally very good agreement between computed and measured ignition delay times. Ciezki and Adomeit [1] carried out reflected shock tube experiments at somewhat lower temperatures and rather high pressures, observing NTC behavior at temperatures between 750 and 1000 K. Computed results are compared with data in Fig. 4, showing overall excellent agreement between computed and measured results. The magnitude of the NTC region is very closely reproduced by the reaction mechanism. Perhaps most importantly, the shift in the NTC region to higher temperatures as pressure is increased is also accurately reproduced. This shift is due to the influence of pressure on the equilibria of the addition reactions of molecular oxygen to the alkyl and hydroperoxyalkyl radicals.

The experiments of Ciezki and Adomeit could cover only small part of the low temperature region because of limitations in measuring long ignition times. Similar conditions have been investigated experimentally by Minetti et al. [9] in a rapid compression machine. These experiments are characterized by ignition time of the order of 20–40 ms. In these experiments at temperatures below about 800 K, a noticeable two-stage ignition process as shown in Fig. 5 is observed. This is particularly sensitive to the accumulation and subsequent decomposition of the ketohydroperoxide species. The variation of the temperature in both the first stage delay period and the total ignition delay time for stoichiometric mixtures is shown in Fig. 6. Both are very well reproduced by the reaction mechanism, showing how the ignition becomes essentially a single-stage ignition as the temperature exceeds 800 K, although the NTC region does not disappear until the temperature exceeds 850 K. The intricate interactions in the reaction mechanism responsible for this complex behavior are severely tested by these experiments. In rapid compression machine experiments, the question often arises as to whether or not significant reaction takes place during the compression stroke, especially when the compression time is comparative to the induction period as is the case in the Minetti et al. experiments (i.e. 60 ms compression time). This process has examined this question with the computational model and found that the amount of n-heptane consumption and other reaction occurring during the compression stroke is very minor and has a negligible influence on the measured first-stage, and overall ignition delay times. However, the model calculations suggest that the

heat losses to the combustion chamber walls may be appreciable and further attention is needed to assess the importance of this effect.

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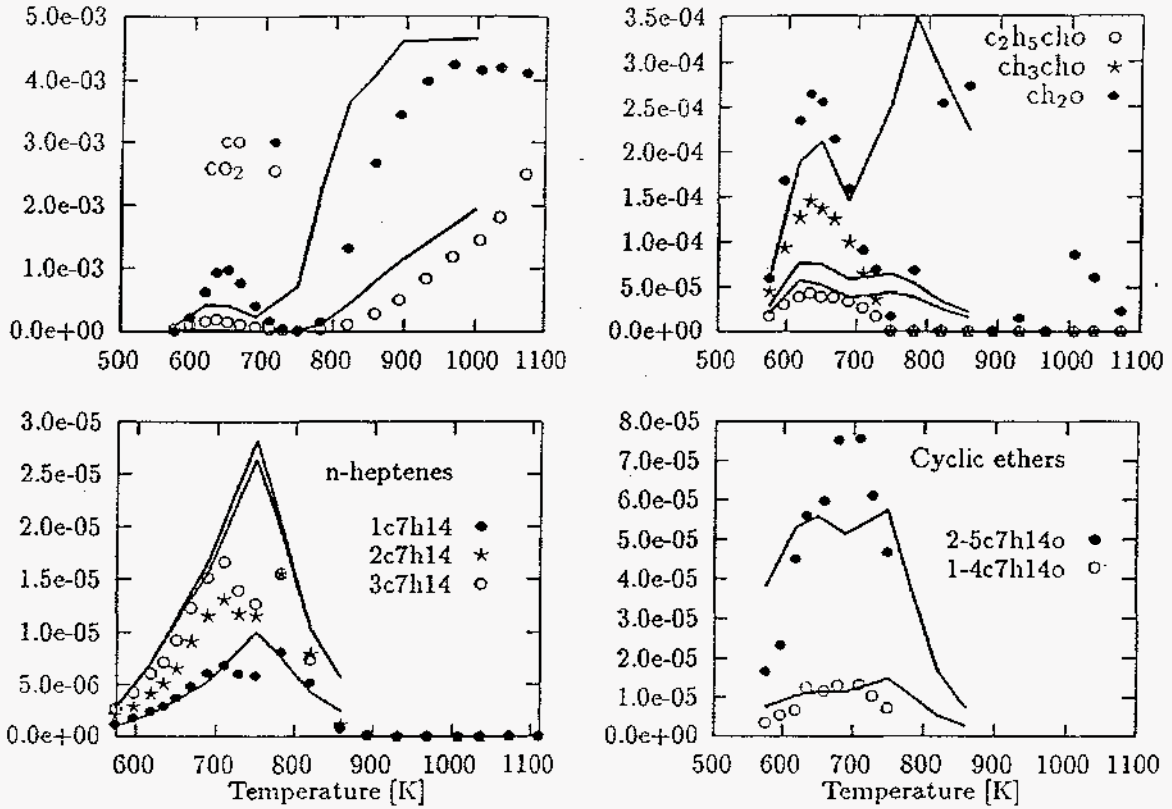


Figure 2: 0.1% n-heptane oxidation at 10 atm, $\phi = 1.0$, $\tau = 1$ s. Experimental (points) [4] and model prediction (lines) mole fraction for some oxygenated compounds, n-heptenes and furans.

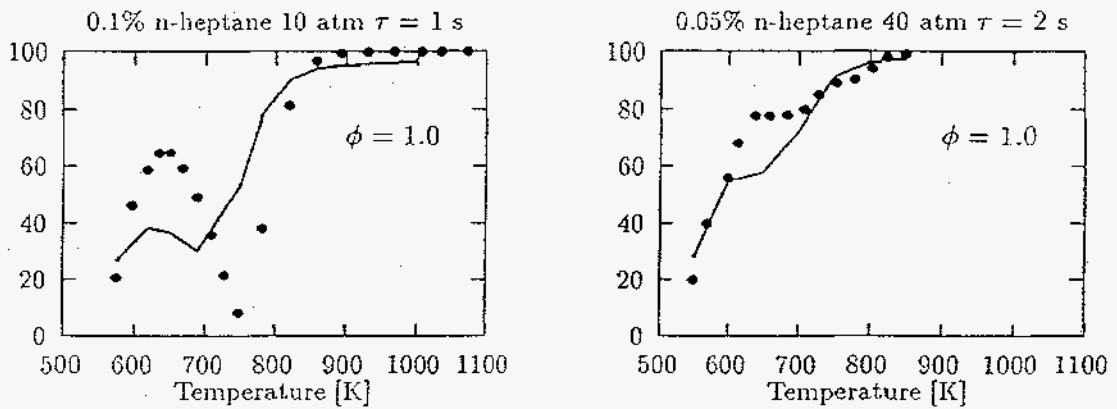


Figure 3: Comparison between experimental (point) [4,5] and model predicted (line) conversion for two different conditions.

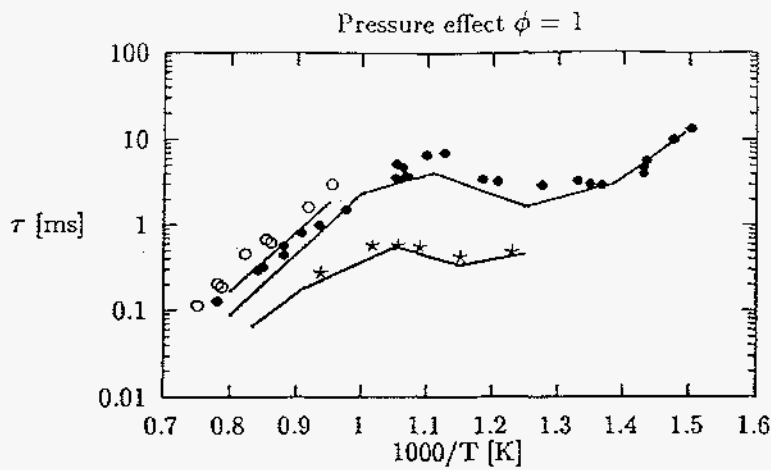


Figure 4: Comparison between experimental (points) [1] and model prediction (lines) times at 6.5 (o), 13.5 (•) and 42 bar (*).

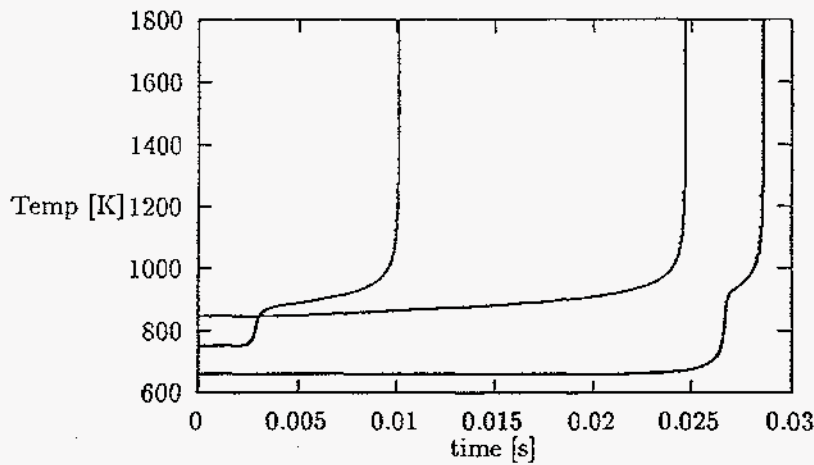


Figure 5: Model predicted temperatures profiles in rapid compression machine experiments [9]. Note the NTC behavior.

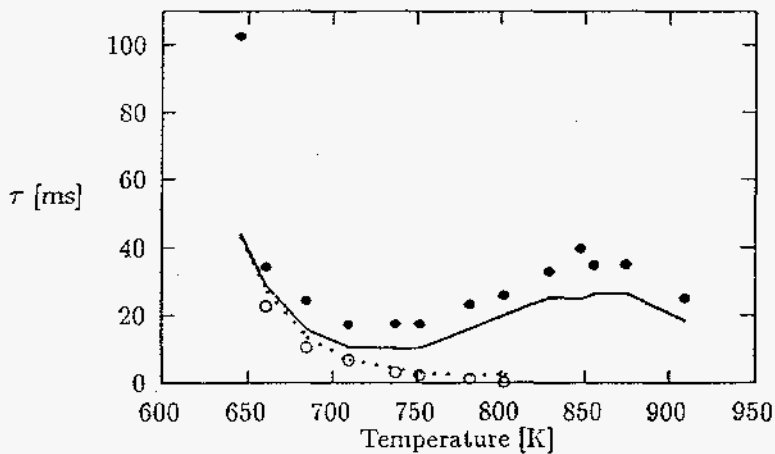


Figure 6: Experimental (points) [9] and model prediction (lines) ignition delay time (•) and first ignition (o).