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Refinement of Reduced Chemical Mechanisms for the Modeling of the Rapid Compression Combustion of Heptane and Octane

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ABSTRACT

Reduced chemical mechanisms for heptane and octane, originally developed by Keck and Hu, have been shown to give excellent agreement with experimental ignition delay times obtained using a rapid compression machine. These mechanisms consist of 20 species and 41 reactions with 10 reactions detailing the initial breakdown sequence of the alkane, 2 global reactions leading to the formation of end products, and the remaining reactions specifying the path to equilibrium products. Until recently, the success of these mechanisms in matching experimental data rested in large part on the fine tuning of forward rates, and the inclusion of specified reverse rates.. For a given reaction, the calculation of the reverse rate from the forward rate and the equilibrium constant—detailed balancing—is the technically correct approach, and the focus of this work was the elimination of the specified reverse rates in favor of this approach. Elimination of the specified reverse rates was found to depend on the accuracy of the thermodynamic property data generated with NASA style polynomial coefficients. Both mechanisms are now able to match experimental data generated with the M.I.T. rapid compression machine with impressive agreement, by employing detailed balancing for the calculation of reverse rates. Current computation techniques include the Detailed and Rate Controlled Constrained Equilibrium methods. However, at the present time, only the detailed method includes the algorithm to model the rapid compression sequence. Work to incorporate the algorithm into the RCCE computation is now underway. KEYWORDS: Kinetics, Reduced Mechanism, Rates, Detailed Balancing, Equilibrium.

INTRODUCTION

In the field of combustion modeling, the simplest computational scheme involves the calculation of temperature and species concentrations, with respect to time, for a system initially consisting of a fuel and oxidant. The evolution of kinetic models has been driven by the need to develop techniques that enabled the solution to problems involving the oxidation of hydrocarbons in the context of practical systems. The fundamental problem encountered is the sheer size of the system that results when a detailed kinetic model is developed for even simple hydrocarbons. Consequently, the development path has forked and two general types of kinetic schemes have evolved: comprehensive detailed kinetic schemes in which every reaction path that can be identified, and all of the associated species are included as part of the mechanism, and reduced schemes, which encompass a number of different approaches, all of which are aimed at reducing the numerical difficulty of the calculation. According to Griffith, who has written an extensive review of the topic, there is no formal definition of what is meant by a reduced scheme [1], whether it is a mathematical or kinetic simplification, or some combination.

The fundamental requirement in a reduced scheme is to introduce a simplifying assumption, and among these, the most basic is to assume that there exists a global reaction in which the reactants go directly to the end products without consideration of the intermediate reactions. Slightly more complex is a skeleton type structure in which global type reactions are accompanied by specific reactions that produce necessary intermediate species. A more sophisticated approach is found in the Quasi Steady State Approximation (QSSA), and the Partial Equilibrium Approximation (PEA). Each of these methods attempts to identify fast acting reactions that are effectively in equilibrium while slow acting reactions are occurring. Once identified, these fast reactions can then be treated as algebraic expressions, reducing the number of ODE's to be integrated. More recently, the simplifying assumptions have involved the application of a sophisticated mathematical technique to identify the most important reactions at each time step, which ideally results in a reduced computational load without significant degradation of data quality. The most prominent examples of this approach are Computational Singular Perturbation (CSP) introduced by Lam and Gousssis [2], Intrinsic Low-Dimensional Manifolds (ILDM) by Mass and Pope [3], and Rate Controlled Constrained Equilibrium (RCCE), by Keck [4].

A fourth method, the subject of this work, has its roots in work done at the Shell Research Ltd. Thornton Research Center during the 1970's by Halstead et al. [5], from which emerged the "Shell Knock Model". This model pioneered a unique representation of an alkane oxidation sequence by utilizing a symbol representative of a group of chemical species undergoing a generalized reaction sequence. This important innovation was justified by the observation, based on experimental data, that a variety of fuels exhibit similar behavior throughout an oxidation reaction, and the radicals which propel the evolution of the fuel species to its products exhibit similar kinetic behavior regardless of the original species. This technique was developed further by Cox and Cole [6] who applied the technique to a more detailed model of an alkane oxidation. In 1986, Keck and Hu [7] developed a mechanism for alkane oxidation to model initiation and chain branching phases of fuel-air mixtures in a constant volume bomb. The Keck and Hu work, like that of Cox and Cole, was built on the foundation of the Shell Knock Model, but included more detailed features of the oxidation sequence. However, Keck and Hu developed the details of their mechanism based on work by Benson, which distinguished it from the Cox and Cole work. In 1987, Hu and Keck [8] published a study that focused on autoignition phenomenon in compressed gas mixtures where a revised version of the mechanism from their earlier work was used for the theoretical modeling. This revised mechanism consisted of 13 active species and 18 chemical reactions, and is the basis of the mechanisms used in this work.

A key feature of this approach to kinetic modeling is that only the very first reactions involving the fuel molecule and its radicals are included. The reaction proceeds by initial abstraction of a hydrogen atom by O_2, and then follows with the most likely reaction to occur given the temperature and constituents. This process repeats, and each time, the most likely reactions, given the new population of O_2, RH (fuel) and fuel radicals present, follow. Chain branching occurs when the high temperature circuit (the outer circuit) begins to dominate and the $\dot{O}H$ radical concentration grows exponentially.

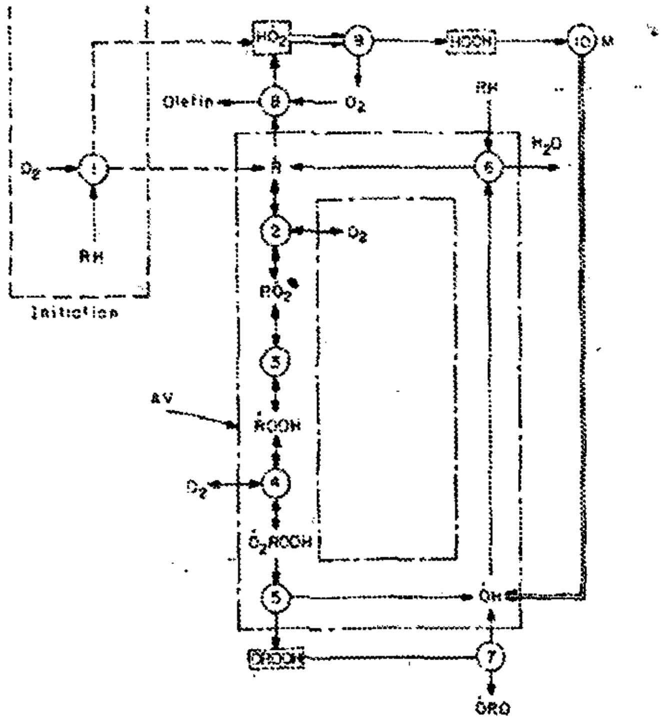

Figure 1: Schematic of high and low temperature reaction paths [8]

The primary focus of both of the earlier Hu and Keck studies was to investigate and model the kinetic mechanism responsible for the two stage induction process observed in the larger alkanes, and consequently, these mechanisms did not include the reactions necessary for the system to go to equilibrium. In 2002, Tanaka, Ferran, and Keck [9] published new work based on the same generalized kinetic mechanism as in the 1987 paper, but with additional elements included to allow the system to go to equilibrium. This was accomplished by imposing 3 global reactions to consume the fuel radicals which occur as the reaction shifts to the high temperature phase, and produce the necessary intermediates for a general set of reactions, taken from the original ChemkinII distribution[10], that lead to the creation of CO2 and H2O, enabling the system to achieve equilibrium.

The MIT rapid compression machine was used to perform experimental studies with n-heptane and iso-octane for a variety of fuel/air mixtures and initial temperatures. The calculation was performed using the Fortran based ChemkinII package incorporating algorithms to model the rapid compression process and boundary layer heat transfer. The rapid compression algorithm consisted of a linear isentropic compression with the RCM piston moving at a constant velocity followed by a parabolic deceleration to a zero velocity at the specified clearance height. A simple, but effective, boundary layer heat transfer model is implemented by considering the volume of the cylinder gas and the boundary layer as an adiabatic core gas of volume V_c. This volume is increased to simulate the growth of the boundary layer, and is accompanied by a proportionate decrease in temperature.

Tanaka's model included 21 species, 40 reactions, and the comparison to experimental data from the rapid compression machine was impressive. It is clear, based on this evidence, that this approach to kinetic modeling, in which only the earliest and slowest reactions involving the fuel and intermediate species, consisting of the same number of carbon atoms as the fuel, can effectively capture all of the important features of the reaction using a very lightweight algorithm. The chemical mechanism is orders of magnitude smaller than a fully detailed set of reactions, which results in a significant reduction in the computational effort required to perform the calculation, regardless of which computational technique, mentioned earlier, is applied.

One drawback to Tanaka's model is the use of reverse Arrhenius coefficients in the chemical mechanisms. An examination of several of the comprehensive mechanisms for large alkanes show that this is a common practice, but is not in adherence with the more widely accepted convention of employing detailed balancing, as in equation 1,

$$k_r = \frac{k_f}{E_C} \qquad (1)$$

using the forward rate and the equilibrium constant E_C, based on Gibbs free energy, to calculate the reverse rate. It is possible that specifying both rates provides a computational advantage, but, if this is the case, care must be taken to insure that the detailed balancing criteria is satisfied for whatever values of k_f and k_r are chosen. If equation 1 is not satisfied then it is unlikely that the reaction will proceed to the correct equilibrium state. Furthermore, since the equilibrium constant is calculated from thermodynamic properties which are known to a much greater degree of accuracy than the rates, calculating the reverse rate from the above relationship results in a more robust mechanism overall.

Removing the reverse rates from Tanaka's mechanisms proved to be problematic. It was assumed from the outset that the existing forward rates were reasonable, and that the calculation should run. Removal of the specified reverse rates in various combinations produced a variety of results ranging from a temperature rise of a few degrees and then steady state, to the calculation blowing up and ending. Plotting the rates for individual reactions showed that the reverse rate for reaction 1 was growing extremely large, effectively terminating the reaction. Calculations comparing the original specified reverse rates with values calculated using detailed balancing showed the latter to be larger by 10 orders of magnitude. Further work to verify the calculation of the equilibrium constant from Chemkin led to the conclusion that the problem was in the thermodynamic property data generated from NASA style polynomials. This original data for most of the C_7 and C_8 species had been assembled from a C_8 mechanism dating from 1994, emailed to a former colleague, by William Pitz [11] at the Lawrence Livermore National Laboratory. Thermodynamic property data for species R_{12}, R_{13}, and R_8 **and** R_9 in the octane set, was generated using a code written by He [12] which produced values of C_p over a range of temperatures for a specified hydrocarbon. The remaining property values were found by integrating the values of $C_p(T)$ to $h(T)$, correcting for $h_f(298)$, *obtained using Benson's Group Additivity [13]*, and fitting the data to a polynomial.

Comparison of the enthalpies calculated using Pitz data at 298 K to $h_f(298)$ calculated using Benson's Group Additivity verified that the property data being used was inaccurate.

		Pitz	**Benson**	**This Work**
		hf (298)	**hf (298)**	**hf (298)**
n-Heptane		**kcal/mole**	**Kcal/mole**	**kcal/mole**
F	**RH**	-44.9	-44.5	-45.03
HE2	**R***	1.3	0.8	1.29
HE3	**C=C**	-17.7	-17.4	-14.94
HE5	**ROO***	-33.6	-32	-33.59
HE6	**R*OOH**	-23.4	-22.3	-23.35
HE7	***OOROOH**	-73.2	-55.1	-58.10
HE8	**OROOH**	-340	-94.4	-94.35
HE9	***ORO**	-231	-61.5	-61.47
HE12	—	-97.5	-97.5	—
HE13	—	-70.5	-70.5	—
		hf (298)	**hf (298)**	**hf (298)**
Iso-Octane		**kcal/mole**	**Kcal/mole**	**kcal/mole**
C8H18	**RH**	-53.4	-56.3	-53.40
OC2	**R***	-10.5	-9.7	-10.50
OC3	**C=C**	-26.9	-27.7	-26.90
OC5	**ROO***	-39.5	-39.6	-39.50
OC6	**R*OOH**	-28.5	-28.6	-28.50
OC7	***OOROOH**	-59	-58.5	-59.00
OC8	**OROOH**	-97	-94.1	—
OC9	***ORO**	-68.6	-61.2	—
OC12	—	-102	-26	—
OC13	—	-72.7	-94.3	—

Table 1: Comparison of enthalpies of formation for the fuel and its variants from the original set, Benson's Group Additivity, and the updated values.

A 1997 preprint of a study of the oxidation of n-heptane by Curran, et. al. [14] obtained from the internet, and a circa 2003, updated version of an iso-octane mechanism published by Curran, et. al. [15] in 2002, also obtained from the internet, were used as sources for the new property data. Table 1 shows the original values of

h_f for heptane and octane obtained from Pitz, and the updated values obtained from the above sources with Benson's value provided for comparison.

For species HE7, HE8, and HE9 in the heptane set, substantial improvements were realized. for species HE12 and HE13 (neither of which are included in any of the comprehensive sets seen to date), a satisfactory match was obtained using the code from He. In the octane set, reasonable matches were obtained at 298K with the original Pitz data, however, the results for species 8, 9, 12, and 13 are not good. This is likely due to an error, or misconfiguration of the He code resulting from the non-linearity of the iso-octane structure. Further work is necessary in this area, because although some of the values appear to match up quite well with Benson's values at 298 K, the calculation would not run at all, with the specified reverse rates removed, for either mechanism with the original data. This suggests that the data diverges significantly as temperature increases.

Substitution of the replacement property data resulted in a kinetic model that ran with only forward rates given, and reverse rates calculated using detailed balancing, for both heptane and octane. The output generated by this configuration did not match up with the experimental data, however. There existed a significant time offset between the model and experimental data that suggested some rate adjustment was needed to compensate for the removal of the reverse rate expressions.

	n-Heptane	Log A	E_a
	Reactions		*kcal/mol*
1	*F+O2<=>HE2+HO2*	*18.3*	*47.5*
2	*HE2+O2<=>HE5*	*12.0*	*0.0*
3	*HE5<=>HE6*	*11.2*	*19.0*
4	*HE6+O2<=>HE7*	*11.5*	*0.0*
5	*HE7=>HE8+OH*	*10.9*	*17.0*
6	*F+OH=>HE2+H2O*	*13.0*	*3.0*
7	*HE2+O2<=>HE3+HO2*	*14.5*	*6.0*
8	*HE3+HO2+7O2=>7CO+7H2O+HO2*	*14.5*	*10.0*
9	*HE8=>HE9+OH*	*15.6*	*43.0*
10	*HE9+O2<=>HE12+HO2*	*11.5*	*6.0*
11	*HO2+HE12+O2 =>H2O2+HE13+HO2*	*13.5*	*10.0*
12	*HO2+HE13+5O2=>7CO+5H2O+HO2*	*13.5*	*10.0*
	Iso-Octane	***Log A***	***E_a***
	Reaction		*kcal/mol*
1	*C8H18+O2<=>OC2+HO2*	*14.6*	*49.0*
2	*OC2+O2<=>OC5*	*12.0*	*0.0*
3	*OC5<=>OC6*	*11.1*	*22.4*
4	*OC6+O2<=>OC7*	*13.5*	*0.0*
5	*OC7=>OC8+OH*	*10.9*	*17.0*
6	*C8H18+OH=>OC2+H2O*	*12.7*	*3.0*
7	*OC2+O2<=>OC3+HO2*	*14.5*	*6.0*
8	*OC3+HO2+7O2=>7CO+7H2O+HO2*	*13.3*	*10.0*
9	*OC8=>OC9+OH*	*15.6*	*43.0*
10	*OC9+O2<=>OC12+HO2*	*13.5*	*6.0*
11	*HO2+OC12+O2=>H2O2+OC13+HO2*	*13.2*	*10.0*
12	*HO2+OC13+5O2=>7CO+5H2O+HO2*	*13.2*	*10.0*

Table 2: Primary reactions from the heptane and iso-octane mechanisms with forward rate data.

A rate sensitivity study was initiated, focusing on only the reactions containing C_7 or C_8 molecules. These reactions and the corresponding rate data are shown in table 2. The rate expressions follow the Arrhenius form, using the three parameter format with Ea in *kcal/mol, R* in kcal/mol•K and *A* in $cm^3/s \cdot K^n$:

$$k_f = AT^n e^{\left[\frac{-E_a}{RT}\right]} \qquad (2)$$

For the reactions shown the value of n is zero, and has been omitted.

The 7th reaction proved to be the limiting reaction in both the n-heptane and iso-octane mechanisms, and when this reaction had its rate adjusted upward, reactions 1, 6 and 8 were also observed to be sensitive to increases in the pre-exponential factor. Table 3 shows the adjustments made to the rates for specific reactions in each of the mechanisms.

	Tanaka		**This Work**	
		n-heptane		
Reaction #	**Log A**	**E_A**	**Log A**	**E_A(kcal/mol)**
1	16.0	46.0	18.3	47.5
7	11.5	6.0	14.5	6.0
8	13.5	10.0	14.5	10.0
		Iso-octane		
	Log A	**E_A**	**Log A**	**E_A(kcal/mol)**
1	16.0	46.0	14.6	49.0
6	13.0	3.0	12.7	3.0
7	11.5	6.0	14.5	6.0
8	13.3	10.0	14.3	10.0

Table 3: Original and modified rate parameters for the heptane and octane mechanisms.

Three pre-exponential terms were modified in the heptane mechanism: reaction 7 was increased by a factor of 1000, reaction 1 by a factor of 100 and reaction 8 by a factor of 10. For iso-octane, the adjustments to reactions 7 and 8 are identical to the n-heptane mechanism, however, reaction 1 had the pre-exponential term reduced by a factor of 100, and it was also necessary to make an adjustment to reaction 6 which had its pre-exponential term reduced by a factor of 2.

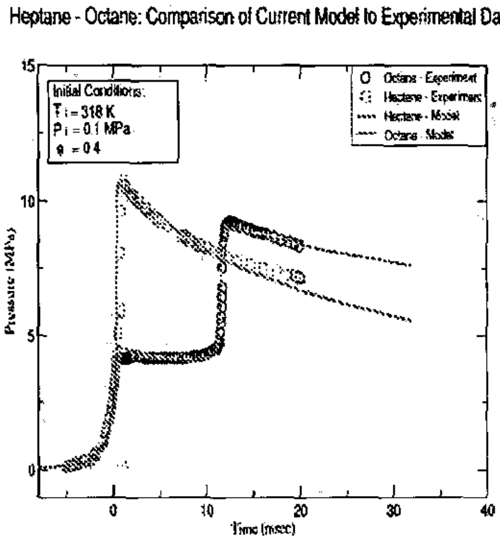

Table 2: Comparison of pressure history for model and experimental data.

Figure 2 is a plot showing a comparison of the pressure history for model data from the current work, and experimental data from Tanaka's work with the MIT Rapid Compression Machine. The data shown was developed from the initial conditions listed near the top of the figure. It is clear that the model is able to match the experimental data very well. And, in fact, the inclusion of the heat transfer model, mentioned above, into the rapid compression algorithm results in an impressively accurate rendering of a complex process with a surprisingly simple model. The degree of accuracy is all the more impressive when one considers the degree of reduction of the chemical mechanism.

Examination of Tanaka's n-heptane and iso-octane mechanisms show that the essential differences between the two mechanisms, aside from the actual species, are the rates for reactions 3, 8, 11 and 12. Although both mechanisms in the current work have had the pre-exponential for reaction 8 increased, the relative difference remains the same. The differences in these rates account for the slower oxidation rate of octane due, essentially, to its iso structure and the resulting scarcity of secondary hydrogen sites in comparison to n-heptane. It was additionally necessary to modify reactions reactions 1 and 7 in both mechanisms, and reaction 6 in the iso-octane mechanism. The need for these modifications is directly attributable to the removal of the reverse rates, and, assuming that the thermodynamic property data is reasonably accurate, the modified rates should be better approximations to the actual values.

Additional work with these mechanisms will likely lead to some fine tuning of the existing rate structure. It would also be beneficial to examine the thermodynamic property data more closely, and seek additional sources for this data. The quality of the data should be determined by comparison to Benson's values, which are still the only reliable source of property data for many of the large hydrocarbons.

CONCLUSION

The reduced mechanism framework for large alkanes presented in this work demonstrates an impressive ability for generating accurate temporal data for the systems investigated with an equally impressive reduction in complexity of the chemical model. The reliance on detailed balancing for the calculation of reverse rates makes the model more robust overall, and reduces the uncertainty associated with the specified reverse rates. It was discovered during the course of this work that some of the thermodynamic property data being used was not sufficiently accurate for the calculation. When enthalpies of formation calculated at 298 K from the polynomials were compared to values calculated using Benson's Group Additivity, significant discrepancies were noted for several species. Updated polynomial data from Curran, et al. effectively remedied the problem, but this raises questions about the accuracy of the thermodynamic property data that is in wide circulation, and has not previously been scrutinized to an appropriate degree. It is clear that inaccurate thermodynamic data will have an impact on rate values. It is equally clear that the practice of specifying reverse rates can mask inaccurate data, and additionally raises the possibility that the system will relax to the wrong equilibrium state.

The purpose of the present work has been to establish a working system from which future investigations can be initiated, and to eliminate unnecessary complications and inaccuracies introduced through the use of reverse rate expressions, in favor of the more rigorous approach available through the application of detailed balancing.

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