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## The Application of the Rate-Controlled Constrained Equilibrium Technique to a Reduced Chemical Mechanism for Iso-Octane

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The reduction of computation times has long been a priority in the field of combustion kinetics. Recently, the trend towards improving calculation times has been towards the development of sophisticated mathematical techniques to reduce the number of equations to be solved without prior reduction of the mechanism. Rate Controlled Constrained Equilibrium is a method that achieves a dramatic reduction in the number of equations to be solved by relaxing the system, at each time step, to a quasi-equilibrium state by minimizing the Gibbs free energy subject to a set of constraints. The system is formulated in terms of the constraint potentials coupled to the energy equation, so for zero-dimensional kinetic calculations, the number of equations to be solved is equal to the number of constraints plus the energy equation. This method is applied to a set of mechanisms for n-heptane and iso-octane that include, primarily, only reactions involving molecules consisting of only the number of carbon atoms as the fuel, and a set of water and carbon dioxide reactions to allow the system to achieve stable equilibrium, subject to the set of constraints imposed. The RCCE technique and the mechanisms are discussed, and comparisons made to the results of a detailed kinetic calculation using the same mechanisms.

### 1. Introduction

In recent years, the field of combustion kinetics has seen the steady development of new techniques aimed at reducing the computation time for chemical kinetic calculations. The primary motivation for this trend is the increasing sophistication of computer models of systems involving hydrocarbon combustion, and the large computation times associated with these models. Fully detailed chemical kinetic mechanisms for even small hydrocarbons can include a large number of species, and a detailed kinetic calculation requires the solution of a rate equation for each one of the species. Most of the traditional techniques employed to reduce computational load fall into one of two categories: Methods falling into the first category focus on the chemical mechanism and attempt to reduce the number of species (through truncation of the species list) and, therefore, the number of rate equations to be solved. An extreme example of this technique would be the reduction of a chemical mechanism to a single global reaction. Methods in the second category focus on the application of mathematical approximations to reduce the number of differential equations through the substitution of algebraic equations. This technique includes well known methods such as Partial Equilibrium Approximation (PEA) and

Quasi-Steady-State Approximation (QSSA) among others. Regardless of the approach, the fundamental objective is to reduce the overall number of equations to be solved so as to reduce the computation time required to obtain a solution [1]. More recently, powerful new techniques have emerged which employ sophisticated mathematical analysis to reduce the system order leading to a shorter computation times while maintaining good accuracy. The most prominent examples of these techniques are Implicit Low Dimensional Manifolds (ILDM) [2] and Computational Singular Perturbation (CSP) [3].

An alternative method for reducing the computation complexity with little or no loss of detail is the Rate Controlled Constrained Equilibrium (RCCE) method developed by J. C. Keck and D. Gillespie [4]. In this work, chemical kinetic calculations are performed by applying this calculation technique to a reduced chemical mechanism for octane that has unique and interesting features in its own right. The RCCE method and the details of the reduced chemical mechanism are presented prior to a discussion of the results.

## 2. The Rate Controlled Constrained Equilibrium Method

The RCCE method is based directly on the Second Law through the Maximum Entropy Formalism which states that the entropy of a system is maximized at its stable equilibrium subject to the constraints imposed. In the RCCE method, it is assumed that a chemically reacting system relaxes to a stable equilibrium state through a series of constrained quasi-equilibrium states determined by slow, rate limiting reactions, while the fast reactions equilibrate the system based on the constraints imposed by the slow reactions. In practice, this is implemented through the application of the Lagrange Multipliers technique to find the minima of the Gibbs Free Energy subject to the imposed constraints:

$$(dG)_{T,P,n} = 0 \quad (1)$$

Three different techniques for the implementation of RCCE have been explored by workers in our group over the past decade. In the first technique, the constraints are integrated directly, and the constraint values are then passed to a generalized equilibrium code such as GNASA or GSTANJAN to determine the constrained system composition at each time step [5]. This approach is cumbersome and inefficient—especially in terms of computation time [6]. The second technique is based on the integration of constraint factors [7]. This method proved to be effective for the H/O system, but could not be easily *generalized* to other systems. In the third technique, the constraint potentials which are conjugate to each constraint are integrated directly. This approach was first proposed by Keck [8] and is now implemented exclusively in this format within our group [9-10] and by others [11,12].

A detailed formulation of the RCCE method in constrained potential form will not be included here, but can be found in earlier publications [9,10,13,14]. For the purposes of this discussion the basic mechanics of the method can be understood through a discussion of the constraints. In an RCCE calculation, the constraints imposed on the system are assumed to have the form

$$C_i = \sum_{j=1}^{Nsp} a_{i,j} N_j, i = 1, \dots, Nc \quad (2)$$

where  $C_i$  represents the  $i^{th}$  constraint,  $Nsp$  is the number of chemical species,  $\mathbf{a}$  is the matrix which defines the relationship between the species and the constraints, and  $a_{i,j}$  is the value of the  $i^{th}$  constraint for the  $j^{th}$  specie. An expression for  $N_j$ , the number of moles of the  $j^{th}$  specie, arises through the application of the Lagrange Multiplier technique. The resulting expression is a

function of the constraint potentials ( $\gamma_i$ ) conjugate to the constraints (Lagrange Multipliers), and  $\mu_j^o$ , the standard state Gibbs Free Energy of the  $j^{\text{th}}$  species:

$$N_j = V \left( \frac{P_o}{R T} \right) e^{\left( \frac{-\mu_j^o}{R T} - \sum_{n=1}^{N_c} a_{n,j} \gamma_n \right)} \quad (3)$$

For chemical kinetic calculations, the RCCE formulation includes 1 rate equation for each constraint, plus the energy equation. In contrast, the detailed kinetic formulation requires a separate rate equation for each specie, plus the energy equation. Consequently, the detailed kinetic calculation requires the solution, at each time step, of the number of species + 1 ( $N_{sp} + 1$ ) equations whereas the RCCE method requires the solution of the number of constraints + 1 ( $N_c + 1$ ) equations. The implication of this is that the application of RCCE eliminates the need to start with a complete reaction model that must then be simplified through the application of various approximations. Instead, one starts with a small number of general constraints to which more can be systematically added to improve the accuracy of the calculation to any desired level. When the number of constraints becomes equal to the number of species in the system, the method becomes similar in computational complexity to a detailed kinetic calculation. However, even when the number of degrees of freedom for the two methods is equal, in the RCCE calculation the constrained equilibrium requirement must still be satisfied at each time step. This is an important and powerful feature of the RCCE technique.

### 3. Selection of Constraints

The need to select constraints and the lack of a clear methodology for their selection have often been cited as a drawback for the RCCE method. However, as experience and understanding of the constraint selection process have accumulated, many insights into the processes involved in hydrocarbon combustion have been gained. Consequently, constraint selection is viewed by our group as the key to successful implementation of RCCE, and a powerful tool for developing a greater understanding of the process.

			1	2	3	4	5	6	7	8	9	10	
		$H_o/RT$	RH	N2	EO	EH	M	EC	FO	$\bar{C}$	FV	$\frac{R}{R}$	OROOH
5	1	C8H18	-135.54	1	0	0	18	1	8	0	0	0	0
6	2	N2	-23.04	0	1	0	0	1	0	0	0	0	0
7	3	O2	-24.68	0	0	2	0	1	0	0	0	0	0
8	4	H2	-15.72	0	0	0	2	1	0	0	0	0	0
9	5	H2O2	-79.61	0	0	2	2	1	0	0	0	0	0
10	6	CO2	-174.55	0	0	2	0	1	1	2	0	0	0
11	7	H2O	-114.18	0	0	1	2	1	0	1	0	0	0
12	8	OC3	-93.05	0	0	0	16	1	8	0	1	0	0
13	9	HO2	-22.82	0	0	2	1	1	0	0	0	1	0
14	10	OC5	-122.09	0	0	2	17	1	8	0	0	1	1
15	11	OC8	-221.87	0	0	3	16	1	8	1	0	0	1
16	12	O	74.86	0	0	1	0	1	0	1	0	2	0
17	13	H	68.65	0	0	0	1	1	0	0	0	1	0
18	14	CO	-65.58	0	0	1	0	1	1	1	0	0	0
19	15	OH	-7.22	0	0	1	1	1	0	1	0	1	0
20	16	OC2	-69.59	0	0	0	17	1	8	0	0	1	1
21	17	OC9	-172.77	0	0	2	15	1	8	2	0	1	0
22	18	OC6	-107.89	0	0	2	17	1	8	0	0	1	1
23	19	OC7	-162.76	0	0	4	17	1	8	0	0	1	1
24	20	OC13	-177.28	0	0	2	12	1	8	2	0	0	0
25	21	OC12	-224	0	0	2	14	1	8	2	0	0	0

Table 1: An  $a_{i,j}$  matrix for iso-octane with 18 species and 10 constraints.

The general requirements for the constraints are that they must: be linearly independent, include the elements, yield the energy and entropy of the system (within experimental accuracy), and hold the system in the specified initial state. In addition, the constraints should reflect any knowledge about slow, rate-limiting reactions that will influence the evolution of the system. Figure 1 shows an  $a_{i,j}$  matrix with 18 species and 10 constraints for iso-octane combustion in  $O_2$ . Table 1 provides a description for each of the constraints listed here.

In the RCCE method, only reactions that changes a constraint are included in the calculation. In theory, one reaction is needed for each constraint. In practice,

#	$C_i$	Constraint Definition
1	EC	Elemental carbon
2	EO	Elemental oxygen
3	EH	Elemental hydrogen
4	M	Total number of moles
5	FV	Moles of free valence (any unpaired valence electron)
6	FO	Moles of free oxygen (any oxygen not directly attached to another oxygen)
7	RH	Moles of Fuel molecule
8	FRP	Moles of Fuel radical and fuel radical peroxides
9	C=C	Moles of Olefin (an <i>alkene</i> )
10	O=ROO	Species created in rate limiting step

Table 2: Description of the 10 constraints used for the iso-octane / O<sub>2</sub> calculation.

more reactions are usually required to obtain the desired detail. The matrix in table 2 is the so-called  $b_{ij}$  matrix for the iso-octane/O<sub>2</sub> system. The  $b_{ij}$  matrix is the product of the stoichiometric coefficient matrix and the constraint, or  $a_{ij}$ , matrix. Each row shows the constraints changed by the adjacent reaction, and the list is sorted so the reactions lower in the list are the ones that

	1	2	3	4	5	6	7
	RH	O=ROOH	M	FO	FRP	C=C	FV
C8H18+OH=>OC2+H2O	-1	0	0	0	1	0	0
C8H18+O2<=>OC2+HO2	-1	0	0	0	1	0	2
OC3+HO2+8O2=>8CO+8H2O+HO2	0	0	7	16	0	-1	0
OC8=>OC9+OH	0	-1	1	2	0	0	2
OC7=>OC8+OH	0	1	1	2	-1	0	0
H+OH+M=H2O+M	0	0	-1	0	0	0	-2
O+O+M=O2+M	0	0	-1	-2	0	0	-4
OH+OH(+M)=H2O2(+M)	0	0	-1	-2	0	0	-2
H+O2(+H2O)=HO2(+H2O)	0	0	-1	0	0	0	0
O+CO(+M)<=>CO2(+M)	0	0	-1	0	0	0	-2
H+O2(+M)=HO2(+M)	0	0	-1	0	0	0	0
O+H+M=OH+M	0	0	-1	0	0	0	-2
H+H+M=H2+M	0	0	-1	0	0	0	-2
H+O2(+H2)=HO2(+H2)	0	0	-1	0	0	0	0
OC2+O2<=>OC5	0	0	-1	0	0	0	0
OC6+O2<=>OC7	0	0	-1	0	0	0	0
O2+CO=O+CO2	0	0	0	2	0	0	2
H+HO2=OH+OH	0	0	0	2	0	0	0
HO2+CO=OH+CO2	0	0	0	2	0	0	0
H+HO2=O+H2O	0	0	0	2	0	0	0
H2O2+H=OH+H2O	0	0	0	2	0	0	0
O+OH=O2+H	0	0	0	-2	0	0	-2
OC2+O2<=>OC3+HO2	0	0	0	0	-1	1	0
HO2+HO2=O2+H2O2	0	0	0	0	0	0	-2
H+HO2=H2+O2	0	0	0	0	0	0	-2
OH+HO2=H2O+O2	0	0	0	0	0	0	-2
HO2+HO2=O2+H2O2	0	0	0	0	0	0	-2
OH+HO2=H2O+O2	0	0	0	0	0	0	-2
O+HO2=O2+OH	0	0	0	0	0	0	-2
H2O2+H=HO2+H2	0	0	0	0	0	0	0
O+H2=OH+H	0	0	0	0	0	0	0
OH+OH=O+H2O	0	0	0	0	0	0	0
OC5<=>OC6	0	0	0	0	0	0	0
CO+OH=CO2+H	0	0	0	0	0	0	0
H2O2+OH=H2O+HO2	0	0	0	0	0	0	0
H2O2+O=OH+HO2	0	0	0	0	0	0	0
OH+H2=H2O+H	0	0	0	0	0	0	0

Table 3: A  $b_{ij}$  matrix showing the equilibrium reactions for the octane system with 7 constraints.

improvements in computational efficiency in its own right, and in combination with a reduced chemical scheme, even greater improvements can be realized.

Modeling the autoignition of combustible charges in a constant-volume constant-energy (CVCE)

change the least number of constraints. The last 8 reactions on the list do not change any constraints and, therefore, do not play a role in an RCCE calculation. The resulting configuration for an RCCE chemical kinetic calculation using this configuration is 18 species, 29 reactions as opposed to the detailed chemical kinetic calculation which would use the full set of 37 reactions and 18 species. The RCCE system could be further reduced through the elimination of reactions that have a minimal effect on the system evolution for the temperature and pressure of interest. The species symbols of the form OC# represent iso-octane species in this case, and are related to the generalized form in table 4.

## 4. Results and Discussion

### 4.1 Reaction Model

The objective of this work is to explore the feasibility of using Rate Controlled Constrained Equilibrium to perform chemical kinetic calculations based on a radically reduced chemical mechanism for large alkanes. The RCCE technique offers the potential for significant

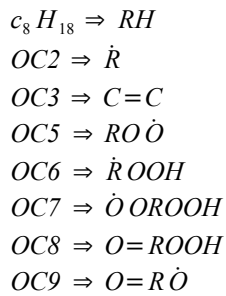


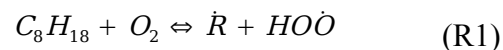
Table 4: Species nomenclature and functional form

environment is a frequently employed technique in combustion kinetics because of its relevance to important kinetically driven processes such as engine knock [15] and distributed combustion [16]. The results presented here were generated by CVCE models based on the RCCE and detailed kinetic calculation techniques. The computer codes for both methods are coupled with the FORTRAN based CHEMKIN II [17] code and the integration is performed by DDASSL [18]. Studies are conducted at an initial temperature of 900K, and 1, 5, 10, and 100 atmospheres pressure

## 4.2 The Chemical Kinetic Mechanism

The chemical mechanism used in this work is based on a mechanism developed by Keck and Hu [19] in the mid 1980's and is based on results that emerged from research conducted by Halstead et al. at the Shell Oil Company Thornton Research Center during the 1970's [20]. The reaction mechanism describes the oxidation of large alkanes (consisting of 4 or more carbon atoms) using a generalized set of reactions based on a symbolic representation of the fuel, its radicals, and isomers that is independent of the actual fuel. This technique allowed the reduction of the number of reactions necessary to model the oxidation of heptane or octane, for example, from several thousand in the largest published mechanisms [21], to 9 for the RCCE calculation and 10 for the detailed kinetic calculation. In the functional format presented in table 3, R could be any alkane with 4 or more carbon atoms, but in this instance refers only to iso-octane based molecules with C = 8.

Figure 1 is a schematic diagram of the reaction sequence for the chemical mechanism. This sequence is general and applies to any alkane, (represented here by  $RH$ ) containing 4 or more carbon atoms. The schematic shows an inner and outer circuit which correspond to a low and high temperature sequence of reactions. The low temperature sequence begins with the initiation reaction at 1 where a hydrogen atom is abstracted from the fuel molecule by  $O_2$  to form the alkyl radical:



At 2, an  $O_2$  attaches to the fuel radical to produce an peroxy alkyl radical followed by an internal isomerization reaction to form a hydroperoxy alkyl radical at 3. A second  $O_2$  addition reaction occurs at 4 followed by the rate limiting irreversible decomposition of the product to an OH radical and a ketohydroperoxide at 5, which further decomposes producing the product at 7 and an OH radical.

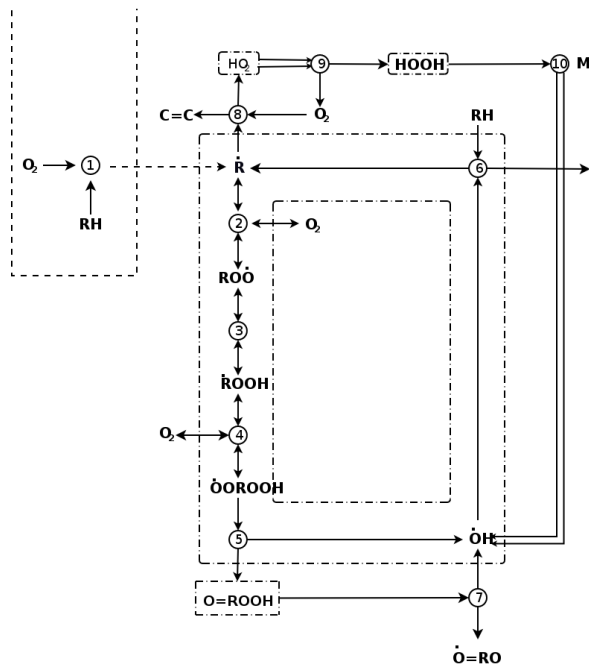


Figure 1: Schematic of reaction sequence for alkane combustion

The associated reaction equations for steps 2 through 7 are:

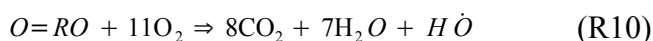
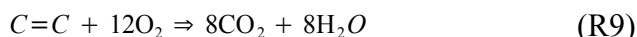


Reactions R2 through R6 are highly exothermic with a  $\Delta H$  of -107.7 kcal/mol, causing a rapid temperature rise during the low temperature cycle. At higher temperatures, the olefin producing reaction



becomes faster than R2 and the high temperature cycle becomes active. R1, R7, R8, and the hydrogen peroxide producing reaction  $HO\dot{O} + HO\dot{O} \Rightarrow HOOH + O_2$  comprise the high temperature cycle which is barely exothermic with a  $\Delta H$  of only -5.4 kcal/mol. The low exothermic yield of the high temperature cycle results in a slow temperature rise, eventually reaching the range where the reaction  $(M) + HOOH \Rightarrow H\dot{O} + H\dot{O} + M$  becomes important, and the chain branching phase begins.

This mechanism was originally developed for a study focused on the ignition phase of alkanes and did not include the chemistry for the system to achieve equilibrium. The mechanism has been adapted in more recent work [20,21] to include the necessary reactions for the system to relax to a constrained stable equilibrium. Specifically, a system of reactions to model  $H_2$  and  $CO$  oxidation, included with the original CHEMKIN II package, has been included as well as the following global reactions:



Reaction 9 (R9) is included in both the detailed kinetic model and the RCCE model. Since the species in reaction 10 (R10) are only constrained through the elemental constraints, reaction 10 is not part of the RCCE calculation, and is, therefore, omitted from the RCCE model. The total number of reactions used for the two different types of calculations are 29 in the RCCE model and 38 in the detailed kinetic model.

### 4.3 Calculation Results

Figure 2 compares the temperature evolution data generated by the RCCE and detailed kinetic models for iso-octane in  $O_2$ , at different initial pressures. In each case  $T_i = 900K$ , and  $\phi = 1.0$ . Agreement between the RCCE and detailed kinetic models is excellent at all pressures, but improves as pressure increases. Another noteworthy feature is decrease in the slope of the curve, during the high temperature run-up, as pressure increases.

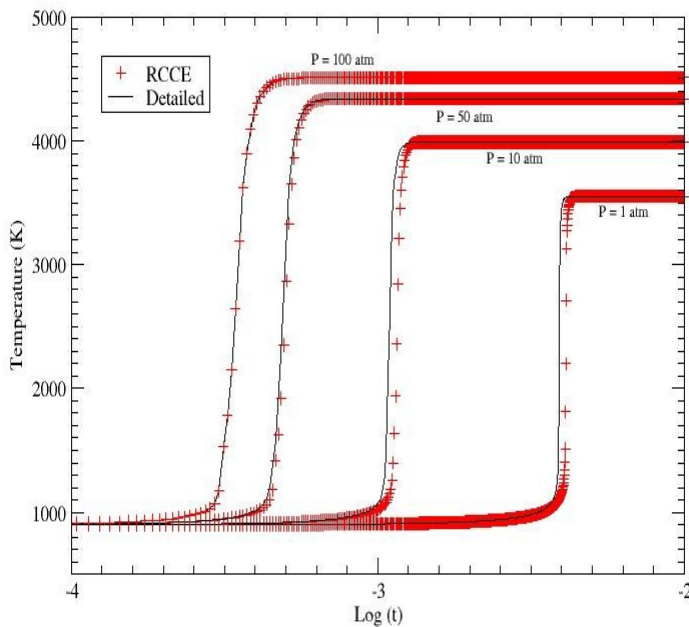


Figure 2: Temperature history plots for  $T_i = 900\text{K}$ ,  $P_i = 1, 10, 50$  and  $100$  atmospheres

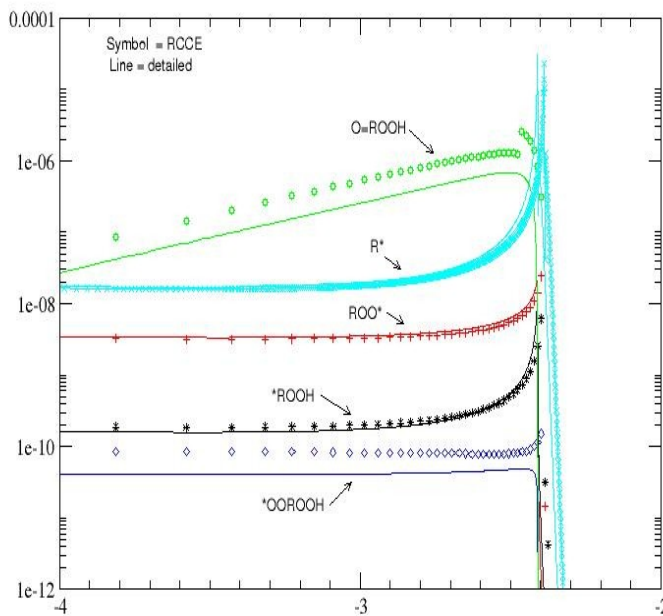


Figure 3: Group 1 specie plot:  $T_i = 900\text{K}$ ,  $P_i = 1$  atm

Figures 3, 4 and 5 show the evolution of important groups of species for RCCE and detailed kinetic calculations with an initial temperature and pressure of 900K and 1 atmosphere.

The highly exothermic reactions producing the fuel radical and the fuel radical peroxides (the FRP group) drive the low temperature part of the reaction cycle. Figure 3 shows the evolution of the FRP species— at one atmosphere— beginning with the mildly exothermic high temperature portion of the cycle where they are in equilibrium. The rate limiting reaction R7 creates a bottle neck, suppressing the production of the FRP group and allowing  $O=ROOH$  to accumulate until the temperature gets high enough for R7 to proceed more rapidly. The rapid drop in the amount of  $O=ROOH$  coincides with an increased production of the highly exothermic FRP group and causes a corresponding rapid increase in temperature and propelling the system into the chain branching phase. Agreement between the RCCE and detailed kinetics calculations is very good with minor differences in the amounts of  $OOROOH$  and  $O=ROOH$ . In each case, RCCE is predicting a larger number of moles of the species. Since the reactions for these species are in both models, and the rates are identical, the difference can be attributed to the additional requirement for equilibrium in the RCCE model.

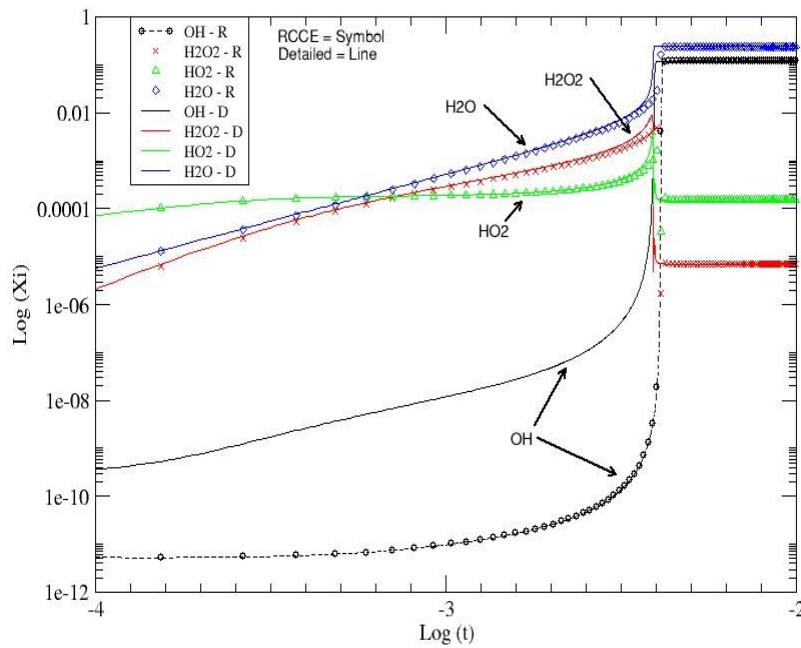


Figure 4: Group 2 specie plots for  $T_i = 900K$ ,  $P_i = 1 atm$

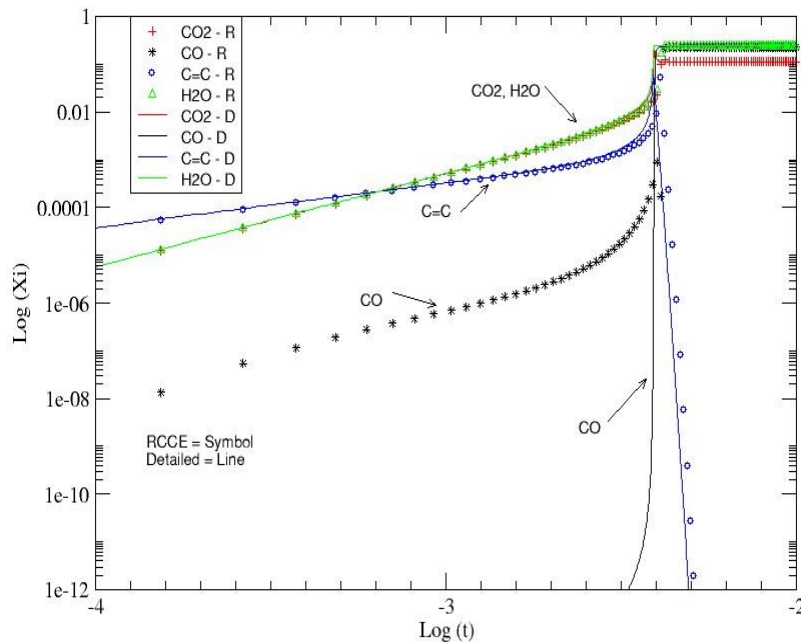


Figure 4 shows the populations of the important radicals  $OH$  and  $HO_2$ , hydrogen peroxide,  $H_2O_2$ , and the end products  $H_2O$ ,  $CO$  and  $CO_2$ . Once again, the overall agreement between the two models is very good with the exception of the predicted amounts of  $OH$ .

Both models show  $HO_2$  to be roughly in equilibrium throughout the high temperature portion of the cycle and increasing amounts of  $H_2O$  and  $H_2O_2$ . The amount of  $H_2O$  is probably artificially high due to the global reaction R10. The discrepancy in the amounts of the  $OH$  radical are the result of there not being a constraint on  $OH$  in the RCCE model. Of the eight reactions that do not change a constraint (see the  $b_{ij}$  matrix in table 3), and are omitted from the RCCE calculation, six involved the production or consumption of  $OH$ . However, the built in requirement for equilibrium in the RCCE calculation produces a credible history even without rate expressions.

The evolution of the olefin, and the end products  $CO$ ,  $CO_2$  and



$H_2O$  are displayed in Figure 5. Again, the RCCE and detailed kinetic models are seen to be in excellent agreement, except in the case of the  $CO$  which is predicted by the RCCE calculation to be steadily increasing with a slope similar to the  $CO_2$  while the detailed kinetic calculation shows the  $CO$  as being near zero and then rising suddenly near the end of the calculation. This behavior can also be attributed to the global reaction R10 which results in the production of artificially large amounts of  $H_2O$  and  $CO_2$ . In the detailed calculation, aside from a global reaction, the only mechanism for  $CO$  generation is the reaction  $CO + O + M \rightleftharpoons CO_2 + M$  which will only occur at high temperatures. In the RCCE model, a similar  $CO/CO_2$  imbalance is introduced by the global reaction. However, the equilibrium requirement in the RCCE model causes the  $CO$  concentration to remain at a credible level, with a slope that is close to the  $CO_2$  and  $H_2O$  values.

## 5. Concluding Remarks

The constant volume, constant energy calculation of the combustion kinetics of iso-octane in  $O_2$  were conducted using a reduced chemical mechanism in a detailed kinetic calculation and a Rate Controlled Constrained Equilibrium calculation. The same reaction rates were used for both models. The calculations were made for stoichiometric conditions with an initial temperature of 900K and initial pressures of 1, 10, 50, and 100 atmospheres. The RCCE and detailed kinetic models showed excellent agreement overall with nearly identical ignition delay times for each pressure. Comparisons between the two models of the predicted histories of selected species at 1 atmosphere showed very good agreement with two notable exceptions: the evolution of  $CO$  and  $OH$ . Both discrepancies are attributed to global reactions used in the mechanisms. It is seen that the RCCE method, and its built in ability to maintain system equilibrium—with or without a reaction mechanism—results in superior performance overall when compared with the detailed kinetic technique. Other unique features of the RCCE method, including the potentially significant improvements in computational efficiency and the method for constraint selection are discussed.

Studies have also been conducted with n-heptane using the same reduced chemical mechanism described above and the RCCE and detailed kinetic calculations. The results for the heptane calculations are similar in all aspects to the ones presented here for iso-octane.

## 6. Acknowledgments

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