High Temperature Compact Mechanism Development for Large Alkanes: *n*-Hexadecane

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Introduction

Improving internal combustion engine efficiency while minimizing pollutant emissions is a topic of continued interest. To this end, robust chemical kinetics models and more accurate numerical tools are needed to improve our understanding of the complex physical and chemical processes taking place in combustion systems. This study focuses on the development of a high temperature mechanism for the oxidation and pyrolysis of *n*-hexadecane. Hexadecane is a primary reference fuel for cetane rating of diesel fuels and is a major component in simple mixtures used to emulate the autoignition and combustion behavior of distillate-type fuels utilized in advanced engine designs (e.g. direct injection and homogeneous charge compression ignition diesel engines). Models of this large hydrocarbon molecule [1, 2] are scarce and involve a large number of reactions and species which make them not readily applicable to the simulation of multi-dimensional fluid flow problems. Recognizing the problem of mechanistic complexity versus predictive robustness, this study aims to develop a partially reduced skeletal mechanism for large alkane molecules.
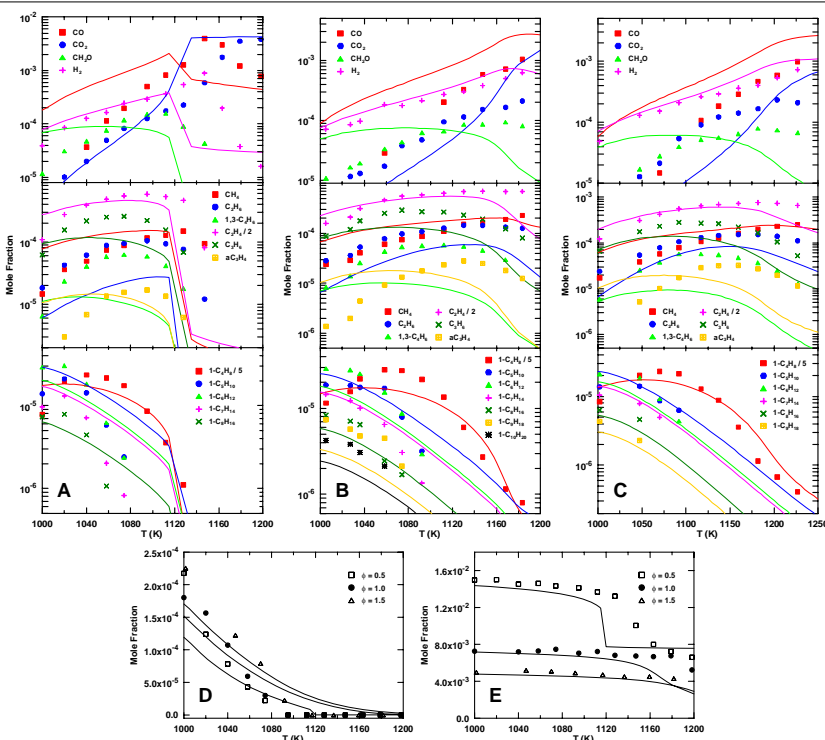

Figure 1. Comparison of experimental [4] and computed species profiles for the oxidation of hexadecane at atmospheric pressure in a Jet Stirred Reactor (JSR) with a mean residence time of 70 ms. (**A**) ϕ = 0.5, 0.03% $C_{16}H_{34}$ / 1.47% O_2 / 98.5% N_2; (**B**) ϕ = 1.0, 0.03% $C_{16}H_{34}$ / 0.735% O_2 / 99.235% N_2; (**C**) ϕ = 1.5, 0.03% $C_{16}H_{34}$ / 0.49% O_2 / 99.48% N_2; (**D**) hexadecane consumption; (**E**) oxygen consumption.

Validation

❖ **Oxidation:** To date, the only detailed experimental study on the oxidation of hexadecane is that of Ristori *et al.* [2]. They studied the gas–phase oxidation of $C_{16}H_{34}$ in a Jet Stirred Reactor (JSR) at atmospheric pressure over 1000-1250K temperature range and for equivalence ratios spanning from 0.5 through 1.5. Concentration profiles were obtained for major and minor species (up to decene). Figure 1 shows the results obtained from the current model compared against the experimental data [4]. As can be seen, the model successfully captures reactivity trends as the equivalence ratio is varied. The model also predicts well the formation of alkenes. Some disparities exist in the prediction of CO and 1,3-butadiene. Such discrepancies have previously been reported [4, 9]; our laboratory is currently further refining the mechanism below the C_3 level in order to improve these results. The model, however, yields comparable results when compared to the model developed in [2] which consists of nearly 300 species and 1,800 reactions.

❖ **Pyrolysis:** In industrial applications, alkenes are usually "manufactured" by pyrolysis of raw materials such as LPG and naphtas. In recent years, however, the use of higher-boiling materials has increased, especially gas-oil. Hexadecane kinetics studies are, thus, beneficial for these applications as the carbon content of gas-oil is similar to that of hexadecane (it is noted, however, that gas-oil is a complex mixture of a large number of paraffins, aromatics, and naphtas). Figure 2 compares computed species profiles against available data [10] obtained during the thermal (steam) cracking of hexadecane at atmospheric pressure in a tubular quartz reactor. Data is plotted with respect to the percentage of fuel conversion, $X = 100 [1 - ([C_{16}]_f / [C_{16}]_o]$ where $[C_{16}]_o$ is the initial hexadecane concentration and $[C_{16}]_f$ is the amount of hexadecane recovered. Reasonable agreement is observed for major species. Trends for large alkenes are also reproduced although it is noted that considerable experimental uncertainty exists for these measurements since the concentration of species larger than 1-pentene was very low. The model does capture the relative higher concentration of 1-hexene which is probably caused by the 1,5 isomerization of alkyl radicals.
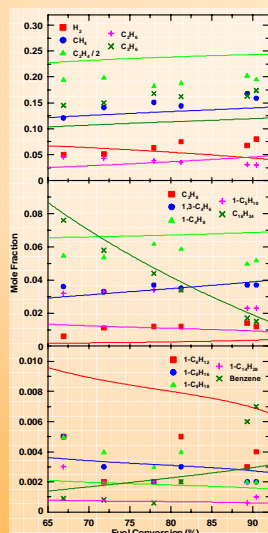

Figure 2. Experimental [10] and calculated species profiles during the steam pyrolysis of hexadecane at a temperature of 973 K and atmospheric pressure.

Mechanism Development

The current mechanism was built in a hierarchal manner. A high temperature hexadecane submechanism was combined with our recent update of the H_2/O_2 kinetic model [3] along with C_1-C_4 kinetics including the modifications listed in [4]. In the hexadecane submechanism, five classes of reactions are treated:

Table 1. H-atom abstraction rates.
(cm³-mol-s-cal)

Radical	Log (A)/H	b	E_a
	Primary sites		
H	6.97	2.00	7,700
O	5.62	2.40	5,500
OH	6.37	1.80	974
HO_2	3.90	2.55	16,500
CH_3	11.34	0.00	11,600
O_2	12.82	0.00	50,900
C_2H_5	10.72	0.00	12,300
C_2H_3	11.22	0.00	18,000
aC_3H_5	11.12	0.00	20,500
	Secondary sites		
H	6.64	2.00	5,000
O	4.76	2.60	1,769
OH (C-**C**-C-)	5.70	2.00	-596
(-C-**C**-C-)	5.47	2.00	-1,391
HO_2	3.68	2.60	13,900
CH_3	11.3	0.00	9,500
O_2	13.3	0.00	47,590
C_2H_5	10.10	0.00	10,400
C_2H_3	11.30	0.00	16,800
aC_3H_5	10.70	0.00	16,100

❖ **C-C, C-H bond homolysis**: Rate constants for these unimolecular fuel decomposition reactions were calculated from the recombination reactions of two radical species to form the stable parent molecule using thermochemistry. For reactions leading to hexadecyl + H, a recombination rate constant of $1x10^{14}$ cm³/(mol s) was assumed [5]. For reactions involving CH_3 the recombination rate was assumed to be $2x10^{13}$ cm³/(mol s) whereas for decompositions where the smallest product is ethyl or larger, the recombination rate was set to $7x10^{12}$ cm³/(mol s) [5].

❖ **H-atom abstraction:** Abstraction by H, O, OH, HO_2, CH_3, O_2, C_2H_5, C_2H_3, and aC_3H_5 is considered. Rates are as listed in Table 1.

❖ **Isomerization:** 1,4/1,5/1,6 internal hydrogen transfers were considered. Rates follow the rules of [6].

❖ **β-scission:** The alkyl radicals formed are assumed to decompose through β-scission into a 1-olefin and a smaller alkyl radical which, in turn, also decomposes following this β-scission pattern. The decomposition of all radicals larger than ethyl is treated in this manner. Rate constant were calculated from the reverse reaction, that is, the addition of an alkyl radical across the double bond of an alkene (Log A = 11, E_a = 7,200 cal/mol [5]).

❖ **Olefin reactions:** Olefins larger than C_4 follow unimolecular decomposition pathways as well as H abstraction (by H, O, OH, and CH_3) from primary, secondary and vynilic sites with subsequent rapid decomposition. Rates listed in [7] and [8] were used.

Mechanism Reduction

An approach similar to that previously applied in our laboratory for *n*-decane [9] is extended here for *n*-hexadecane. The originally developed **detailed mechanism** (above) included detailed treatment of the alkyl radicals formed, incorporating both internal hydrogen isomerization and β-scission reactions and consisted of **151 species** undergoing **1,155 reactions**. In order to reduce the number of required species and simultaneously maintain the desired mechanistic detail, it was assumed that each of the alkyl radicals in the system exists in isomeric partial equilibrium above the C_4 level. Using the corresponding isomerization rates, the relative concentrations of each isomer within a given radical group were calculated as a function of temperature and an Arrhenius-type expression (i.e. $k = A\ T^b\ exp\ (E_a/RT)$) was fitted to the results. The calculated Arrhenius parameters were used to modify the rates associated with the decomposition of each isomer radical. As a result, only a single radical species was needed to represent all the isomers associated with it and the respective reaction channels associated with each isomer. Using this approach, the resulting **reduced model** consisted of **98 species** and **944 reactions**.

A Note on Laminar Flame Speed

The laminar flame speed embodies the fundamental diffusive, reactive, and exothermic properties of a given fuel/oxidizer mixture and is commonly used to partially validate kinetic models. No hexadecane flame speed experimental data are currently available in the literature. However, Davis and Law [11] showed that normal alkanes (from ethane through heptane) have almost the same flame speeds (since they have similar structure and flame temperature). It is safe to assume, thus, that hexadecane flame speeds will be similar to those of other alkanes and, in fact, the current model shows this (Figure 3). The ability of the mechanism to accurately predict these flame speeds depends on the small-molecule kinetics as discussed in [4].
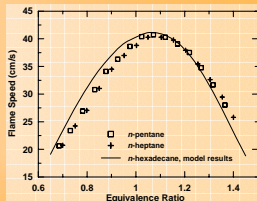

Figure 3. Calculated hexadecane laminar flame speed compared with experimental data [11] for other large alkanes.

Summary

A partially reduced skeletal reaction mechanism for the high temperature oxidation and pyrolysis of *n*-hexadecane has been developed consisting of 98 species and 944 reactions. By assuming that the alkyl radicals formed during these processes are in isomeric partial equilibrium, a considerable reduction in the required number of species was achieved while still maintaining the desired level of detail. The mechanism has been shown to reproduce the limited available experimental data and its performance is comparable to that of other much larger mechanisms available in the literature. The method described here can, thus, be successfully applied to the generation of compact mechanisms for other large alkanes found in modern fuels. Future measurements using Princeton's Variable Pressure Flow Reactor (VPFR) will be performed to generate additional validation data to further refine the mechanism.

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