

The influence of thermal coupling and diffusion on the importance of reactions: The case study of hydrogen–air combustion†

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Detailed chemical kinetics mechanisms are usually developed on the basis of spatially homogeneous calculations, but utilized in the simulation of very complex physical models. A fundamental question is if the importance of reactions is determined solely by the temperature and the actual concentration set or if it is also influenced by the thermal and diffusion couplings present in the physical model. A 46-step detailed mechanism of hydrogen oxidation was studied at equivalence ratios 0.5, 1.0, 2.0, and 4.0. Six physical models were designed (homogeneous explosion, burner-stabilized and freely propagating laminar flames, with and without thermal coupling), which provided very similar concentration curves as a function of temperature, while the local sensitivity functions revealed that the couplings in these models were very different. The importance of the reactions in every model was investigated by the principal component analysis of the rate sensitivity matrix F (PCAF method), exploiting that the results of this method depend only on the concentrations and temperature. A fundamentally different method, the principal component analysis of the local sensitivity matrix S (PCAS method) was used to extract information on the importance of reactions from the sensitivity functions. The PCAF and PCAS methods selected identical reduced mechanisms at all conditions, which shows that these are equally effective methods for determining a minimal reduced mechanism. The good agreement between the results of the two methods in the case of all models demonstrated that the importance of reactions was independent of the physical model into which the mechanism had been embedded. Thermal coupling did not have any effect on the selection of the reduced mechanisms. The difference between the importance of reactions in explosions and flames was caused by the difference of the concentrations in the low-temperature regions and not by the presence of diffusion. The reduced mechanisms contained 15 to 28 reaction steps, depending on the equivalence ratio and the type of the model. All species were retained in models of the combustion of lean and stoichiometric mixtures, while species H_2O_2 could be eliminated at rich conditions. Description of near stoichiometric conditions required more reaction steps, while rich combustion could be described by few reactions. An overall reduced mechanism, applicable in a wide range of conditions, contained 31 reaction steps. Results of the PCAS method revealed the global similarity relations of the sensitivity matrices of adiabatic explosions.

Introduction

As a result of the fast progress of reaction kinetics, detailed reaction mechanisms are available for many chemical processes. Usually, these mechanisms are developed on the basis of spatially homogeneous simulations assuming some special conditions. However, the mechanisms are frequently applied for the simulation of spatially inhomogeneous systems, where diffusion of the species may change the significance of the reactions. Thermal coupling can also be different at the conditions of the development and the applications of the mechanisms. An extreme case is an *adiabatic* system, where there is no heat exchange and the temperature profile is determined by the heat effect of the chemical reactions. The other possible extreme case is a *constrained temperature* system, where the temperature profile is fully prescribed externally and is independent of the heat release of the chemical reactions. A vital question is whether the importance of reactions changes if the mechanism is embedded into a different physical model. In other

words, is it possible to use the same reaction mechanism in spatially inhomogeneous multidimensional simulations that have been developed at spatially homogeneous conditions?

Vajda *et al.*¹ have investigated the effect of thermal coupling and diffusion on the mechanism of hydrogen oxidation. They concluded that the description of spatially homogeneous systems requires a very detailed mechanism and the same reactions are important with and without thermal coupling. They stated that the presence of simultaneous thermal and diffusion couplings makes most of the reactions unimportant and therefore the flames can be simulated using a much simpler mechanism. One of the basic ideas of the article¹ is that the effects of thermal and diffusion couplings have to be investigated by comparing similar systems with and without such couplings. Vajda *et al.* explored the combustion of atmospheric, stoichiometric hydrogen–air mixtures and compared the sensitivities calculated in the following systems: (V1) isothermal explosion, $T = 920$ K; (V2) isothermal explosion, $T = 1500$ K; (V3) adiabatic explosion, $T_0 = 920$ K; (V4) explosion with constrained temperature profile using the adiabatic curve of V3; (V5) adiabatic burner-stabilized flame $T_c = 298$ K; (V6) burner-stabilized flame with constrained temperature profile to the adiabatic curve of V5. The importance of the reactions was determined for systems V1, V2, V3, and V5 by the principal

† Electronic Supplementary Information (ESI) available: four PCAF results (for systems Z1, Z2, Z3/Z5, and Z4/Z6) given for each equivalence ratio, as a function of temperature in 100 K steps (Table S1). See <http://www.rsc.org/suppdata/cp/b3/b303628f/>

component analysis of the concentration sensitivity matrices. However, as Fig. 1 shows, the enthalpy profiles for the homogeneous explosion cases are very different from each other and also from that of the laminar flame. Consequently, the concentration profiles are also very different for these cases, as shown in Fig. 2.

Brown *et al.*² also investigated the reduction of identical reaction mechanisms for conditions of different physical models. They stated that “combustor type influences mechanism reduction substantially because of the different couplings between the fluid mechanics and chemistry”. Brown *et al.* studied an updated version of a hydrogen oxidation mechanism and the hydrogen oxidation part of the GRI mechanism³ version 1.2, at equivalence ratios 0.8, 1.0, and 1.6. In addition, they explored the reduction of two methane oxidation mechanisms. Brown *et al.* investigated the following hydrogen oxidation systems: (B1) adiabatic explosion, $T_0 = 970$ K; (B2) stationary perfectly stirred reactor with residence time of 3×10^{-3} s and inlet temperature of 300 K; (B3) adiabatic freely propagating flame $T_c = 300$ K. In the case of combustion of stoichiometric hydrogen–air mixtures and their own model, the full mechanism contained 28 reversible reactions, while the reduced mechanisms included 19, 18, and 19 reactions for the cases of explosion, laminar flame, and perfectly stirred reactor, respectively. In the discussion, they attributed the differences in the reduced mechanisms to the fact that no initiation reactions were needed in the models of flames and perfectly stirred reactors, because “each has a source of radicals during ignition due to either diffusion or perfect mixing”. As Figs. 1 and 2 show, the conditions that Brown *et al.* chose were not designed to separate the effect of diffusion coupling from the effect of different radical concentration levels.

In this paper, conditions and methods were selected in order to investigate specifically the thermal and diffusion couplings. The initial and boundary conditions were chosen in such a way that the concentrations in all systems with and without thermal and diffusion couplings be as close as possible to each other. Compared to the previously referred two papers, the methods and the conditions of investigations were extended.

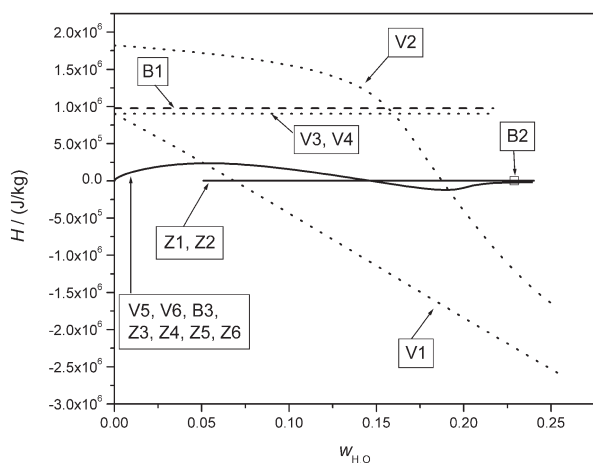


Fig. 1 Specific enthalpy as a function of the mass fraction of H_2O in various systems of stoichiometric, atmospheric hydrogen–air combustion. The V and B series of systems were investigated by Vajda *et al.*¹ and Brown *et al.*² respectively, and the Z series are the systems investigated here. The systems included isothermal explosions (V1, V2), adiabatic explosions (V3, B1, Z1), constrained temperature profile explosions (V4, Z2), perfectly stirred reactor (B2), adiabatic premixed freely propagating (B3, Z3) and burner-stabilized (V5, Z5) laminar flames and constrained temperature profile premixed freely propagating (B3, Z4) and burner-stabilized (Z6) laminar flames. Initial and boundary conditions for all systems are defined in the text.

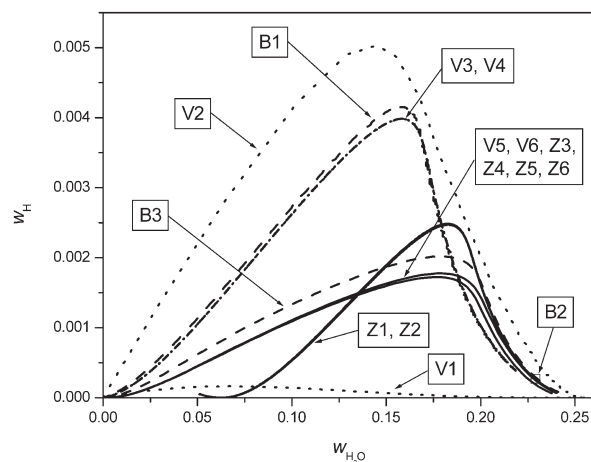


Fig. 2 Mass fraction of H-atom as a function of the mass fraction of H_2O in the various systems. The conditions and the notations are identical to those in Fig. 1.

The importance of reactions was investigated in all systems in a wide range of equivalence ratios. In the Vajda *et al.*¹ and Brown *et al.*² articles, the importance of reactions was determined by the principal component analysis of the local concentration sensitivity matrices (PCAS method).⁴ Besides this tool, we also examined the change of the importance of reaction steps during the course of the combustion process by the principal component analysis of the rate sensitivity matrices (PCAF method).⁵ Vajda *et al.*¹ investigated burner-stabilized flames, while Brown *et al.*² studied freely propagating flames. In our studies, mechanism reduction results for these two types of flames were cross-examined. In addition, reaction importance was also investigated in all flames without thermal couplings.

Because of the additional kinetic analysis and the more similar conditions in the explosion and flame systems, the calculations presented here may reveal more information about the effects of thermal and diffusion couplings. In the next section, the reaction mechanism investigated, the initial and boundary conditions, and the simulation programs are defined. In the subsequent section, methods for the identification of important species and reactions in a complex mechanism are reviewed. Then, the results of the application of these methods to the analysis of hydrogen–air explosion and flame systems are described. Conclusions are summarized in the last section.

Similar kinetic systems with and without thermal and diffusion couplings

The starting point of the investigations was a detailed mechanism for hydrogen oxidation, which included 9 species and 46 irreversible reaction steps. This was a submechanism of the Leeds methane oxidation mechanism⁶ that contained the hydrogen oxidation steps only. In the calculations, the programs of the CHEMKIN-II package⁷ were used. Homogeneous explosions were calculated by the program SENKIN⁸ and premixed stationary one-dimensional laminar flames were simulated by the program PREMIX.⁹ In all calculations, a constant pressure of $p = 1$ atm was assumed. All systems were investigated at equivalence ratios $\phi = 0.5$, $\phi = 1.0$, $\phi = 2.0$, and $\phi = 4.0$. These values corresponded to lean, stoichiometric, moderately rich and rich compositions, respectively. The aim was to find different physical systems, where the concentration and temperature profiles were as close to each other as possible. The following six systems were investigated:

Z1 adiabatic explosion

The initial composition and temperature were obtained by a linear interpolation between the following two states: (A) a hydrogen-air mixture having temperature $T = 298.15$ K, (B) a burnt equilibrium state corresponding to state A with the same enthalpy. By definition, in both states the systems have specific enthalpy $H = 0$ J kg⁻¹. All mixtures obtained by linear interpolations in the concentrations have the same specific enthalpy and element composition, but below a threshold temperature the mixture does not explode at adiabatic conditions. The initial composition was selected in such a way that it be just above the explosion limit.

Z2 constrained temperature explosion

The temperature-time curve at the simulation of system Z1 was recorded and during the simulation of system Z2, only concentration changes were calculated, while temperature was changed according to the recorded curve. The calculated concentration curves in system Z2 were identical to those of Z1, but in such a system there are no couplings due to the heat effects of reactions. On changing a parameter value during sensitivity analysis, there is no change in the temperature profile unlike in the case of system Z1.

Z3 adiabatic burner-stabilized flame

The cold boundary temperature of the premixed laminar flame was $T_c = 298.15$ K. At the hot boundary, the gradients of concentrations and temperature were zero; therefore, the hot boundary state corresponded to the burnt equilibrium state. It was an adiabatic flame, therefore the cold and hot boundary gas mixtures had the same specific enthalpy, which was equal to the specific enthalpy of systems Z1 and Z2. Due to heat and species diffusion, specific enthalpy was not constant $H = 0$ J kg⁻¹ as a function of distance. The mass flow rate used corresponded to that of the freely propagating flame having the same cold boundary composition and therefore the heat loss at the cold boundary was zero. In the case of burner-stabilized flames, the starting point of the coordinate system is attached to the burner surface and is independent of the values of parameters of the kinetic mechanism. However, the calculated distance of the flame front from the burner surface changes as a function of parameter values.

Z4 constrained temperature burner-stabilized flame

The temperature-distance curve of flame Z3 was recorded and used for the simulation of flame Z4. The calculated concentration-distance curves in system Z4 were identical to those of Z3, but changing a parameter value causes no change in the temperature profile unlike in the case of flame Z3.

Z5 adiabatic freely propagating flame

The cold and hot boundaries were identical to that of flame Z3. Consequently, the calculated concentration and temperature profiles were also identical. The difference is that for the stationary simulation of freely propagating flames, the coordinate system moves with the flame front and is fixed to a given temperature point of the flame. In our calculations, this reference temperature was always 400 K. Therefore, the calculated distance of the flame front from the reference point is not very sensitive to the parameter changes of the kinetic mechanism.

Z6 constrained temperature freely propagating flame

The temperature-distance curve of flame Z5 was recorded and used for the simulation of flame Z6. This way, the temperature

profile was made independent of the changes of the kinetic parameters.

The calculated concentrations and sensitivities for explosions (Z1–Z2) and flames (Z3–Z6) can be compared easily, if the results are plotted as a function of temperature instead of time or distance. Temperature is continuously increasing with time and distance in adiabatic explosions and laminar flames, respectively; therefore, this is an equivalent representation of the data. Fig. 3 shows the mass fractions of species H, OH, H₂, and H₂O as function of temperature for systems Z1 to Z6 in the case of equivalence ratio $\phi = 2$. The concentration profiles of flames Z3 to Z6 are identical. Remarkably, there is good coincidence between the concentration-temperature profiles of explosions and premixed laminar flames above *ca.* 1300 K. One might expect that, because of the identical reaction mechanisms and similar concentration curves, the sensitivity profiles $\partial Y_i / \partial \ln A_k$ are also similar, where A_k is the pre-exponential factor of reaction k . Fig. 4 shows that this is not the case. The diffusion and thermal couplings and the coordinate systems are different in the six cases; therefore the sensitivity functions are also very different for all systems apart from Z4 and Z6. The sensitivity functions of the adiabatic burner stabilized (Z3) and freely propagating (Z5) flames are different, because in the former system the distance of the flame front from burner surface may change due to parameter perturbations. In constrained temperature flames the location of the flame front is fixed due to the fixed temperature profile, therefore the sensitivity functions of Z4 burner-stabilized and Z6 freely propagating flames are identical.

In some chemical kinetic systems, the rank order and the relative magnitude of the sensitivity coefficients are identical in a wide range of the independent variable z (time or distance) for each variable. This results in a characteristic shape of the sensitivity functions; the sensitivity curves of system Z1 in Fig. 4 represent a good example. This means that the ratio of the sensitivity coefficients is independent of the selection of the model result Y_i and the independent variable z within an interval: $\mu_{ki} = s_{ik}(z)/s_{ij}(z)$. This property was called *self-similarity* in papers from refs. 1 and 10 and *global similarity* in the article from ref. 11. Inspection of the sensitivity functions in Fig. 4 reveals that global similarity for all parameters is present in adiabatic explosion Z1, it also fulfils for a part of the parameters in adiabatic burner-stabilized flames Z3 and this feature is missing in the other cases. Note that Vajda *et al.*¹ found global similarity in the case of adiabatic burner-stabilized flames only.

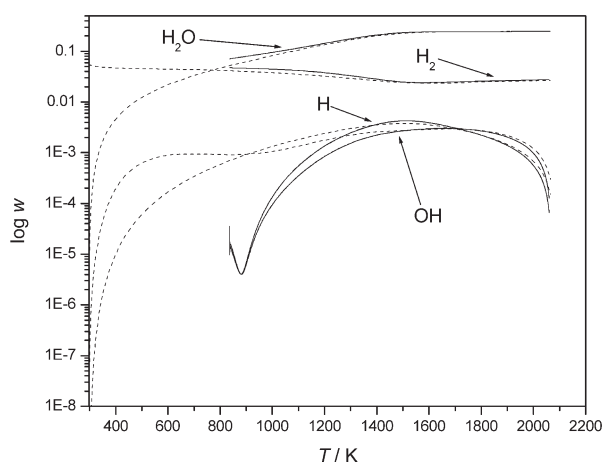


Fig. 3 Mass fractions of species H, OH, H₂, and H₂O as functions of temperature at adiabatic combustion of slightly rich ($\phi = 2$) hydrogen-air mixtures. Solid lines and dashed lines belong to homogeneous explosions (Z1–Z2) and laminar flames (Z3–Z6), respectively.

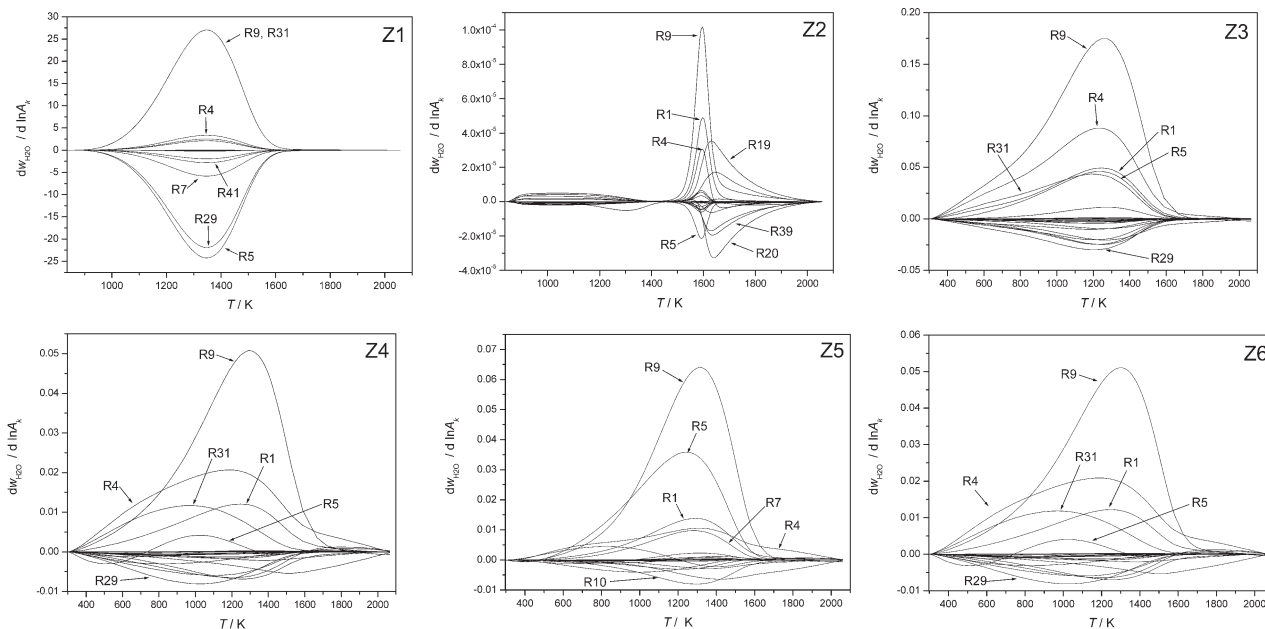


Fig. 4 Sensitivity of the mass fraction of H_2O with respect to the preexponential factors A_k of reactions as function of temperature in systems Z1 to Z6 for equivalence ratio $\phi = 2$. The sensitivity curves were normalized with the parameter value to make them of similar magnitude: $A_k(\partial w_{\text{H}_2\text{O}}/\partial A_k) = \partial w_{\text{H}_2\text{O}}/\partial \ln A_k$.

Systems Z1–Z6 seem to be well suitable for our purposes, because the calculated concentrations as a function of temperature are either identical or very similar to each other, while the calculated sensitivity functions are very different. The latter means that perturbation of parameters in the various systems causes very different effects on the simulation results, due to the different thermal and diffusion couplings.

Determination of the importance of species and reactions

Changes of concentrations and temperature in a constant pressure spatially homogeneous reaction system can be described by the following initial value problem:

$$d\mathbf{w}/dt = \mathbf{f}_w(T, \mathbf{w}, \mathbf{p}) \quad \mathbf{w}(0) = \mathbf{w}^0 \quad (1a)$$

$$dT/dt = f_T(T, \mathbf{w}, \mathbf{p}) \quad T(0) = T^0 \quad (1b)$$

where T is temperature, t is time, \mathbf{w} is the N -vector of mass fractions, \mathbf{p} is the M -vector of parameters and T^0 and \mathbf{w}^0 are the initial values of temperature and mass fractions, respectively. In the case of adiabatic systems, function f_T is defined in such a way to ensure constant specific enthalpy of the mixture during the reaction. In this case, \mathbf{Y} denotes the vector of variables, that is $\mathbf{Y} = (\mathbf{w}, T)$ and accordingly, $\mathbf{f} = (\mathbf{f}_w, f_T)$. In the case of constrained temperature calculations, $T(t)$ is a predefined function, eqn. (1b) is missing, and variable vector \mathbf{Y} includes the mass fractions only.

Local sensitivity analysis is a widely used tool in chemical kinetics.^{12–14} The local sensitivity coefficient $s_{ik} = \partial Y_i/\partial p_k$ gives information on the effect of the small change of parameter p_k on model output Y_i . The sensitivity coefficients constitute the first order local sensitivity matrix $\mathbf{S} = \{\partial Y_i/\partial p_k\}$. This sensitivity matrix can be calculated by solving the following initial value problem:

$$\dot{\mathbf{S}} = \mathbf{J}\mathbf{S} + \mathbf{F} \quad \mathbf{S}(0) = \mathbf{0} \quad (2)$$

where $\mathbf{J} = \partial \mathbf{f}/\partial \mathbf{Y}$ is the Jacobian and $\mathbf{F} = \partial \mathbf{f}/\partial \mathbf{p}$.

In spatially inhomogeneous systems, the change in concentrations and temperature can be described by an appropriate system of partial differential equations (PDEs). The most

frequently simulated 1D reaction–diffusion systems are stationary premixed laminar flames. The general form of the corresponding PDEs is given by:

$$\mathbf{L}(\mathbf{Y}, \mathbf{p}) = 0 \quad (3)$$

where \mathbf{L} is a second order differential operator. In this case, the right-hand-side of eqn. (1) is part of this operator as the chemical source term. A detailed description of operator \mathbf{L} for laminar flames and the corresponding boundary conditions can be found in many articles (see, e.g., ref. 1), and are not reproduced here. As previously, vector \mathbf{Y} either includes temperature and the mass fractions or \mathbf{Y} includes the mass fractions only and the temperature–distance function is prescribed externally. Like in the cases of temporal systems, the local sensitivity matrix as a function of distance can be calculated by solving the appropriate sensitivity differential equation corresponding to eqn. (2).

The aim of chemical kinetic models is to provide information about the concentration of the *important species* or to reproduce some *important features*, like the laminar flame velocity. Kinetic models usually include *necessary species* that are not important, but the presence of them is required for the accurate calculation of the concentrations of important species and of important features. Any other species present in a kinetic mechanism are *redundant*. A possible algorithm¹⁵ for the detection of redundant species can be based on the inspection of the Jacobian. An element of the normalized Jacobian $\partial \ln f_j/\partial \ln w_i$ provides information about how the production rate of species j changes if the concentration of species i is perturbed. If the square of changes is summed up for all important species, then the value of B_i characterizes the strength of the direct link of species i to the group of important species:

$$B_i = \sum_j (\partial \ln f_j/\partial \ln w_i)^2 \quad (4)$$

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 importance of species has to be investigated at several concentration sets. This algorithm has been encoded as option CONNECT in the program KINALC for the analysis of gas kinetic mechanisms.¹⁶ If a species is redundant, then all its consuming reactions can be eliminated from the mechanism. Details of the detection of redundant species are discussed in the article from ref. 15

The principal component analysis of the concentration sensitivity matrix⁴ (called below the *PCAS method*) investigates the effect of parameter perturbation on the following objective function:

$$e(\mathbf{p}) = \int_{z_1}^{z_2} \sum_{i=1}^K \left(\frac{Y_i^*(z) - Y_i(z)}{Y_i(z)} \right)^2 dz \quad (5)$$

Here, $Y_i(z)$ is the calculated i th model result using the nominal parameter set at value z of the independent variable, while $Y_i^*(z)$ is the same model result using a perturbed parameter set. The integrated squared deviation is investigated in the interval (z_1, z_2) of the independent variable. The summation may refer to all model results or only some of them and K is the number of model results considered in the objective function. It has been shown⁴ that the objective function e can be approximated around the nominal parameter set using the local sensitivity matrix:

$$e(\mathbf{a}) \approx (\Delta\mathbf{a})^T \tilde{\mathbf{S}}^T \tilde{\mathbf{S}} \Delta\mathbf{a}, \quad (6)$$

where $\Delta\mathbf{a} = \Delta \ln \mathbf{p}$, superscript T denotes the transpose and matrix $\tilde{\mathbf{S}}$ has been composed from a series of normalized local sensitivity matrices:

$$\tilde{\mathbf{s}} = \begin{bmatrix} \tilde{s}_1 \\ \tilde{s}_2 \\ \vdots \\ \tilde{s}_n \end{bmatrix} \quad (7)$$

Since the integral in eqn. (5) is approximated by summation, the $\tilde{\mathbf{S}}_m = \{\partial \ln Y_i(z_m) / \partial \ln p_k\}$ sensitivity matrices have to belong to several independent variable values within the interval (z_1, z_2) . The rows of these matrices correspond to the variables present in the objective function (5). Using the vector of eigenvalues λ and the matrix of eigenvectors \mathbf{U} of matrix $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$, the objective function (6) can be transformed to

$$e(\mathbf{a}) = \sum_i \lambda_i (\Delta \Psi_i)^2 \quad (8)$$

where $\Delta \Psi = \mathbf{U}^T \Delta \mathbf{a}$ are the transformed parameters called principal components. The eigenvectors define which parameters are grouped together. These parameter groups have a joint effect on the objective function and the corresponding eigenvalues show the effectiveness of the parameter groups. Parameters having a high eigenvector element in the parameter group characterized by a high eigenvalue are influential on the simulated curves of variables present in the objective function (5). It has been shown^{4,15} that if the objective function includes all important and necessary species, then the PCAS method provides a reduced mechanism that reproduces the important features and the concentration profiles of all the important species, but contains the important reactions only. Important reactions can be identified, because the pre-exponential factors of the important reactions appear as parameters, having high eigenvector element in a parameter group characterized by an eigenvalue above the threshold. In practice, the minimal mechanism is searched for in such a way that several reduced mechanisms, belonging to gradually decreasing threshold values of the eigenvalues and the eigenvectors are produced, the simulation results of the reduced mechanisms are

compared with that of the full mechanism, and the smallest reduced mechanism that meets the requirements is accepted. Mechanism reduction by the PCAS method can be carried out efficiently by using option PCAS of program KINALC.¹⁶

If the global similarity relation exists among the sensitivity functions of model output i in the interval (z_1, z_2) of the independent variable, then relation

$$\frac{\partial Y_i}{\partial p_k} = \mu_{kl} \frac{\partial Y_i}{\partial p_l} \quad (9)$$

holds between the sensitivity coefficients.¹¹ This also means global similarity of the normalized sensitivity functions:

$$\frac{p_k}{Y_i} \frac{\partial Y_i}{\partial p_k} = \frac{p_k}{p_l} \mu_{kl} \frac{p_l}{Y_i} \frac{\partial Y_i}{\partial p_l} \quad (10)$$

$$\frac{\partial \ln Y_i}{\partial \ln p_k} = \tilde{\mu}_{kl} \frac{\partial \ln Y_i}{\partial \ln p_l} \quad (11)$$

where the factor $\tilde{\mu}_{kl}$ is independent of z in interval (z_1, z_2) and the model output i investigated. This means that the normalized sensitivity matrix $\tilde{\mathbf{S}}_m = \{\partial \ln Y_i(z_m) / \partial \ln p_k\}$ can be calculated as the product of two vectors:

$$\tilde{\mathbf{S}}_r = \tilde{\boldsymbol{\mu}}_i \tilde{\mathbf{s}}_i^T(z_m) \quad (12)$$

where vector $\tilde{\boldsymbol{\mu}}_i^T = \{\tilde{\mu}_{i1}, \tilde{\mu}_{i2}, \dots, \tilde{\mu}_{iM}\}$ contains the multiplication factors and non-zero vector $\tilde{\mathbf{s}}_i^T(z_m) = \{\partial \ln Y_i(z_m) / \partial \ln p_1, \partial \ln Y_i(z_m) / \partial \ln p_2, \dots, \partial \ln Y_i(z_m) / \partial \ln p_n\}$ is a column of the normalized sensitivity matrix belonging to parameter l and independent variable value z_m . Matrix $\tilde{\mathbf{S}}$, defined in eqn. (7), can also be obtained as a product of two vectors: $\tilde{\mathbf{S}} = \tilde{\boldsymbol{\mu}}_i \tilde{\mathbf{s}}_i^T$, where $\tilde{\boldsymbol{\mu}}_i^T = \{\tilde{\boldsymbol{\mu}}_i^T, \tilde{\boldsymbol{\mu}}_i^T, \dots, \tilde{\boldsymbol{\mu}}_i^T\}$ and $\tilde{\mathbf{s}}_i^T = \{\tilde{\mathbf{s}}_i^T(z_1), \tilde{\mathbf{s}}_i^T(z_2), \dots, \tilde{\mathbf{s}}_i^T(z_n)\}$. Non-zero vectors $\tilde{\boldsymbol{\mu}}_i^T$ and $\tilde{\mathbf{s}}_i^T$ have rank of one, therefore the rank of matrix $\tilde{\mathbf{S}}$ is also one, consequently the rank of matrix $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ is also one. Hence, if the global similarity relation exists among the sensitivity vectors of all variables present in the objective function of the principal component analysis in the investigated interval (z_1, z_2) , then matrix $\tilde{\mathbf{S}}^T \tilde{\mathbf{S}}$ has only one non-zero eigenvalue. If the global similarity is not exactly true but is a good approximation, then one of the eigenvalues is much higher than the others and usually only one eigenvalue is higher than the threshold. If the global similarity relation is valid for the sensitivity coefficients belonging to all parameters but one, then the number of effective eigenvalues is two, etc. In general, if objective function (5) of the PCAS method can be well approximated by an expression of type (8) that contains low number r of eigenvalues, then similarity relations exist among the sensitivity vectors and strong couplings are present among the variables. If the number of effective principal components is one, then the effect of the change of one parameter can be fully compensated for all variables present in the objective function at any value of the independent variable within interval (z_1, z_2) by changing other parameter(s). If number r of the effective eigenvalues is two, then the results for all variables present in the objective function in the whole interval (z_1, z_2) can be effectively tuned by changing two parameters, each selected from one of the parameter groups. The minimal number of parameters that are needed to change for an effective tuning of the model is equal to number r of the effective principal components. This statement is, however, based on a local analysis and is not true therefore for large parameter changes.

An alternative method for the reduction of detailed reaction mechanisms is the principal component analysis of the rate sensitivity matrix \mathbf{F} (*PCAF method*).⁵ In this case the objective function is defined by:

$$e' = \sum_{i=1}^m \left(\frac{f_i^*(z) - f_i(z)}{f_i(z)} \right)^2 \quad (13)$$

where f_i and f_i^* can be calculated using eqn. (1) for variable Y_i at the original and the perturbed parameter sets, respectively. This objective function can be approximated by

$$e'(\alpha) \approx (\Delta\alpha)^T \tilde{F}^T \tilde{F}(\Delta\alpha) \quad (14)$$

where the matrix $\tilde{F} = \{(p_k/f_i)(\partial f_i/\partial p_k)\}$ is the normalised sensitivity matrix of production rates for the variables present in the objective function. The elements of matrix \tilde{F} can be calculated by simple analytical expressions derived from eqn. (1) at a given variable vector Y . Note that the sensitivity matrix S can be calculated only by solving additional differential equations. If the parameters investigated are the pre-exponential factors of reactions, then the corresponding elements of matrix \tilde{F} can be calculated⁵ from the rates of reactions, the production rates of species and the stoichiometric matrix. If temperature is one of the variables in the objective function, then calculation of the parametric sensitivity of the rate of temperature requires also the utilization of reaction enthalpies and the mean heat capacity of the mixture. As previously, eigenvector–eigenvalue analysis of the $\tilde{F}^T \tilde{F}$ matrix provides a list of important reactions, if the objective function includes all important and necessary species. The rate parameters of all the important reactions have high eigenvector elements in a parameter group characterized by an eigenvalue above a threshold. Usually, the best thresholds for the eigenvalues and the eigenvector elements are searched for by probing several values as described at the PCAS method. Option PCAF of program KINALC¹⁶ allows a quick start for using this method for the reduction of mechanisms.

Although the PCAS and PCAF methods may look technically similar, the two methods are fundamentally different. Objective function (13) of the PCAF method investigates the change of rates, which are functions of variables Y only in autonomous systems. Therefore, this method provides information on the importance of reactions that belong to a given temperature and concentration set. If the importance of reactions is investigated in an interval of time or distance, the analysis has to be repeated at several values of the independent variable. If two different physical models provide identical concentration sets and temperature using the same reaction mechanism, and the same variables are considered in the objective function, the PCAF method will indicate identical importance of reactions. On the other hand, the PCAS method investigates the *results of parameter perturbation*. This information is present in the local sensitivity matrices, which depend also on the physical model in which the kinetic mechanism is embedded. As Fig. 4 shows, very different sensitivity functions may belong to an identical kinetic mechanism and similar concentration functions. Because the PCAS method investigates integrated deviations [see eqn. (5)], it provides information on the importance of parameters that belongs to an interval of the independent variable.

Comparing the results of kinetic analyses

The aim of our investigations was to produce reduced mechanisms that were practically indistinguishable from the full mechanism. Therefore, the reduced mechanisms had to fulfil the following requirements: deviation from the full mechanism in the mole fractions of species H_2 , O_2 , and H_2O should be less than 5% at every time or distance, except for at low concentrations. A concentration was considered low if it was one hundred times lower than the peak concentration. It also meant that the deviations of the mole fractions of all other species were usually also below 5%. In the case of adiabatic simulations, deviation in the calculated temperature had to be less than 10 K, in the case of freely propagating flames the deviation in the flame velocity had to be less than 2%, and in the

case of adiabatic explosions the deviation in the ignition time had to be less than 10%. These values roughly correspond to the precision of the measurements that can be used to discriminate two detailed combustion mechanisms. The reduced mechanisms were tested automatically and the deviations were screened in the whole range of time or distance. This procedure allowed a non-biased selection of the minimal reduced mechanisms that met the above thresholds.

As a first step, the importance of species was determined by the CONNECT method described in the previous section. It showed that H_2O_2 was redundant in the case of all models at equivalence ratios $\phi = 2.0$ and $\phi = 4.0$. This result was checked by eliminating all reactions of H_2O_2 from the mechanism and repeating all simulations. The deviations between the results using the full and the reduced mechanisms were always below the thresholds in all models. In the following mechanism reduction studies, using either the PCAS or the PCAF methods, the objective function included the concentrations of all species at equivalence ratios $\phi = 0.5$ and $\phi = 1.0$ and the concentrations of all species but H_2O_2 at equivalence ratios $\phi = 2.0$ and $\phi = 4.0$. In addition, temperature was included in the objective function at the investigation of the adiabatic models.

In the next step, the change of the importance of the reactions as a function of temperature was determined in the various models. Using the PCAF method, the result depends on the reaction mechanism, the temperature, and the concentration set only and is independent from the local sensitivity functions. Although the corresponding adiabatic–constrained temperature pairs of models provided identical concentration and temperature profiles, the results of the PCAF analyses were slightly different, because at the investigation of the former models temperature was also considered in the objective function. The corresponding burner-stabilized-freely propagating flame model pairs (Z3 and Z5; Z4 and Z6) gave identical simulation results and therefore the PCAF results were also identical for these pairs. The four PCAF results (for systems Z1, Z2, Z3/Z5, and Z4/Z6) are given for each equivalence ratio, as a function of temperature in 100 K steps in the table of the Electronic Supplementary Information.† This table shows that the importance of the reactions usually change at *ca.* 1300 K. For example, in the case of stoichiometric systems and laminar flames, reactions 13, 17, 33, and 37 are important at low temperatures, while reactions 2, 3, 20, 21, 25, and 40 are important at high temperatures. Reactions 1, 4, 5, 7, 9, 10, 19, 27, 29, 31, and 39 are important in the whole temperature region. The chemical reactions belonging to these reaction numbers can be identified in Fig. 5.

A reaction was considered important in a model by the PCAF method if it was found important at any of the conditions investigated. In Fig. 5, which summarizes the importance of reactions, the columns belong to models Z1–Z6 at each equivalence ratio and the rows belong to the reaction steps. The shaded lower bar in a cell of Fig. 5 shows that the corresponding reaction was found important by the PCAF method in the appropriate model at any investigated condition.

Using the PCAS method, the whole time or distance intervals of the models were investigated and therefore the importance of reactions belongs to the whole simulation interval of the model. Shaded upper bar in a cell of Fig. 5 indicates that the corresponding reaction was found important in the model by the PCAS method.

We have shown in the previous section that if all sensitivity matrices are selected from the region of global similarity of the sensitivity functions, then the rank of matrix $\tilde{S}^T \tilde{S}$ is one and the objective function (8) includes a single eigenvalue. The number of eigenvalues used at the selection of the important parameters provides the number of parameters that can be tuned independently to improve the agreement between the simulation results and the experimental data to be modelled. For this reason, the number of ‘effective’ eigenvalues is an

Table 1 The first three eigenvalues of the PCAS method for each model and equivalence ratio. The bold eigenvalues were considered only in the objective function (8)

	Equivalence ratio			
	0.5	1.0	2.0	4.0
Z1	7.02E+07 1.47E+01 1.37E+01	1.12E+08 3.52E+01 2.15E+01	1.09E+07 9.36E+01 1.56E+01	9.07E+04 3.44E+01 2.29E+01
Z2	7.71E+03 2.61E+01 1.19E+01	6.49E+03 7.09E+01 3.32E+01	3.59E+03 1.08E+02 4.58E+01	1.90E+03 3.62E+01 3.02E+01
Z3	6.01E+03 1.92E+01 1.31E+01	5.71E+02 4.17E+01 1.52E+01	6.17E+02 5.15E+01 1.21E+01	1.28E+03 2.29E+01 1.25E+01
Z4	3.24E+01 1.74E+01 1.13E+01	4.23E+01 2.74E+01 1.35E+01	1.18E+02 2.73E+01 1.25E+01	6.51E+01 2.20E+01 1.17E+01
Z5	2.80E+02 1.82E+01 1.30E+01	5.89E+01 3.65E+01 1.55E+01	1.09E+02 4.08E+01 1.09E+01	9.34E+01 2.29E+01 9.14E+00
Z6	3.22E+01 1.74E+01 1.13E+01	4.23E+01 2.74E+01 1.35E+01	1.18E+02 2.73E+01 1.25E+01	6.51E+01 2.20E+01 1.17E+01

important result of the PCAS analysis. Table 1 shows the first three eigenvalues for each model and for each equivalence ratio. Bold numbers indicate the eigenvalues used at the approximation of the objective function by equation (8). In all cases, only the first or the first two eigenvalues were used.

Plotting ratio $\mu_{kl} = (\partial Y_i / \partial p_k) / (\partial Y_i / \partial p_l)$ as a function of temperature shows that global similarity is valid for all pairs of sensitivity functions in the case of adiabatic explosions (Z1) only (see ref. 11 for stoichiometric mixtures).

In this model, the domain of global similarity spans from ca. 900 K to 50 K below the thermodynamic equilibrium temperature. Global similarity was valid for some sensitivity coefficients in a restricted temperature domain in adiabatic burner-stabilized flames and was not found in the other models.¹¹ Accordingly, there was a large separation between the first and the second eigenvalues for model Z1 at all equivalence ratios (see Table 1). However, two eigenvalues were needed in the objective function (8) at equivalence ratios 0.5 and 1.0. In these cases, the reaction steps defined by the first eigenvector provided a reduced mechanism that was applicable in the region of global similarity, while the reaction steps defined by the second eigenvector were also needed to create a reduced mechanism that was applicable also in the region near the equilibrium state. It is more surprising that all other reduced mechanisms were defined by the first eigenvector. This means that all the results of all models can be effectively tuned by changing a single effective parameter.

Both the PCAS and the PCAF methods include a linearized approach to a nonlinear kinetic system. Some of the reaction parameters are just above the thresholds, but in fact can be eliminated from the mechanism. The importance of reactions close to the threshold values was tested by comparing the simulation results with and without these reaction steps. If a reaction proved unimportant in this test, it was indicated by light shading in Fig. 5. The full and the reduced mechanisms provided very similar simulation results; an example is given in Fig. 6. In the forthcoming discussions, this corrected importance of reactions will be analysed.

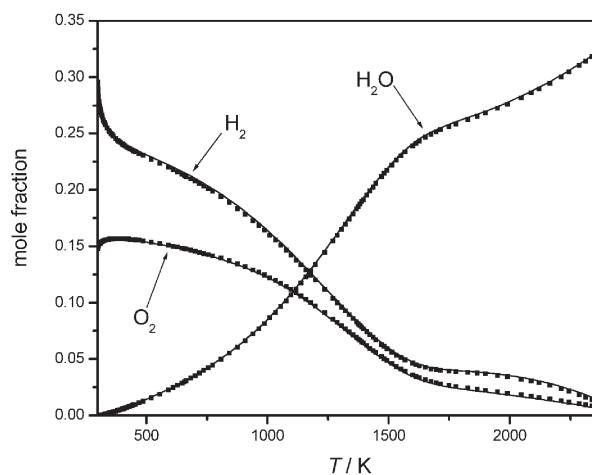


Fig. 6 Agreement between the full and the reduced mechanisms in the case of stoichiometric burner-stabilized flame. Dots: 25-step reduced mechanism; solid lines: 46-step full mechanism.

(i) Comparison of the effectiveness of the PCAS and PCAF methods

These two methods represent basically different ways of finding a minimal reaction set and one of the methods could be more efficient than the other. In the bottom rows of Fig. 5, the number of reaction steps in the minimal reduced mechanisms, as proposed by the two methods, is indicated. The results are compared for the 24 cases (4 equivalence ratios times 6 models) and the numbers of reaction steps in the reduced mechanisms are always identical. Comparing the upper and lower lines of each row demonstrates that the reduced mechanisms selected by the two methods are identical in all cases. Therefore, the PCAS and PCAF methods seem to be equally effective and provide identical result.

The result of the PCAF method depends on the concentrations and temperature, while the outcome of the PCAS method depends on the sensitivity functions that are determined by the physical model. The good agreement between the results of the two mechanism analysis methods in the cases of all models demonstrated that the importance of reactions was independent of the physical model in which the mechanism had been embedded.

(ii) Effect of thermal coupling on the importance of reactions

Comparing the importance of reactions for pairs of models Z1–Z2, Z3–Z4, and Z5–Z6 reveals how thermal coupling influences the importance of reactions. There is no difference for any of the model pairs at any equivalence ratio. This means that in the hydrogen–air combustion mechanism, the importance of the reactions does not change when the thermal coupling is switched off. This finding is in accordance with that of Vajda *et al.*¹ In principle, it would be possible that a reaction step had significant contribution to the heat release, but had no significant contribution to the concentration profiles of important species.

The detailed PCAF analysis results (see the Electronic Supplementary Information) indicate that above 900 K, reaction 41 (at $\varphi = 2.0$ and 4.0) and reaction 45 (at $\varphi = 0.5$ and 1.0) are important in the adiabatic models and not important in the constrained temperature models. This behaviour does not appear in the summary of Fig. 5, because these reactions have identical importance according to the PCAF method below 900 K.

(iii) Effect of diffusion on the importance of reactions

Comparison of the results for explosions (Z1, Z2) and flames (Z3 to Z6) reveals the effect of diffusion. In general,

the importance of reactions is identical in explosions and flames, with few exceptions. Fig. 5 shows that reactions 42, 43, and 45 are important in explosions, but not important in flames at equivalence ratios $\varphi = 0.5$ and $\varphi = 1.0$. The detailed PCAF analysis indicates that reactions 43 and 45 are important at low temperature (below 900 K) at the initial recombination of radical HO_2 . Reaction 42 is important only in stoichiometric explosions near the equilibrium temperature. In an opposite way, reactions 37 and 41 are important in flames, but not important in explosions at equivalence ratio $\varphi = 4$. These are also HO_2 radical reactions and according to the detailed PCAF analysis, these are important in the flames below 800 K. The explosions started from a higher temperature and therefore the importance of reactions could not be investigated there. In our models, explosions always started from high radical concentrations and therefore the initiation reactions had no special role. Consequently, basically the same reactions were important in flames and explosions, indicating that the diffusion itself does not modify the importance of reactions.

(iv) Importance of reactions in burner-stabilized and freely propagating flames

The difference between the importance of reactions for these two types of flames can be investigated by comparing model pairs Z3–Z5 and Z4–Z6. Fig. 5 shows that the importance of reactions is identical in these columns. It is somewhat surprising that the PCAS analysis provided exactly identical lists of important reactions for these flames, because Fig. 4 shows that the shapes of the sensitivity functions are very different. This result proves the robustness of the PCAS method.

(v) Change of the importance of reactions with the equivalence ratio

Most reactions are either unimportant or important in the whole range of equivalence ratio. However, some reactions are important in near stoichiometric mixtures only (reactions 8, 28, 32). Several reactions of H_2O_2 (reactions 13, 17, 19, 20) are important in lean and stoichiometric mixtures only, because H_2O_2 is not an important species in rich mixtures. The recombination reactions of the H-atoms (reactions 21 and 23) are the only ones that become important in rich mixtures.

The columns of Fig. 5 define 24 reduced mechanisms and these can replace the full mechanism in the corresponding model. The joint mechanism is applicable in models Z1 to Z6 in the $\varphi = 0.5$ to $\varphi = 4.0$ equivalence ratio range. This joint mechanism contains the following 29 reaction steps: 1–5, 7–10, 13, 17, 19–21, 23, 25, 27–29, 31–33, 37, 39–43, and 45. Conditions of the explosion Z1 and Z2 were designed to be close to that of flames Z3 to Z6. Therefore, the concentrations of the radicals are high already at the start of the explosions and therefore no initiation reactions were needed in the reduced models. The 29-step reduced mechanism is therefore not applicable in the explosion cases V1–V4 and B1, which start from a $\text{H}_2/\text{O}_2/\text{N}_2$ mixture with zero radical concentrations. Our examples did not include a perfectly stirred reactor like system B2. Flames V5 and V6 of Vajda *et al.* and flame B3 of Brown *et al.* were similar to our flames Z3, Z4, and Z5. As a by-product of our study, we wanted to create a joint reduced mechanism that is applicable in models V1–V6, B1–B3 and Z1–Z6, that is practically at all usual conditions of applicability of the hydrogen–air reaction mechanism. The PCAF analysis was carried out at the conditions of models V1–V4 and B1–B2, considering not only stoichiometric mixtures, but also equivalence ratios $\varphi = 0.5$, 2.0, and 4.0. The analysis revealed that in these systems two more reaction steps are also important: reactions 12 and 30. The joint reduced model, applicable

at all conditions, consists of 31 reaction steps: 1–5, 7–10, 12–13, 17, 19–21, 23, 25, 27–33, 37, 39–43, and 45.

Results of the previous investigations of Vajda *et al.*¹ showed that both adiabatic and constrained temperature explosions could be described by a 23-step reduced mechanism. Deviations from the results of the 38-step full mechanism were less than 5% for all species and temperature in all points of the simulated interval. These requirements were similar to ours. In the case of the adiabatic burner-stabilized flame, their reduced mechanism contained only 15 reaction steps. However, the deviations were rather high even if these were investigated at three distances only. Considering also the lean and rich flames, the highest deviations were 42 K in the calculated temperature, 11.6% in the flame velocity and 12% in the mass fraction of water (see Table 5 in¹). Vajda *et al.* explained the results on the basis that the sensitivity functions are globally similar in the case of adiabatic flames and are not similar in the case of explosions. However, as Fig. 4 in this paper shows, the sensitivity functions are similar in the case of adiabatic explosions and burner-stabilized flames, but are not similar in the case of constrained temperature simulations and freely propagating flames. Therefore, the explanation above does not seem to be valid. We consider that the basic reason of the great difference between the sizes of the two reduced mechanisms of Vajda *et al.* is the difference of the accuracy requirements and is not related to the couplings in the models.

Most combustion mechanisms, as used in the simulations, contain only reversible reaction steps. In these cases, the rates of forward reactions are calculated from the Arrhenius expressions and the rates of reverse reactions are calculated from the forward rates and the thermodynamic data. In our suggested 31-step reduced mechanism, most of the reaction steps found unimportant were the reverse reaction steps of important ones. Brown *et al.*² investigated the importance of reversible reactions and noted that “more reactions could have been eliminated if forward and reverse reactions were specified” (p. 404). If our mechanism was defined by 23 reversible reactions, only reversible reaction steps 15–16 and 35–36 could be eliminated from the mechanism. The latter reaction pair $2\text{O} + \text{M} = \text{O}_2 + \text{M}$ was also found to be redundant by Brown *et al.*² Reaction pair 15–16 ($\text{H}_2\text{O}_2 + \text{O} = \text{OH} + \text{HO}_2$) was present in the GRI mechanism as reaction B5 and was found to be important by Brown *et al.* This reaction was not needed in our 31-step reduced mechanism to reproduce the results of models B1–B3.

Conclusions

In the studies described in this paper, six physical models were designed (homogeneous explosions, burner-stabilized and freely propagating laminar flames, with and without thermal coupling), which provided very similar concentration curves as a function of temperature, while the thermal and diffusion couplings were very different. If the allowed deviations between the full and the reduced mechanisms are uniformly demanded in the cases of all types of models, then the reduced mechanisms will be almost identical at a given equivalence ratio. This means that detailed reaction mechanisms can be developed on the basis of spatially homogeneous experiments and calculations. The obtained mechanisms can be used in spatially inhomogeneous simulations, like 2D and 3D air pollution modelling or flame calculations, if the temperature and concentration curves at the development and the applications are similar.

Principal component analysis of the concentration sensitivity matrix (the PCAS method)⁴ has been used many times for the analysis and reduction of detailed reaction mechanisms. The principal component analysis of the rate sensitivity matrix (PCAF method)⁵ has also been frequently applied for finding

reduced mechanisms that contain important species and important reactions only. These two methods are substantially different, because the PCAF method investigates the rates in the chemical source term, while the PCAS method studies the dependence of model results on parameter changes. These methods have not been tested against each other previously. This work indicated that the PCAS and PCAF methods are equally effective in finding a minimal subset mechanism that produces practically the same simulation results as the full mechanism. The PCAF method is faster, simpler, and allows a pointwise investigation of the mechanisms in the space of concentrations, while the PCAS method provides additional information about the couplings in the physical models.

The theoretical description of the PCAS and PCAF methods, given in the articles from refs. 4, 5 and 12, has been extended here by the inclusion of temperature as one of the variables in the objective function for application of these methods in chemical systems with calculated temperature profile. Also, it was shown that if interval (z_1, z_2) investigated by the PCAS method is within the interval of global similarity of the sensitivity functions, then there is a large separation between the first and the second eigenvalues. Therefore, the PCAS method provides information about the existence of global similarity relations, which have been investigated by other methods in the article from ref. 11. It is recommended that the number of effective principal components should be noted, because this is equal to the minimal number of parameters that can be tuned to optimise the calculated profiles of all variables that were included to the objective function. This information can be important when starting from a physical model, a minimal number of parameters are adjusted to improve the agreement between the measured data and the simulation results.

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