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Kinetic analysis of mechanisms of complex pyrolytic reactions

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Abstract

Detailed reaction mechanisms are available for the description of the pyrolysis of many compounds. These mechanisms may consist of hundreds of species and thousands of reactions. Effective analysis of large reaction mechanisms includes uncertainty analysis, which provides information on the reliability of the mechanism and reaction flux analysis, which facilitates the chemical understanding of the process. Reduction of large mechanisms may include the detection and elimination of redundant species and reactions. Another branch of methods, like the QSSA, ILDM, or repro-modelling utilize the very different timescales that are usually present in chemical kinetic systems.

The methane pyrolysis mechanism of Dean et al. containing 1604 irreversible reactions of 189 species was investigated at atmospheric pressure and 1100 K temperature. According to uncertainty analysis, for this system the rate coefficients of all crucial reaction steps are relatively well known. This mechanism was reduced to 338 reactions of 62 species, which could be simulated 11.5 times faster, while the calculated concentration profiles of the main products remained almost identical. Dimension analysis revealed that the process could be modelled by a system of differential equations having 18 variables only. These results were obtained using computer codes KINALC, MECHMOD and Flux Viewer, which are freely available through the Web. © 2006 Published by Elsevier B.V.

Keywords: Complex reaction mechanisms; Uncertainty analysis; Reaction fluxes; Reduction of mechanisms; Quasi-steady-state approximation; Dimension analysis

1. Introduction

The primary aim of most recent research in applied and industrial chemistry is to contribute to the protection of the environment. Environmental friendly design and control of chemical processes means that fewer pollutants are produced and fewer by-products are formed. To achieve it, very detailed knowledge of chemical processes is needed. The ultimate level of information is when the process is described by a detailed reaction mechanism. Such reaction mechanisms are available for many important processes. These may contain several thousand reactions of several hundred species, and the parameterised temperature and pressure dependence of all rate coefficients.

Large reaction mechanisms are usually utilized in the following three steps. First, the detailed reaction mechanism is created and validated using all available experimental information. The next step should be the analysis of the mechanism and a characterization of the limits of its application. Simulation

of a large reaction mechanism might consume too much computer time, when applied for real-time process control or in a computational fluid dynamics (CFD) code that simulates a complex flow field. Therefore, the final step can be the reduction of the reaction mechanism to an almost equivalent smaller computation model. This paper does not deal with the creation of a detailed reaction mechanism, but discusses possible ways for the analysis and reduction of such mechanisms.

2. Computer codes for the simulation and analysis of gas kinetic mechanisms

Probably the CHEMKIN-II package [1] made the highest influence on the simulation of gas kinetic processes. This package was made in the SANDIA National Laboratories and it was distributed as a freeware till 1995. The CHEMKIN package consists of not only a collection of Fortran codes but also thermodynamic and transport databases. The package includes a series of simulation programs for various frequently applied conditions and a collection of utility subroutines for the calculation of thermodynamic and chemical kinetic quantities. The CHEMKIN project was later taken over by the Reaction Design, Inc. [2], which released the CHEMKIN 3.x, and

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CHEMKIN 4.x versions. The “CHEMKIN format” became a standard for the representation of high temperature gas kinetic mechanisms, used also by other simulation codes.

KINALC [3] is a program that was created for the analysis of gas kinetic mechanisms. It was written as an extension to the CHEMKIN-II package and can be used for the analysis of CHEMKIN-format mechanisms. KINALC is not applicable for carrying out simulations, but can read the concentrations and sensitivities calculated by the CHEMKIN simulation codes. Although it was prepared in accordance with the CHEMKIN-II package, recently it was made compatible also with Chemkin versions 3.x and 4.x. KINALC contains 17 different methods for the analysis of complex reaction mechanisms and a part of these will be discussed in this paper.

KINALC is accompanied by two utility programs. MECHMOD can be used for modification of reaction mechanisms, like changing reversible reaction steps to pairs of irreversible ones, automatic changing of units, elimination of species from the mechanism, and modification of thermodynamic data. FluxViewer is a code for the animation of reaction fluxes. Computer codes KINALC, MECHMOD and FluxViewer are freeware and can be downloaded from the Web [4].

3. Pyrolysis of methane

The various methods for the kinetic analysis of mechanisms of complex pyrolytic reactions will be illustrated on the analysis of a methane decomposition mechanism. Sheng and Dean [5] created a reaction mechanism to simulate the pyrolysis of *n*-butane, and also *n*-butane–steam vapour and *n*-

butane–N₂ mixtures. This mechanism was used to describe the chemical reactions within the anode channel of a solid-oxide fuel cell and it contains 2498 irreversible reactions of 291 species. It was the starting point for the creation [6] of a reaction mechanism to describe the gas-phase reactions of methane and natural gas with air and steam in non-catalytic regions of a solid-oxide fuel cell. This mechanism, containing 6914 irreversible reactions of 349 species, describes both the pyrolysis and the fuel-rich oxidation of methane. The authors of the mechanism, Gupta et al., reported the testing of it against the methane pyrolysis measurements of Back and co-workers [7] (see Fig. 1 in article [6]). We have received a slightly updated version of the mechanism [8]. Since we wanted to use it to describe the pyrolysis and not the oxidation of methane, all oxygen-containing species were removed by MECHMOD. This resulted in a mechanism containing 1604 irreversible reactions of 189 species. From now on, this mechanism will be referred to as the ‘Dean mechanism’ in this paper. Using the Dean mechanism and the SENKIN simulation code of the CHEMKIN-II package, we successfully reproduced Fig. 1 of the Gupta et al. article [6].

The Dean methane pyrolysis mechanism was investigated at the following conditions: the pressure is constant 1 atm, temperature is constant 1100 K, the gas initially contains pure methane and the process is simulated until 2000 s. Analysis and reduction of the mechanism was carried out at 12 reaction times located at 10⁻², 3.6 × 10⁻², 10⁻¹, 3.6 × 10⁻¹ s, etc. These points were selected to be equidistantly spaced in a logarithmic timescale. The calculated concentration–time curves are indicated by solid lines in Fig. 1.

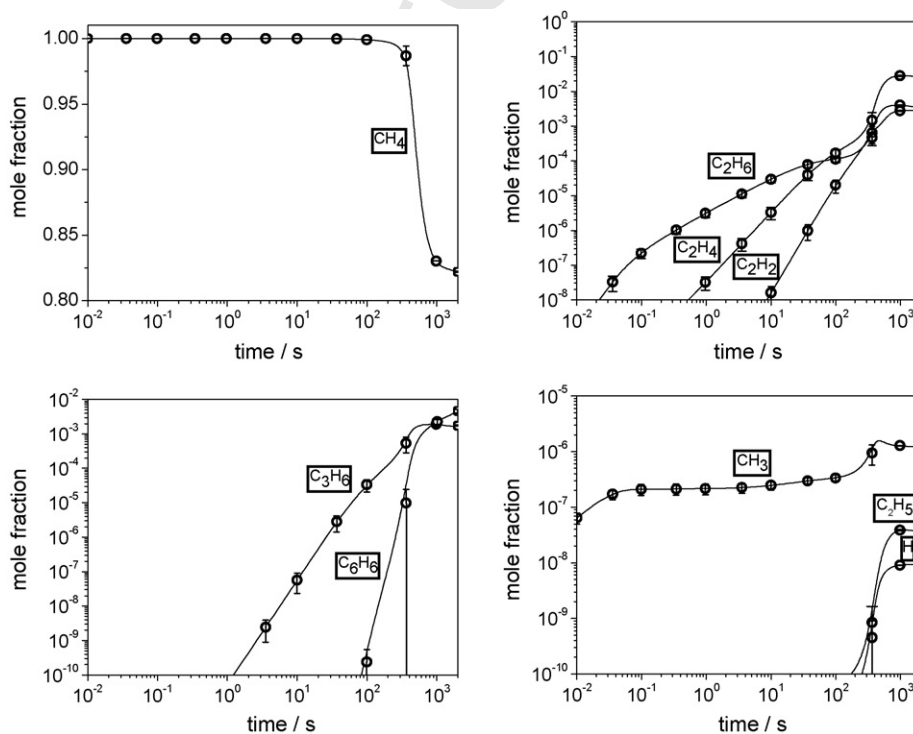


Fig. 1. Calculated concentration–time curves of methane pyrolysis at conditions $X_0(\text{CH}_4) = 1.0$, $T = 1100 \text{ K}$, $p = 1 \text{ atm}$. The solid lines are related to the original Dean mechanism (189 species and 1604 irreversible reactions), while the open circles belong to the reduced mechanism of 62 species and 338 irreversible reactions (see text). The vertical error bars show 1σ uncertainty of the calculated concentrations.

4. Uncertainty analysis: assessment of the reliability of kinetic models

All parameters of models are uncertain causing an uncertainty to the model results. Uncertainty analysis is the common name of a branch of mathematical methods for the calculation of the uncertainty of models. Uncertainty analysis methods, from a practical point of view, can be sorted to three main groups. Using the local uncertainty analysis [9], the uncertainty of only one parameter is investigated at a time. This method is based on partial derivatives and it is computationally very cheap. Using a screening method, like the Morris method [9,10], the effect of changing several parameters simultaneously is investigated in a wide range of parameters. This method requires moderate computer time, but provides only qualitative information on the effect of the uncertainty of parameters.

Global uncertainty analysis methods provide the most information and are computationally the most expensive. Using these methods, all parameters are changed simultaneously, and their joint probability density function (pdf) is taken into account. Examples for global methods are Monte Carlo analysis using Latin Hypercube sampling [9] and the Sobol' method [11].

We have recently published a series of papers on the uncertainty analysis of combustion [12–14] and atmospheric chemical [15–17] systems using a wide range of methods. We found that the method of local uncertainty analysis provided results in good agreement with the more sophisticated global methods in the cases of the investigated chemical kinetic systems.

The first step of uncertainty analysis of chemical kinetic systems is the determination of the uncertainty of rate parameters. Uncertainty factor f_j is given in several data collections [18–22]. This factor is defined in the following way:

$$f_j = \log_{10} \left(\frac{k_j^0}{k_j^{\min}} \right) = \log_{10} \left(\frac{k_j^{\max}}{k_j^0} \right) \quad (1)$$

where k_j^0 is the recommended value of the rate coefficient of reaction j , while k_j^{\min} and k_j^{\max} are the possible minimal and maximal values of k_j , respectively. Assuming that the deviation of $\ln k_j^{\min}$ and $\ln k_j^{\max}$ are 3σ from $\ln k_j^0$, the variance of $\ln k_j$ can be calculated:

$$\sigma^2(\ln k_j) = \left(\frac{f_j \ln 10}{3} \right)^2 \quad (2)$$

Using the rules of error propagation and assuming the independency of rate coefficients, the variance of model result y_i due to the uncertainty of kinetic parameters, denoted by $\sigma_{K_j}^2(y_i)$, can be calculated:

$$\sigma_{K_j}^2(y_i) = \left(\frac{\partial y_i}{\partial \ln k_j} \right)^2 \sigma^2(\ln k_j) \quad (3)$$

$$\sigma_K^2(y_i) = \sum_j \sigma_{K_j}^2(y_i) \quad (4)$$

$$S_K \%_{ij} = \frac{\sigma_{K_j}^2(y_i)}{\sigma_K^2(y_i)} \times 100 \quad (5)$$

Here, $\partial y_i / \partial \ln k_j$ is the semi-normalized local sensitivity coefficient, and $S_K \%_{ij}$ is the percentage contribution of parameter j to the variance of model output i . Local uncertainty analysis of chemical kinetic models is encoded to KINALC as option UNC_ANAL.

Local uncertainty analysis of the Dean mechanism was carried out at the conditions given in Section 3. For all reactions that are also present in the Leeds methane oxidation mechanism [4,23], the same uncertainty factors were used as in the article of Zádor et al. [14]. The uncertainty factors of the other reactions were looked for in data collections [18–22], and when not found, these were set to $f_i = 0.5$, which is a typical value for less known reactions. Error bars in Fig. 1 show the calculated 1σ uncertainty of the simulated concentrations. At small reaction times (small conversion of methane) the uncertainties are relatively low and these are also low at high reaction times near the equilibrium. The concentrations of some species (e.g. benzene, hydrogen atom) have significant uncertainties at 360 s, in the time interval of rapid concentration changes. The general picture is rather satisfying because it shows that the calculated concentration profiles have usually small uncertainty. It is recommended in general that all published simulation results should be accompanied with uncertainty calculation to show the reliability of the calculated results.

KINALC calculates not only the uncertainty of model results, but also the percentage contribution of the uncertainty of kinetic parameters to the uncertainty of results according to Eq. (5). Fig. 2 shows contributions $S_K \%_{ij}$ to the uncertainty of methane concentration at 360 s. Reaction $\text{CH}_3 + \text{H}(+\text{M}) \Rightarrow \text{CH}_4(+\text{M})$ gives the main part of the uncertainty, and only 5 reactions of the 1604 reactions contribute more than 5%! Using more accurate rate parameters for these five reactions, more accurate methane concentration could be calculated. The accuracy of the other reaction rate parameters does not influence significantly the calculated CH_4 concentration. Although a great part of the 1604 reaction steps of the mechanism are kinetically not well known, low uncertainty of the simulation results indicate that the reaction parameters that are crucial for the simulation of the concentration profiles of the main products have low enough uncertainty.

5. Rate-of-production and reaction flux analysis

The classic method for the investigation of reaction mechanisms is the rate-of-production analysis (ROPA). Using this method, the contribution of each reaction step to the production rate of each species is monitored at several reaction times. KINALC provides such lists in a detailed (option ROPAD) or in a brief form (option ROPAB). As an example, Fig. 3 shows the main contributions of the reaction steps to the production rate of methane at 360 s. In principle, rate-of-production analysis provides all information that is needed for the analysis and reduction of detailed mechanisms. However,

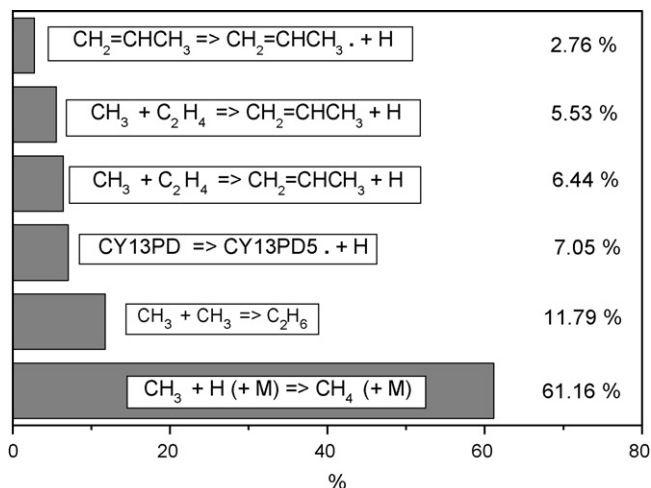


Fig. 2. Relative contribution of the uncertainty of rate coefficients to the uncertainty of the calculated methane concentration at $t = 360$ s. CY13PD denotes cyclo-1,3-pentadiene and CY13PD5 denotes the corresponding radical with a missing H on carbon atom 5.

224 this method provides huge amount of numbers and therefore
225 other methods are more appropriate.

226 Transformation of one species to another is traditionally
227 depicted by reaction flux plots. Such figures frequently appear
228 in textbooks (see, e.g. [24,25]). In the Turns book [25] the
229 reaction flux plot is explained in such a way that each arrow
230 represents an elementary reaction, and the width of an arrow is
231 proportional to the destruction rate of the reactant. However,
232 definition of reaction fluxes should be based on a conserved
233 property, like the number of element atoms in the species. Revel
234 et al. [26] defined the proper calculation of element fluxes and
235 this calculation is encoded to KINALC as option ATOMFLOW.
236 The output of KINALC is the ordered list of element fluxes
237 from one species to another at each reaction time investigated.
238 This information can be interpreted by graphical postprocessor
239 code FluxViewer.

240 FluxViewer is a Java code that puts one label for each
241 species on the screen. These labels can be moved around using
242 the drag-'n'-drop method allowing a proper arrangement of
243

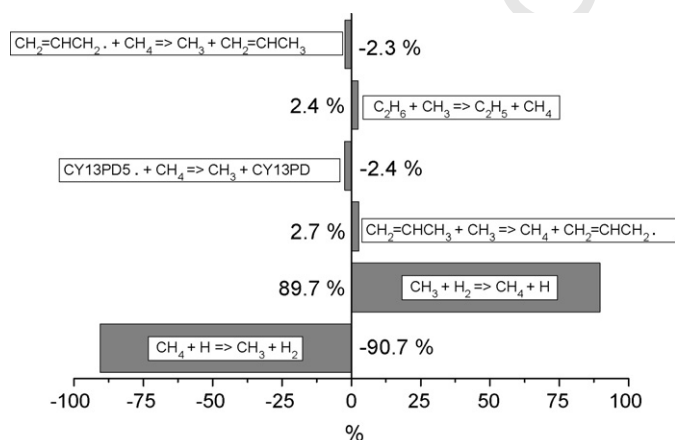


Fig. 3. Contribution of the reaction steps to the production rate of methane at $t = 360$ s.

243 species. The program interconnects the labels with arrows; the
244 widths of the arrows are proportional to the logarithm of the
245 element fluxes. FluxViewer produces movies about the change
246 of fluxes as a function of time, temperature or (in the case of
247 flames) distance. Also, frames from the movie can be saved.
248 Fig. 4 is a frame from the reaction flux movie, which shows the
249 main C-atom fluxes in the Dean mechanism at 360 s.
250

251 6. Elimination of redundant species and redundant 252 reactions

253 Most published reaction mechanisms contain redundant
254 species and reactions, because the authors of the mechanisms
255 are cautious and regularly include marginally important species
256 and reactions. Also, the mechanisms are usually created for a
257 wide range of conditions, while these are utilized in a narrower
258 range of circumstances. Elimination of redundant species and
259 reactions from a mechanism has two benefits: (i) a smaller
260 mechanism is better interpretable from a chemical point of
261 view; (ii) simulation of a smaller mechanism requires less
262 computer time.

263 The aim of chemical kinetic models is to provide
264 information about the concentration of the *important species*
265 or to reproduce some *important features*, like laminar flame
266 velocity. Kinetic models usually include *necessary species* that
267 are not important, but the presence of them is required for the
268 accurate calculation of the concentration of important species
269 and of important features. Any other species present in a kinetic
270 mechanism are *redundant*. A possible algorithm [27] for the
271 detection of redundant species can be based on the inspection of
272 the Jacobian. An element of the normalized Jacobian $(y_i/f_j)(\partial f_j/\partial y_i)$
273 provides information about how the production rate of
274 species j changes if the concentration of species i is perturbed.
275 If the square of changes is summed up for all important species,
276 then the obtained value B_i characterizes the strength of the

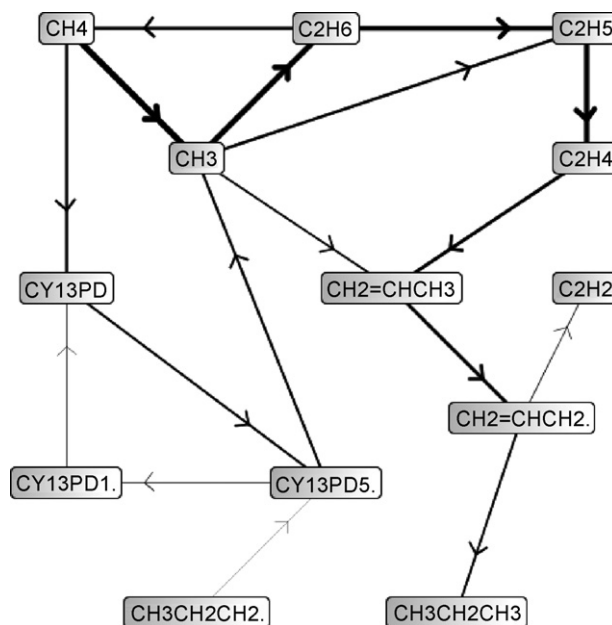


Fig. 4. The main C-atom fluxes at $t = 360$ s.

direct link of species i to the group of important species:

$$B_i = \sum_{j=1} \left(\frac{y_i}{f_j} \frac{\partial f_j}{\partial y_i} \right)^2 \quad (6)$$

Species having high B_i values are closely linked to the important species. In the next step, the species having the highest B_i value is also included into the summation and vector \mathbf{B} is recalculated. This procedure is repeated until a gap appears in the series of the ordered B_i values. Species having B_i values above the gap are closely linked directly or through other species to the important species and these are the necessary species. Because the Jacobian depends on the concentrations, the redundancy of species has to be investigated at several reaction times. A species is redundant, if it is redundant at each time investigated. All consuming reactions of the redundant species can be eliminated from the mechanism. More details about the detection of redundant species are discussed in articles [27,28]. This algorithm is encoded as option CONNECT in KINALC.

A possible method for the reduction of detailed reaction mechanisms is the principal component analysis of the rate sensitivity matrix \mathbf{F} (PCAF method) [29]. Eigenvector–eigenvalue analysis of matrix $\tilde{\mathbf{F}}^T \tilde{\mathbf{F}}$ provides the list of important reactions, where in matrix $\tilde{\mathbf{F}} = \{(k_j/f_i)(\partial f_i/\partial k_j)\}$ index i refers to the important and necessary species. All important reactions have large eigenvector elements in a parameter group characterized by a large eigenvalue. A reaction is redundant, if it is found redundant at each time investigated. Option PCAF of program KINALC allows a quick start for using this method for the reduction of mechanisms.

As a first step, the importance of species was determined by option CONNECT of KINALC. We considered CH_4 and its main decomposition products, C_2H_4 , C_2H_2 , C_3H_6 , and C_6H_6 as important. The necessary species were determined using the method above at each reaction time investigated. All in all, 127 species were found redundant at all reaction times. These species had 618 irreversible reactions; therefore, after the elimination of redundant species and all their reactions the mechanism contained 986 irreversible reactions of 62 species.

In the next step, further redundant reactions were identified using option PCAF of KINALC. The importance of reactions was determined at the same reaction times, and the thresholds for eigenvalues and eigenvectors were 10^{10} and 0.01, respectively. In this step, the number of species remained identical, but the number of reactions decreased radically further to 338. Fig. 1 demonstrates the good agreement between the results of the full mechanism and the reduced mechanism after the elimination of both the redundant species and reactions. The deviation between the two simulation results for the important species is less than 1%.

The original mechanism contained 189 species and 1604 irreversible reactions, while the obtained reduced mechanism contained 62 species and 338 reactions. It is expected that the simulation time is roughly proportional to the square of the number of species, thus $189^2/62^2 = 9.3$ times increase of simulation speed was anticipated. Handling less reactions

allows further savings in computer time and, by comparing the actual CPU times, 11.5 times increase of the simulation speed was measured.

7. Mechanism reduction based on timescales

Elimination of redundant species and reactions from the mechanism resulted in significant savings in simulation time. However, in many practical applications spatially inhomogeneous problems are simulated, occasionally at complex geometries. Therefore, further reduction in computer time is needed that can be achieved on the basis of the existence of very different timescales in chemical kinetic systems.

The traditional mechanism reduction method that is based on timescales is the quasi-steady-state approximation (QSSA). The key of the application of the QSSA is the proper selection of the QSSA-species. Let the original concentration vector \mathbf{y} be split to $\mathbf{y}^{(1)}$ and $\mathbf{y}^{(2)}$, according to the non-QSSA and QSSA-species, respectively. This means that the original Jacobian $\partial\mathbf{f}/\partial\mathbf{y}$ can also be partitioned accordingly, e.g. $\partial\mathbf{f}^{(2)}/\partial\mathbf{y}^{(2)}$ shows the effect of changing the concentration of QSSA-species on the production rate of QSSA-species.

Denote $\mathbf{y}^{(2)}$ the concentration of QSSA-species calculated by the solution of the kinetic system of differential equations and $\mathbf{Y}^{(2)}$ the same concentration set calculated using the QSSA. This means that $\Delta\mathbf{y}^{(2)} = \mathbf{y}^{(2)} - \mathbf{Y}^{(2)}$ denotes the error of the quasi-steady-state approximation. If $\Delta\mathbf{y}_i^{(2)}$ is small, then species i is a good candidate for being a QSSA-species.

Error $\Delta\mathbf{y}^{(2)}$ of the quasi-steady-state approximation can be calculated [30] via solving the following algebraic system of equations:

$$\frac{d\mathbf{y}^{(2)}}{dt} = \mathbf{J}^{(22)} \Delta\mathbf{y}^{(2)} \quad (7)$$

If the QSSA is applied for a single species only, then the corresponding error can be calculated in the following way:

$$-\Delta y_i = \left(-\frac{1}{J_{ii}} \right) \frac{dy_i}{dt} \quad (8)$$

This means that the QSSA error for species i is equal to the product of the lifetime of this species and the production rate of the species [30]. KINALC calculates the QSSA error for a group of species (option QSSAG) and for each species separately (option QSSAS).

The error of the QSSA for each species was calculated for the reduced Dean mechanism and the list of species having the smallest estimated QSSA error at time 360 s is given in Fig. 5. Similar calculations were carried out at each reaction time. A species can be a QSSA-species if its calculated QSSA error is small at each time investigated. The analysis revealed that the QSSA could be applied for 36 species out of the 62 ones, therefore the concentrations of only 26 species should be calculated by solving the kinetic system of differential equations.

The concept of intrinsic low-dimensional manifolds [31] (ILDM) can be considered as a further development of the

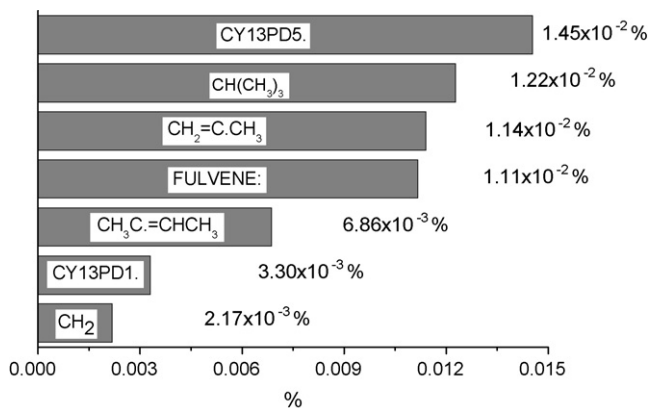


Fig. 5. Species causing the lowest error when considered as a QSSA-species and the estimated related QSSA error at $t = 360$ s.

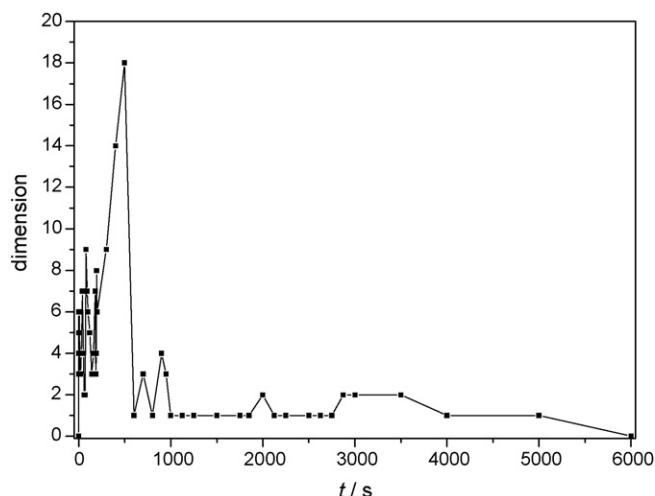


Fig. 6. Change of the dynamical dimension of the methane pyrolysis model with reaction time (see text).

quasi-steady-state approximation. With some simplification, low-dimensional manifolds are attracting geometric forms in the space of concentrations that the trajectories of simulations approach. The speed of approaching these manifolds depends on the timescales of the system. These timescales at any reaction time can be determined by the eigenvalue–eigenvector decomposition of the Jacobian:

$$\mathbf{\Lambda} = \mathbf{W}\mathbf{J}\mathbf{V} \quad (9)$$

where $\mathbf{J} = \partial\mathbf{f}/\partial\mathbf{y}$ is the Jacobian, \mathbf{W} and \mathbf{V} are the matrices of left and right eigenvectors, respectively; $\mathbf{\Lambda}$ is a diagonal matrix and its diagonal elements are the eigenvalues of the Jacobian. Denote λ_j the j th eigenvalue of the Jacobian and \mathbf{w}_j the corresponding left eigenvector. Measures $1/|\lambda_j|$ are called the timescales of dynamical systems. In non-linear systems, these timescales change with the values of variables and therefore with time.

A simple method was suggested for the calculation of the dimension of the manifold [32]. In a dynamical system of n variables, the degree of freedom of the movement in the space of variables is $n_1 = n - n_c$, where n_c is the number of conservation relations, which is equal to the number of zero eigenvalues of the Jacobian. The columns of matrix \mathbf{W} indicate the basic excitation directions (called modes) in a dynamical system at a given point in the space of variables. In all these directions, distance from the stationary point *in this direction* can be calculated by equation:

$$\Delta z_i = \frac{\mathbf{w}_i \mathbf{f}}{\lambda_i} \quad (10)$$

If the state of the system is close to the stationary value of mode i , that is if $\Delta z_i < z_{\text{thres}}$, then the system is not moving towards this direction. Let n_r denote the number of such so called relaxed modes. The actual dynamical dimension of the evolution of the system is $n_D = n - n_c - n_r$. For justification and details see [32]. This method is encoded as option ILDM in program KINALC.

The change of the dynamical dimension of the Dean mechanism was calculated till 6000 s. Fig. 6 shows that the dimension is between 2 and 9 till 200 s. After this time, it

increases up to 18 and then sharply decreases to 1–3. At larger reaction times the dimension is two or one, while at the equilibrium it reaches zero. The time interval of high dimension coincides with the interval of fast concentration changes.

Dimension analysis revealed that the dynamical description of the system can be based on an only 18-variate system of differential equations and the values of the other variables can be calculated by algebraic equations. It is a usual result of dimension analysis that the minimum number of variables is less than the number of non-QSSA-species, indicating that the QSSA is not optimal for the utilization of very different timescales.

An approach for the reduction of the methane pyrolysis model, alternative to the ILDM [31] or the QSSA [30], would be to carry out thousands of simulations using the original detailed reaction mechanism and fitting the coefficients of an 18-variate system of difference equations to the simulation results. This method is called repro-modelling and it had been shown [33,34] to allow very fast (in some cases several thousand times faster), but accurate simulations of complex chemical kinetic systems.

8. Summary

As a result of the fast progress of experimental and theoretical reaction kinetics, detailed reaction mechanisms are available for many chemical processes, including the pyrolysis of several compounds. These mechanisms may consist of hundreds of species and thousands of reactions. Several methods exist for the analysis of large reaction mechanisms. Many of these methods were discussed in a review paper [35] and these methods are readily available in computer code KINALC [3]. KINALC is a kinetic analysis postprocessor to the CHEMKIN gas kinetics simulation packages (versions CHEMKIN-II, 3.x and 4.x).

Reliability of reaction kinetic models can be assessed by uncertainty analysis. Chemical interpretation and understanding of complex reactions is very important and it can be based

on reaction flux analysis. A graphical tool called FluxViewer is available to visualize the main chemical pathways and their change with conversion.

The applicable methods include the identification of the redundant species in the mechanism via the analysis of the Jacobian of the system of kinetic differential equations. Using the principal component analysis of the rate sensitivity matrix, the redundant reaction steps can be identified. In most cases, one third of the species and two third of the reaction steps can be eliminated from mechanisms published in the literature.

Further reduction of reaction mechanisms can be achieved by considering the very different timescales of kinetic models. KINALC can be used for the estimation of the error of the quasi-steady-state approximation, and therefore it is applicable for the selection of the QSSA-species. The quasi-steady-state approximation is not the most effective method for the reduction of large reaction mechanisms and the minimal number of variables in an equivalent kinetic model can be determined by dimension analysis.

All methods were illustrated on the analysis and reduction of a methane pyrolysis mechanism, which contained 1604 irreversible reactions of 189 species.

Acknowledgements

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