Rate-Controlled Constrained-Equilibrium Calculations of Methane–Oxygen Kinetics Using Reduced Chemistry

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ABSTRACT: According to the underlying concept of the rate-controlled constrained-equilibrium (RCCE) method, the relaxation of a complex reacting system towards the final equilibrium state is governed by a set of active and passive constraints imposed by the internal dynamics of the system, which is considerably smaller in dimension than the original system. A set of 12 constraints, able to accurately model the dynamic evolution of the methane oxidation over a wide range of initial temperatures and pressures is proposed. Based on rational analysis of the important rate-limiting steps a further reduced set is obtained, which when is used in conjunction with RCCE is able to give excellent predictions for dynamic evolution of the system at low temperatures at different pressures. Some salient features of RCCE are explored and the RCCE method is proposed as a physics-based, rational alternative approach for the conventional detailed kinetics. The kinetic scheme involves only C_1 chemistry and comprises 132 reactions along with 29 species without nitrogen chemistry.

Keywords: Rate-Controlled Constrained-Equilibrium (RCCE) Method, Maximum-Entropy Principle, C_1-Chemistry, Reduced Chemistry.

NOMENCLATURE

C_i = i^{th} constraint
N_j = Number of moles of species j
N_c = Total number of constraints
N_s = Total number of species
V = Volume
R = Universal gas constant
T = Temperature
h_j^0 = Enthalpy of species j
s_j^0 = Entropy of species j
μ_j^0 = Standard Gibbs free energy of species j
g = Constraint potential

1. INTRODUCTION

The development of models for describing the time evolution of chemically reacting systems is a fundamental objective of chemical kinetics. The conventional approach to this problem involves (1) specifying the state and species variables included in the model, (2) compiling a “full set” of rate-equations for these variables, and (3) integrating this set of equations to obtain the time-dependent behaviour of the system. Such calculations are frequently referred to as “comprehensive” or “detailed kinetics”. However, detailed kinetics of hydrocarbon systems can easily grow to thousands of chemical species and isomers, and millions of reactions. Consequently, "detailed" solution is difficult, if not impossible to achieve. The gravity of this problem is even more apparent when considering reacting turbulent flows where the effort required to resolve the complexity of turbulence is similar to that required for the determination of the chemistry.

Several powerful methods for simplifying the chemical kinetics calculations for large chemical systems have been developed over the past couple of decades, which are based on the physico-mathematical considerations of the dynamical evolution of the system. Works on intrinsic low dimensional manifolds (ILDM) [1], computational singular perturbation (CSP) [2], the so-called adaptive chemistry [3] and the Rate-Controlled Constrained-Equilibrium (RCCE) method [4], on which we will focus in this work, are the most prominent.

The RCCE method, originally proposed by Keck and Gillespie [4] and later developed and applied to different cases by Keck and co-workers [5-9], is based on the maximum-entropy principle of thermodynamics and involves the fundamental observation that slow reactions in a complex reacting system impose constraints on its composition, which control the rate at which it relaxes to chemical equilibrium, while the fast reactions equilibrate the system subject to the constraints imposed by the slow reactions. Consequently, the system relaxes to chemical equilibrium through a sequence of constrained-equilibrium states at a rate controlled by the slowly changing constraints.

A major advantage of the RCCE method over the above-mentioned simplifying methods is that it is unnecessary to start with a complete reaction model that must be then simplified by various approximations. Instead, one starts with a small number of constraints to which more can be systematically added to improve the accuracy of the calculations, to any desired level. In the limit where the number of constraints equals the number of species specified for a system, the method becomes similar to an exact calculation with the important caveat that the equilibrium requirement must be satisfied at each time step. However, as with all thermodynamic systems, the number of constraints necessary to describe the state of the system within measurable accuracy is in general very much smaller than the number of species in the system. In addition, reactions that do not change any constraint do not affect the evolution of the system. Thus, only the rates of slow reactions which change the constraints are required and these are the ones most likely to be known.

Reduction of the system of reactions for different reduced mechanisms can be trivially obtained subject to different sets of constraints. However, the careful and informed selection of constraints is the key to the successful implementation of RCCE which requires careful examination of the underlying chemistry.

In this study, we consider the stoichiometric oxidation of methane with pure oxygen over a wide range of initial temperatures (900K-1500K) and pressures (1atm-100atm) in a constant volume reactor. The kinetic scheme involves only C_1 chemistry and comprises 132 reactions along with 29 species without nitrogen chemistry. Based on a careful examination of the chemistry of oxidation, a set of 12 constraints have been determined which are capable of exactly reproducing the results from a detailed kinetic calculation, with the set of 132 reactions, over the specified range of initial conditions.

The application of the RCCE method will result in a reduction of the system through the elimination of reactions that do not change a constraint, and are, therefore, in equilibrium. This results in an initial reduction of the system to 111 reactions. In principle, only one reaction is needed for each constraint to achieve the correct final equilibrium state, and the reaction chosen for each constraint should be the fastest one from the group of reactions which change the constraint. However, a single reaction for each constraint may not, in general, predict the correct evolution of the system. In this work, 18 reactions and 15 species provide an excellent match with the ignition delay times from the detailed kinetic calculation based on 132 reactions. The importance of these drastic reductions will be underscored when dealing with situations involving reacting gas dynamics such as detonation studies, homogeneous combustion in gas turbine engines [10], etc.

2. RATE CONTROLLED CONSTRAINED EQUILIBRIUM METHOD

2.1. DIFFERENT FORMULATIONS

The Rate Controlled Constrained Equilibrium (RCCE) method can be implemented in three different formulations, that have been explored to various extents by our research group over the past decade. The first method is based on the direct integration of the constraints and the determination of their values at each time step. The results of such calculations have to be coupled with a generalized equilibrium program (GNASA or GSTANJAN) to determine the constrained-equilibrium state of the system as a function of time [6]. This method has been proved to be inefficient and time consuming [6]. The second method is based on integration of the constraint factors which proved to be superior to the first method [7]. The third approach involves the direct integration of the constrained potentials conjugate to each constraint. This method was originally proposed by Keck in a review paper [11] and explored and implemented in later works [12-13]. There have been recently published similar formulations and, in some respects, extensions in literature [14,15].

2.2. RATE CONTROLLED CONSTRAINED EQUILIBRIUM IN CONSTRAINT-POTENTIALS FORM

The detailed formulation of RCCE in constrained-potential form can be found in earlier works [9,12,13]. So we avoid repeating the procedure in detail here and address important points. In the present work, as well as all previous applications of RCCE method, the constraints imposed on the system by the reactions have been assumed to be a linear combination of the mole number of the species present in the system,

$$C_i = \sum_{j=1}^{ns} a_{ij} N_j,\ i=1,\ldots,Nc \qquad (1)$$

where a_{ij} is the value of the i^{th} constraint for the j^{th} species and N_c is the number of constraints. The constrained-equilibrium composition of a system found by maximizing the entropy or minimizing the Gibbs Free Energy subject to a set of constraints using the method of LaGrange multipliers is

$$N_j = (V/RT)\exp(-m_j^0 - \sum_{i=1}^{nc} a_{ij} g_i),\ j=1,\ldots,Ns \qquad (2)$$

where $m_j^0 = (h_j^0 - Ts_j^0)/RT$ is the standard Gibbs free energy of species j and g_i is the constraint potential (LaGrange multiplier) conjugate to the constraint i. N_s is also the number of species in the system. Upon solving the differential equations governing g_i vector, the constrained-equilibrium composition of the system can be found from eqn. 2 at each time step.

3. SELECTION OF CONSTRAINTS

The selection of appropriate constraints is the key to the successful application of the RCCE method. Among the general requirements for the constraints are that they must (1) be linearly independent combinations of the species mole numbers, (2) include the elements, (3) determine the energy and entropy of the system within experimental accuracy, and (4) hold the system in the specified initial state. In addition, they should reflect whatever information is available about rate-limiting reactions controlling the time evolution of the system. After a thorough examination of the oxidation chemistry of Methane at low temperatures-high pressures (knock related applications) and high temperatures-low pressures (flame propagation applications) the following set of constraints were identified:

EC, EO, EH (elemental carbon, oxygen and hydrogen respectively), M (total number of moles), FO (moles of free oxygen, defined as any oxygen not directly attached to another oxygen), FV (moles of free valence, defined as any unpaired valence electron), FU (Fuel Molecule, CH_4), FR (Fuel Radical, CH_3), OHO (O+OH), PEROXY ($CH_3OO+CH_3OOH+CH_2OOH$), ALC ($CH_3O+CH_3OH+CH_2OH+CH_2O$), CO (CHO+CO)**.**

It should be noted that if only the elements are used as constraints, the RCCE method is identical to the element potential method used by STANJAN [18] to calculate the chemical equilibrium composition of a system, while if the number of independent constraints equals the number of species in a system the RCCE method is equivalent, in degrees of freedom, to the detailed kinetics approach. It is certainly true that our current ability to model systems using constraints as unknowns is not as well developed as our ability to model systems using species. However, just the fact that so little is known about the chemical kinetics of the rate-controlled constrained-equilibrium states makes this topic such a promising area of research.

4. RESULTS AND DISCUSSIONS

4.1. REACTOR MODEL

Auto-ignition of combustible charges is one of the most basic combustion processes, and determining the chemical kinetic mechanism involved has been a major goal of combustion research for the past half century [16]. The importance of such analysis relates back to strictly kinetically-controlled processes such as engine knock [16,17] and newly increased interest in distributed combustion in gas turbines to reduce the pollution and engine susceptibility to combustion instabilities [10]. For these reasons we have employed a constant volume, constant energy reactor in this study. The time dependent dynamics of the system are determined by N_c equations for constraints and one energy equation, totalling N_c+1 overall. These equations were integrated using DDASSL [19].

Studies include temperatures as low as 900K up to 1500K and pressures as low as 1 atm up to 100 atm. The low temperature-high pressures results are relevant to "knock" applications whereas the high temperature-low-to-high pressures results are of interest to both flame-propagation and distributed (flameless) combustion applications.

4.2. KINETIC MECHANISM

The kinetic mechanism used in this study is based on the scheme used in [8], and includes 132 reactions with 29 species

(Table 1). Twenty species and 102 reactions were taken from GRI-Mech 3.0 [20] and 9 species along with 30 additional reactions from [21] and estimations by authors.

Table1: List of species involved in the model.

H, H_2, HO_2, H_2O_2, OH, H_2O, O, O_2, C, CH, CH_2, CH_3, CH_4, CH_3O, CH_2OH, CH_3OH, HCO, H_2CO, CH_3OO, CH_2OOH, CH_3OOH, OCHO, HOCO, HOCHO, OOCHO, HOOCO, HOOCHO, CO, CO_2.

4.3. LOW TEMPERATURE - HIGH PRESSURES

Time-dependent temperature profiles of stoichiometric mixtures of methane and oxygen at different pressures are shown in fig.1.

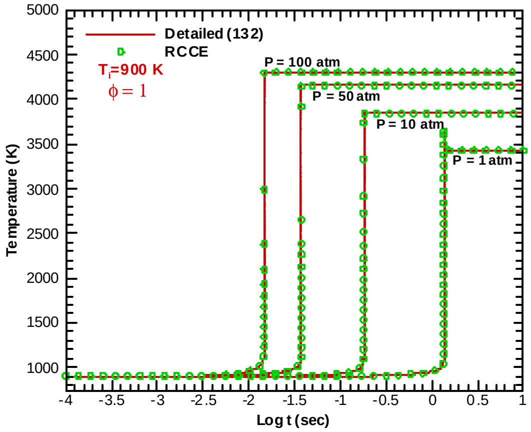

Fig.1: temperature profiles at different pressures for initial stoichiometric mixture of fuel and oxidizer.

The mixture's initial temperature is 900 K. A set of 12 constraints has been used. The set includes EO, EC, EH, FV, FO, M, FU, FR, OHO, PEROXY, ALC and CO. The definition of these constraints can be found in section 3. Clearly, the set of chosen constraints yields excellent results over the entire range of pressures and are able to capture the dissociation effects relevant at low pressures which are reflected in the overshoot above the final equilibrium temperature. From the full set of 132 reactions, referred to as Detailed (132), 21 reactions do not change any constraints, and are, therefore, in equilibrium. These reactions are redundant.

The time-dependent histories of the species for a stoichiometric mixture at initial temperature of 900K and initial pressure of 100 atm are also shown on log-log plots in fig.2–fig.4. Clearly, the agreement is extremely good.

Fig.2 shows that during the early stages of ignition, CH_3 and HO_2 are the dominant radicals in the radical pool with CH_3OO playing a minor role.

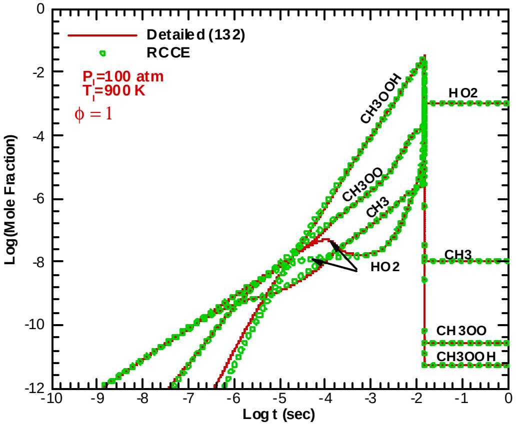

Fig.2: Profiles of CH3, CH3OO and CH3OOH versus time at initial pressure of 100 atm and initial temperature of 900 K

This is a consequence of the initiation reaction, being the only active reaction during this period that converts CH_4 into CH_3 and O_2 into HO_2;

R.1 $CH_4+O_2=CH_3+HO_2$

R.1 is an endothermic reaction and is, therefore, slow. The next important attacks on the fuel molecule are by the newly-generated HO_2 radicals through

R.2 $CH_4+HO_2=CH_3+H_2O_2$

which does not change the generalized constraints of FO, FV and M but converts fuel into the fuel radical. The Methyl radicals react readily with oxygen to form the corresponding Methylperoxy radicals,

CH_3OO, which most probably abstract hydrogen from the fuel molecules and form the Methylhydroperoxide, CH_3OOH:

R.3 $CH_3+O_2+M=CH_3OO+M$

R.4 $CH_3OO+CH_4=CH_3OOH+CH_3$

R.3 is an important source for the generation of Methylperoxy radical, particularly at high pressures, because of increased collision frequency. The rate-limiting bimolecular counterpart of R.3 produces free oxygen through

R.5 $CH_3+O_2=CH_3O+O$

Other important rate-limiting steps for formation of free oxygen are

R.6 $CH_3+HO_2=CH_3O+OH$

R.7 $CH_3+O_2=CH_2O+OH$

R.7 is a four-center reaction and is very slow. The O and OH radicals generated here quickly go to water through:

R8 $O+CH_4=CH_3+OH$

and

R.9 $OH+CH_4=CH_3+H_2O$

which are both very fast and, thus, keep the concentrations of O and OH very small. R.9 is the major route for early water formation shown in fig. 3.

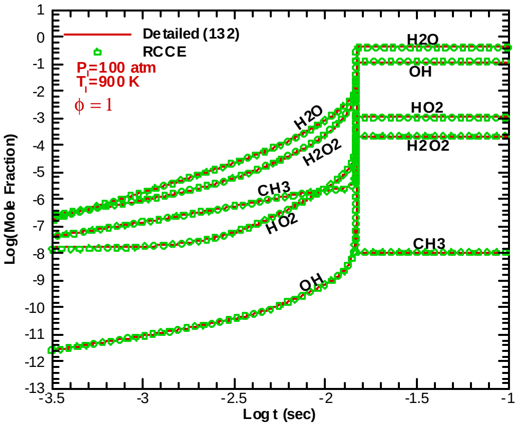

Fig.3: Profiles of the most important H2-O2 system at initial pressure of 100 atm and initial temperature of 900 K

Among the steps involving HO_2, other than those mentioned above, the followings steps are of more importance:

R.10 $HO_2+HO_2=H_2O_2+O2$

R.11 $H+O_2+M=HO2+M$

The generated H_2O_2 breaks on the weak O-O bond and produces free oxygen by converting to OH:

R.12 $H_2O_2+M=OH+OH+M$

The other important steps involve conversion of the intermediate species CH_3O and CH2O down to CO, which are listed in table 2. The time-dependent evolution of the major stable species and HCO radical are shown in fig.4

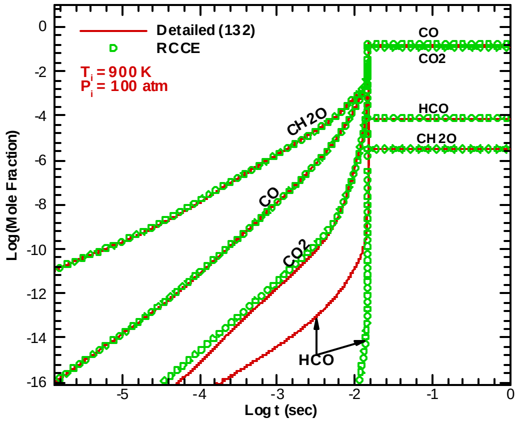

Fig.4: Profiles of CO, CO2 and CHO versus time at initial pressure of 100 atm and initial temperature of 900 K

4.4. REDUCED REACTION SET

Based on the above observations of the important steps of the ignition mechanism a reduced set of 18 reactions, table 2, is obtained which when is used in conjunction with RCCE is able to give perfect predictions for ignition delay times at both low and high pressures. The low pressure results are shown in (fig. 5)

The real value of RCCE becomes evident when comparing the results of such reduced reactions, based on observations of fundamental chemical processes, with RCCE against the detailed kinetics calculations with the full mechanism comprising 132 reactions (fig. 5).

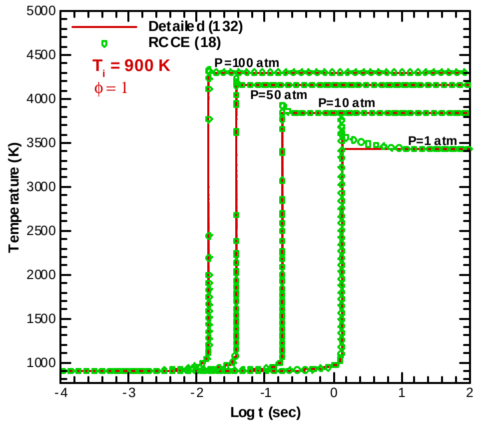

Fig.5: RCCE predictions of temperature profiles at different pressures using the reduced reaction list (table 2) compared with the detailed kinetics predictions using the original 132 reactions.

							M	FU	FR	PEROXY	FO	ALC	OHO	CO	FV
1	CH3	+ O2	+ M	=	CH3OO	+ M	-1	0	-1	1	0	0	0	0	0
2	OH	+ OH	+ M	=	H2O2	+ M	-1	0	0	0	-2	0	-2	0	-2
3	H	+ O2	+ H2O	=	HO2	+ H2O	-1	0	0	0	0	0	0	0	0
4	CH3	+ CH2O	+	=	CH4	+ HCO	0	1	-1	0	0	-1	0	1	0
5	CH4	+ O2	+	=	CH3	+ HO2	0	-1	1	0	0	0	0	0	2
6	CH4	+ OH	+	=	H2O	+ CH3	0	-1	1	0	0	0	-1	0	0
7	CH3OO	+ CH4	+	=	CH3OOH	+ CH3	0	-1	1	0	0	0	0	0	0
8	CH4	+ HO2	+	=	CH3	+ H2O2	0	-1	1	0	0	0	0	0	0
9	CH3	+ O2	+	=	CH3O	+ O	0	0	-1	0	2	1	1	0	2
10	CH3	+ HO2	+	=	OH	+ CH3O	0	0	-1	0	2	1	1	0	0
11	CH3	+ O2	+	=	CH2O	+ OH	0	0	-1	0	2	1	1	0	0
12	CO	+ HO2	+	=	CO2	+ OH	0	0	0	0	2	0	1	-1	0
13	O2	+ H	+	=	OH	+ O	0	0	0	0	2	0	2	0	2
14	CH2O	+ OH	+	=	H2O	+ HCO	0	0	0	0	0	-1	-1	1	0
15	CH2O	+ O2	+	=	HCO	+ HO2	0	0	0	0	0	-1	0	1	2
16	CH2O	+ HO2	+	=	HCO	+ H2O2	0	0	0	0	0	-1	0	1	0
17	CH3OO	+ HO2	+	=	CH3OOH	+ O2	0	0	0	0	0	0	0	0	-2
18	HO2	+ HO2	+	=	H2O2	+ O2	0	0	0	0	0	0	0	0	-2

Table 2: Reduced Mechanism

The results of the RCCE calculations with the 18-reaction set, referred to as RCCE (18), are compared against detailed calculations using the full mechanism referred to as Detailed (132). All RCCE calculations reach the correct final state, although at low pressures additional legitimate recombination reactions have to be included in the reduced model.

The effect of such reactions is effectively felt during the burning time, when the energy released acts to dissociate some of the newly-formed species and reduce the temperature. This is equivalent to saying these reactions shorten the relaxation time of the system to its final equilibrium state at low pressures.

It is also of interest to see how the RCCE calculations with the reduced set, RCCE (18), compares against the detailed calculations with the same reduced reactions, referred to as Detailed (18). Fig. 6 represents such comparison.

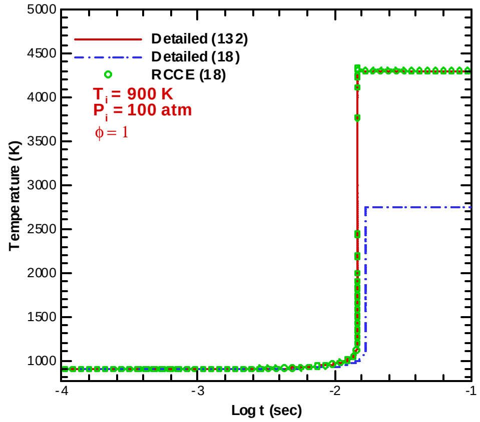

Fig.6: RCCE predictions of the temperature profile using the reduced reaction mechanism, RCCE(18), compared with the detailed kinetics using the original 132 reactions, Detailed (132), and the detailed kinetics using the same reduced reaction mechanism, Detailed (18)

Clearly, the later one does have problem in achieving the correct final equilibrium state.

In the detailed kinetic approach, the set of chemical species is explicitly defined by the mechanism (set of reactions), i.e. no information is available for non-participating species. Conversely, in the RCCE approach, the amount of any constituent can be found from eqn. 2, which can be seen to be a function of the Gibbs free energy of the species, the constraint potentials, and the $a_{i,j}$ matrix. The $a_{i,j}$ matrix expresses the relationship between the species and the specified constraints. It can be immediately seen that any species represented in the $a_{i,j}$ matrix will evolve dynamically even if there is no kinetic path provided in the mechanism. This guarantees the achievement of the correct final equilibrium state.

Fig.7 confirms this notion, as H_2 is clearly not included in the reduced reaction list, yet its evolution is accurately predicted by RCCE. It also achieves the correct final equilibrium state. This feature uniquely distinguishes RCCE from *all* other methods available for kinetics modelling: *the built in requirement to achieve the correct final equilibrium state independently of the reaction paths of the species*. This distinct character of RCCE enables one to have a very good estimate of the kinetic behaviour of the system through very small number of legitimate kinetic steps and avoiding estimating about the uncertain fast steps.

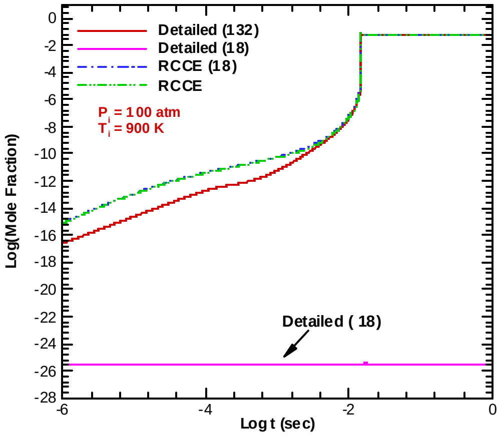

Fig. 7: RCCE predictions of the H_2 concentration using the full mechanism (RCCE) compared against RCCE using the reduced reaction list (RCCE (18)), detailed calculations using the same reduced list (Detailed (18)) and the detailed kinetics using the full mechanism (Detailed (132)). Note that H_2 is not included in the reduced reaction mechanism.

Based on these observations, another salient feature of RCCE is that the number of reactions could be as small as one reaction for each constraint in order for the system to go to the correct final equilibrium state. However, a single reaction for each constraint may not, in general, predict the correct evolution of the system and, therefore, more reactions can be added to have more accurate predictions of the dynamic evolution of the system. This is so that the list of species, depending on the complexity of the reacting system, could be, indeed, endless. With regard to the above-mentioned points, we propose RCCE as an alternative approach for the conventional detailed kinetics method in combustion treatment.

4.5. HIGH TEMPERATURES

RCCE calculations of the high-temperature ignition problem were performed with the first 11 constraints in conjunction with the full mechanism. The sample result of such calculations is shown in fig. 8. Predicted temperature profiles are in excellent agreement with the detailed calculations.

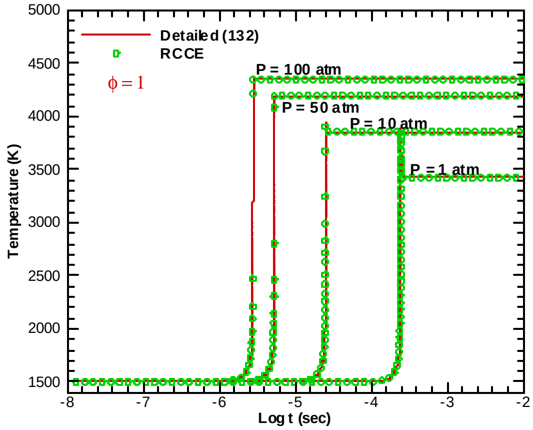

Fig.8 High-temperature results for a stoichiometric mixture at T_i=1500K and different initial pressures. The first 11 constraints have been used to carry out the calculations.

5. CONCLUSION

RCCE calculations of methane oxidation over a wide range of initial temperatures and pressures have been made using 12 constraints and 132 reactions and good agreement with “detailed” calculations using 29 species and 132 has been obtained. In addition a reduced set of 18 reactions has been identified which when employed in the RCCE calculations gives results identical to those obtained using the full 132 reactions.

Among the unique features that distinguish the RCCE method from all other methods available for kinetics studies are: 1) it enables one to obtain a good estimate of the kinetic behaviour of a complex chemically reacting system using a relatively small number of known reactions thus avoiding the necessity of having to estimate the rates of a large number of uncertain fast reactions, 2) the entropy always increases as the system evolves and an approach to the correct final equilibrium is guaranteed,. 3) an estimate of the concentrations of any species for which the standard Gibbs free energy is known can be obtained even though the species is not explicitly included in the reaction set used, 4) the accuracy of the results can be systematically improved by adding reactions on at a time, and finally 5) it is based on the well established Maximal Entropy Principle of thermodynamics rather than mathematical approximations.

5. ACKNOWLEDGMENT

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