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Proceedings of the Combustion Institute 30 (2005) 1273–1281

Proceedings
of the
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Uncertainty analysis of updated hydrogen and carbon monoxide oxidation mechanisms

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Abstract

Uncertainty analysis was used to investigate H₂/air and wet CO/air combustion mechanisms. The hydrogen/carbon monoxide submechanism of the Leeds Methane Oxidation Mechanism was updated on the basis of the latest reaction kinetic and thermodynamic data. The updated mechanism was tested against three hydrogen oxidation and two wet CO bulk experiments. Uncertainties of the simulation results, caused by the uncertainties of the kinetic parameters and the heat of formation data, were analysed. The methods used were the local uncertainty analysis and Monte Carlo analysis with Latin hypercube sampling. The simulated flame velocity had a relatively large uncertainty in both hydrogen–air and wet CO flames. In the case of ignition experiments, for both fuels the uncertainties of the simulated ignition delay times were small and comparable with the scatter of the experimental data. There was a good agreement between the simulation results and the measured temperature and concentration profiles of hydrogen oxidation in a flow reactor. However, accurate ignition delay is not a result of the flow reactor experiments. The uncertainty of the required time correction for matching the simulated 50% consumption of H₂ to that of the experimental one (corresponding to the simulated ignition delay) was found to be very large. This means that very different parameter sets provide very different ignition delays, but very similar concentration curves after the time correction. Local uncertainty analysis of the wet CO flame revealed that uncertainties of the rate parameters of reactions O₂ + H (+M) = HO₂ (+M), and CO + OH = CO₂ + H cause high uncertainty to the calculated flame velocity, temperature, and peak concentrations of radicals. Reaction H + HO₂ = H₂ + O₂ also causes high uncertainty for the calculated flame velocity. The uncertainty of the enthalpy of formation of OH is highly responsible for the uncertainty of the calculated peak OH concentration.

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Keywords: Uncertainty analysis; Mechanism development; H₂ oxidation; CO oxidation

1. Introduction

Direct experimental data for the elementary reactions are always utilised for the development

of detailed combustion mechanisms. Experimental data for species, e.g., thermodynamic data, are also used in combustion models. Applicability of the obtained combustion mechanism is usually tested against bulk experimental data. The simulations provide the output of the model at the nominal parameter set only and do not reveal the uncertainty of the simulation results. However, comparison of the experimental and

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simulation uncertainties is very important for the development of reaction mechanisms that are needed to be accurate in a wide range of conditions. Uncertainty analysis reveals which results are well supported by the model and which ones are merely nominal values that were obtained using the selected set of input parameters.

In combustion kinetics, Warnatz [1] was the first who considered the uncertainty of kinetic parameters. His ‘sensitivity-uncertainty indices’ were based on the uncertainty of kinetic parameters and the local sensitivity coefficients, and provided an unbiased order of reactions that caused the highest uncertainty of simulation results. These indices, however, do not characterize the uncertainty of simulation results. Bromly et al. [2] carried out a local joint kinetic and thermodynamic uncertainty analysis of a model of the low-temperature NO-sensitised oxidation of methane. The ‘impact factors’ of Bromly et al. had features similar to the Warnatz’ indices. Brown et al. [3] estimated the variance of the calculated hydrogen–air flame velocity from the uncertainties of the kinetic parameters. These methods have been discussed in more detail in the paper of Turányi et al. [4]. This paper also provides an algorithmic procedure for the calculation of the variance of simulation results from thermodynamic and kinetic uncertainties using the local uncertainty analysis approach. Oxidation reactions in supercritical water have been investigated by various global uncertainty analysis methods [5,6]. In the current work, besides the local uncertainty analysis, global uncertainty analysis was also carried out. Development of an updated mechanism for the combustion of hydrogen and wet CO is reported, and agreement of the model results with the measurement data characterised by uncertainty results, demonstrating the reliability of the mechanism developed.

2. Reaction mechanism and simulation codes

The Leeds Methane Oxidation Mechanism [7] provided the basis for the further development of the H₂/air and wet CO/air combustion mechanisms. The hydrogen oxidation mechanism can be easily obtained from the methane oxidation mechanism by selecting non-carbon species only. The species considered in the hydrogen–air combustion mechanism were H₂, O₂, H₂O, H₂O₂, H, O, OH, HO₂, N₂, and Ar. The wet CO oxidation mechanism consisted of all the above species and also included CO, CO₂, and HCO. Accordingly, the wet CO oxidation mechanism incorporated the whole hydrogen oxidation mechanism and also included the reactions of the above carbon-atom species.

The rate parameters of all reactions were revised using the latest CEC evaluation [8]. All new recommendations were accepted. The enthalpies of formation of species were updated according to a recent review by Ruscic et al. [9]. Surprisingly, the rate coefficients of many key reactions were changed by about 50%, typically. The changes can be traced back by comparing the Leeds Methane Oxidation Mechanism version 1.5 [7] with the updated mechanism published as a Supplementary Material of this paper. Uncertainty factors f of the rate parameters were taken from data evaluation [8]. The uncertainty factors were converted to the variances of rate coefficients using the method described in [4]. The assumed variances of enthalpies of formation were identical to those of article [4].

The calculations were carried out with the CHEMKIN-II package [10]. Programs SENKIN [11] and PREMIX [12] were modified to carry out sequential calculations with many altered parameter sets required by the global uncertainty analysis methods. Local and global uncertainty analyses were carried out with purpose-written Fortran codes.

3. Local uncertainty analysis

Sensitivity analysis is the common name for a family of tools for investigating the relations between the input parameters and output values of mathematical models [13]. Local sensitivity analysis is widely used in chemical kinetics to explore and understand complex reaction mechanisms (see, e.g. [14,15]). Local sensitivity coefficients are the partial derivatives of the output values with respect to the input parameters. As described, e.g., by Turányi et al. [4] using the rules of error propagation, the contribution of the uncertainty of kinetic parameter k_j to the uncertainty of modelling result Y_i can be calculated

$$\sigma_{k_j}^2(Y_i) = \left(\frac{\partial Y_i}{\partial \ln k_j} \right)^2 \sigma^2(\ln k_j),$$

where $\sigma^2(\ln k_j)$ is the variance of the logarithm of rate coefficient k_j and $\partial Y_i / \partial \ln k_j$ is the semi-normalized sensitivity coefficient. The contributions of the uncertainties of standard enthalpies of formation $H_{298}^0(j)$ can be calculated in a similar way

$$\sigma_{T_j}^2(Y_i) = \left(\frac{\partial Y_i}{\partial \Delta_f H_{298}^0(j)} \right)^2 \sigma^2(\Delta_f H_{298}^0(j)),$$

where $\sigma^2(\Delta_f H_{298}^0(j))$ is the variance of the standard enthalpy of formation and $\partial Y_i / \partial \Delta_f H_{298}^0(j)$ is the corresponding sensitivity coefficient. The sum of the contributions of kinetic and thermodynamic uncertainties provides the variance of modelling result Y_i

$$\sigma^2(Y_i) = \sum_j \sigma_{k_j}^2(Y_i) + \sum_j \sigma_{T_j}^2(Y_i).$$

The percentage share $S_{%ij}$ is a good indication of the contribution of the partial variance of kinetic or thermodynamic parameter j to variance $\sigma^2(Y_i)$

$$S_{ij}\% = \frac{\sigma_j^2(Y_i)}{\sigma^2(Y_i)} \times 100.$$

The calculated variances are exact for linear models and are only estimates for highly non-linear chemical kinetic models. However, we have found that these local estimates are not far from the corresponding more precise values, determined by the methods of global uncertainty analysis for the systems investigated. All programs of the CHEMKIN package [10] calculate local sensitivity coefficients, therefore local uncertainty analysis can be performed easily for most combustion systems.

4. Monte Carlo analysis with Latin hypercube sampling

Monte Carlo (MC) simulations have become increasingly common in atmospheric kinetics for global uncertainty analysis [16–21]. Monte Carlo analysis [13] includes that large number of parameter sets are generated according to the probability density functions of these parameters. The model is simulated with each of these parameter sets, and the results are processed with statistical methods. The cornerstone of this approach is the application of an efficient and unbiased method for the selection of the parameter sets.

Using the method of Latin hypercube sampling (LHS) [13], the range of parameters to be varied during the MC simulations is divided into intervals of equal probability. The parameter values are then randomly and independently sampled from each interval, and the selected values of the parameters are randomly grouped. This ensures that the parameter space is represented with a good approximation of full coverage. The distributions of the parameters were all truncated at the physically realistic bounds taken as 3σ . In the Monte Carlo analysis with Latin hypercube sampling (LHS MC) calculations presented in this paper, the models were simulated with 1000 parameter sets. The analysis of the simulation results included the calculation of the means and the variances of the model output.

5. Uncertainties of hydrogen combustion models

Laminar flame velocity of hydrogen/air mixtures at atmospheric pressure was simulated in a wide range of equivalence ratios. The simulation results were compared with recent experimental

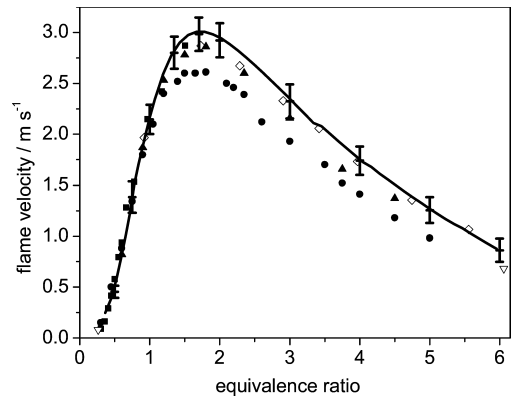


Fig. 1. Flame velocity as a function of equivalence ratio in hydrogen/air mixtures. The solid line is the simulation result and the vertical intervals represent the 1σ uncertainty of the simulation results due to the uncertainty of the kinetic and thermodynamic data. The dots refer to the experimental data: ■, Law and coworkers [22,23]; ◇, Dowdy et al. [24]; ●, Aung et al. [25,26]; ▲, Kwon and Faeth [27]; ▽, Karpov et al. [28].

data [22–28]. Figure 1 shows the calculated laminar flame velocity as a function of equivalence ratio, the 1σ uncertainty of simulation results calculated by Monte Carlo analysis with Latin hypercube sampling, and the experimental data. The measured laminar flame velocity values of lean mixtures were in good agreement with each other and with the simulation results. Interestingly, the calculated modelling uncertainty was also small in this region. For moderately rich and rich mixtures, there was systematic deviation between the experimental results of Dowdy et al. [24] Aung et al. [25,26] and Kwon and Faeth [27]. Our simulation results were closer to the data of Dowdy et al., but the LHS MC uncertainty analysis revealed that the data of Kwon and Faeth were also within the range of uncertainty.

Figure 2 presents the ignition delay τ data of Skinner and Ringrose [29], and Schott and Kinsey [30] measured in shock tube experiments. The compositions of the investigated mixtures were 8% H_2 –2% O_2 –Ar, $p = 5$ atm [29], 1% H_2 –2% O_2 –Ar, $p = 1$ atm, 0.688% H_2 –0.43% O_2 –Ar, $p = 1$ atm, 0.98% H_2 –0.49% O_2 –Ar, $p = 1$ atm, and 3.781% H_2 –1.99% O_2 –Ar, $p = 1$ atm [30]. The published experimental data are the product of the ignition delay time and the initial oxygen concentration in logarithmic scale versus $1000/(T/K)$. Above 1100 K, the simulation results agree very well with the experimental data; below this temperature, the deviation is also not significant. The error bars become smaller as the temperature increases, but the standard deviation remains about 10% of the average value.

Yetter et al., [31] measured the temperature and the concentration profiles of H_2 , O_2 , and H_2O in a flow reactor at 1 atm using a 0.842% H_2

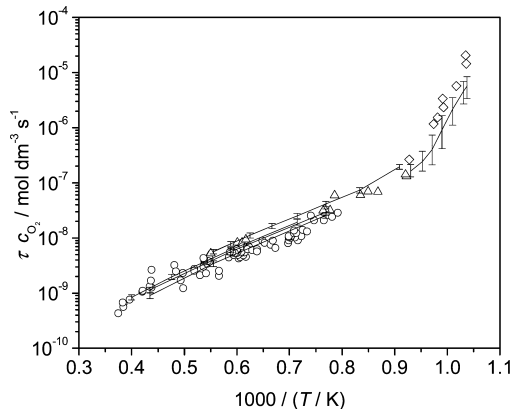


Fig. 2. Ignition delay times in various mixtures measured in shock tubes. \diamond , 8% H_2 –2% O_2 –Ar, $p = 5$ atm of Skinner and Ringrose [29]; Δ , 1% H_2 –2% O_2 –Ar, $p = 1$ atm; \circ , 0.688% H_2 –0.43% O_2 –Ar, $p = 1$ atm, 0.98% H_2 –0.49% O_2 –Ar, $p = 1$ atm, and 3.781% H_2 –1.99% O_2 –Ar, $p = 1$ atm of Schott and Kinsey [30]. The presented data are the product of the ignition delay time and of the initial oxygen concentration. The lines correspond to the calculated nominal values, and the vertical intervals represent the 1σ uncertainty of simulation results.

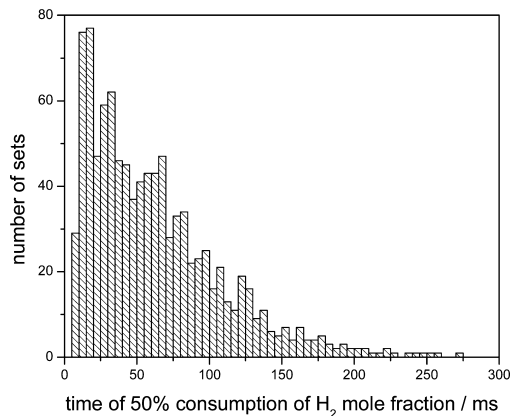


Fig. 3. Histogram of the ignition time obtained in the MC calculations corresponding to the Yetter et al. [31] flow reactor experiment. For details see the text.

H_2 , 1.52% O_2 and 97.638% N_2 mixture. In this experiment, the ignition time τ , defined by the 50% consumption time of H_2 mole fraction, was found to be of the order of 15 ms, but its exact value could not be determined. Figure 3 presents the histogram of the ignition times showing that the distribution is very wide. The majority of the calculated ignition times are between 5 and 200 ms. Note that all the parameter sets used in the calculations were within the physically realistic limits of the parameter values. Figure 4 shows the uncertainty of the concentration and temperature profiles after the time correction. The vertical and

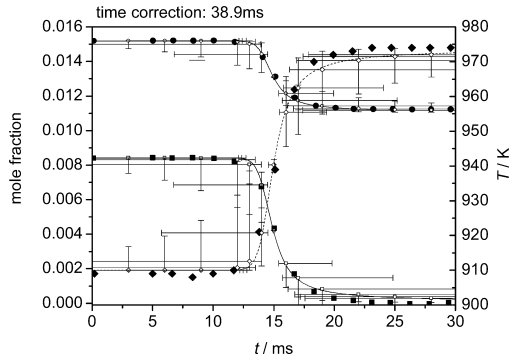


Fig. 4. Temperature and H_2 concentration profiles during the combustion of a lean $\text{H}_2/\text{O}_2/\text{N}_2$ mixture at 1 atm. The solid line is the simulation result; the vertical and the horizontal intervals represent the achievable simulation results in concentration and time, respectively, using any combination of the possible rate parameters. The empty symbols correspond to the average of the MC simulation results, and the dots refer to the experimental data of Yetter et al. [31].

horizontal intervals represent the range of the achievable simulation results (i.e., the endpoints are the minimal and maximal values) in concentration and time, respectively, if all parameters are varied between their allowed minimal and maximal values. Notice that in all other figures the intervals represent the variance of the data. The uncertainty is very small near the point to which the curves were fitted (i.e., 50% consumption of H_2) and is larger diverging from it. Far from the reaction zone, the time uncertainties are large, and the concentration and temperature uncertainties are small. The simulation results based on the nominal parameter set agree well with the experimental curves. Thus, modifications of the parameters result in very different ignition delays, but very similar concentration and temperature curves after the time correction. Consequently, the existing good agreement does not mean that the system is very well known. Very different parameter sets can describe this experiment appropriately.

6. Uncertainties of wet CO combustion models

Laminar flame velocity of atmospheric (95% carbon monoxide + 5% hydrogen)/air mixture was simulated in the equivalence ratio range $\varphi = 0.5$ –6.0. Figure 5 shows the simulated flame velocity as a function of equivalence ratio, its 1σ uncertainty calculated by the LHS MC method and the experimental data of McLean et al. [32]. The simulated values are somewhat larger than the experimental data, but the experimental data are close to the 1σ uncertainty margins.

Local uncertainty analysis was used to investigate further this laminar wet CO flame. Table 1 contains the calculated value of laminar flame

Table 2

Percentage share ($S_{ij}^{\%}$) of the partial variances of kinetic parameters of reactions and enthalpies of formation of species, calculated for the laminar flame velocity ($v_L/\text{cm s}^{-1}$), maximum temperature (T_{\max}/K), and maximum concentrations of H, O, and OH, at the conditions described in the caption of Table 1

φ	0.5		1.0	
	Parameter	$S_{ij}^{\%}$	Parameter	$S_{ij}^{\%}$
v_L	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	68.1	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	33.6
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	14.5	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	20.4
	OH	3.5	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	12.2
	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	3.2	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	6.3
	$\text{H} + \text{HO}_2 = 2\text{OH}$	3.1	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	4.4
T_{\max}	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	45.9	CO	36.8
	CO	18.1	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	23.1
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	11.7	CO_2	21.5
	CO_2	10.6	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	7.2
c_H	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	88.0	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	4.1
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	5.4	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	46.9
			$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	30.6
			$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	7.8
			$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	5.4
c_O	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	87.7	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	4.6
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	5.2	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	38.1
			$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	37.3
c_{OH}	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	66.4	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	8.4
	OH	22.7	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	6.9
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	3.4	OH	82.3
		$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	3.9	
φ	2.0		4.0	
	Parameter	S_{ij}	Parameter	S_{ij}
v_L	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	16.7	HCO	15.4
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	15.4	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	14.6
	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	14.7	$\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$	14.5
	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	13.1	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	12.2
	$\text{H} + \text{HO}_2 = 2\text{OH}$	12.6	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	8.7
	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	10.5	$\text{H} + \text{HO}_2 = 2\text{OH}$	8.5
T_{\max}	CO	60.0	CO	61.6
	CO_2	35.0	CO_2	35.4
	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	3.2		
c_H	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	49.2	HCO	16.5
	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	15.0	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	16.2
	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	12.7	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	14.6
	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	12.4	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	9.1
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	4.2	$2\text{H} + \text{M} = \text{H}_2 + \text{M}$	8.6
c_O	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	54.0	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	7.8
	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	13.8	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	7.6
	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	13.2	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	45.7
	$\text{O}_2 + \text{H} (+\text{M}) = \text{HO}_2 (+\text{M})$	8.5	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	20.5
	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	3.9	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	13.5
c_{OH}	OH	68.6	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	4.7
	$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	11.2	HCO	4.7
	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	7.2	$\text{O}_2 + \text{H} = \text{OH} + \text{O}$	44.1
	$\text{H} + \text{O} + \text{M} = \text{OH} + \text{M}$	5.6	$\text{H}_2 + \text{O} = \text{OH} + \text{H}$	12.1
			HCO	7.9
		$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	7.4	
		$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$	5.9	

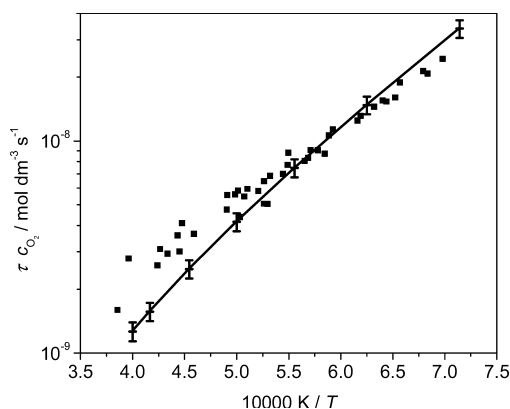


Fig. 6. Ignition delays in a 1% H₂, 3% CO, 5% O₂, 91% Ar mixture as a function of initial temperature. The solid line is the simulation result, the vertical intervals represent the 1 σ uncertainty of simulation results, and the dots refer to the experimental data of Gardiner et al. [33].

Figure 6 compares the experimental [33] and the simulated ignition delay times in a 1% H₂, 3% CO, 5% O₂, 91% Ar mixture as a function of initial temperature. The temperature dependence of the simulated and the experimental ignition delays were similar, and also the simulated and experimental uncertainties were of similar magnitude, but there is a small systematic deviation between the gradients of the two curves.

7. Conclusions

Detailed combustion mechanisms are created using experimental data for the rate coefficients of elementary reactions, if these are available, and specific experimental data for the participating species. Predictions based on these mechanisms, like oxidation of the fuel at various conditions or pollutant formations, are tested by bulk experiments. In the cases of most proposed detailed reaction mechanisms, the agreement between the simulated and the experimental data is reasonably good, but usually not perfect. Realistic comparison of experimental data and simulation results should be based on a quantitative characterization of their deviation, which can be based on the assessment of the experimental errors and the uncertainty analysis of the model.

In this paper, the simulation results were always accompanied by uncertainty analysis results. Both local and global (Monte Carlo) uncertainty analyses were used. The method of local uncertainty analysis allows fast calculation of linear estimates of uncertainties and provides information about the origin of uncertainty. This means that not only the variances of simulation results can be calculated, but also the contribution of the partial variances of kinetic and thermodynamic parameters to the overall variances

of simulation results can be obtained. Monte Carlo analysis provides accurate uncertainties, but the 'naïve' version of this method requires a large number of simulations. The Latin hypercube sampling methodology offers an efficient Monte Carlo analysis, while the results remain unbiased.

The hydrogen and CO oxidation submechanism of the Leeds Methane Oxidation Mechanism was updated using the latest evaluated kinetic and thermodynamic data. The updated mechanism was tested against three hydrogen oxidation and two wet CO bulk experiments. The simulation results were in good agreement with the experimental ignition delays data, but there were some deviations between the simulated and the experimental flame velocities. All calculated flame velocities were larger than the experimental ones. The simulated flame velocity has a relatively large uncertainty due to the uncertainties of the kinetic and thermodynamic data in both hydrogen–air and wet CO flames.

In the case of ignition experiments, for both fuels the uncertainties of the simulated ignition delay times were small and comparable with the scatter of the experimental data.

There was a good agreement between the temperature and concentration profiles of hydrogen oxidation, measured in a flow reactor by Yetter et al., and the simulated curves. However, the uncertainty of the calculated ignition delay (the required time correction) was found to be very large. The uncertainties of the temperature and the concentrations of H₂ and O₂ were small after the appropriate time correction. This means that modifications of the parameters provide very different ignition delays, but very similar curves after the time correction. Consequently, the good agreement does not mean that the system is very well known.

Local uncertainty analysis of the wet CO flame revealed that uncertainties of the rate parameters of reactions O₂ + H (+M) = HO₂ (+M), and CO + OH = CO₂ + H cause high uncertainty to the calculated flame velocity, temperature, and the peak concentrations of radicals. The uncertainty of the enthalpy of formation of OH is highly responsible for the uncertainty of the calculated peak OH concentration and that of the enthalpy of formation of HCO was important at very rich mixtures for both the flame velocity and the concentrations.

Acknowledgments

The authors acknowledge the helpful discussions with D.L. Baulch, T. Bérces, S. Dóbbé, K.J. Hughes, A. Konnov, T. Perger, M.J. Pilling, and A.S. Tomlin and the support of OTKA (Grant No. T43770) and HIAL (Grant No. ENK5-2001-00517).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.proci.2004.08.172.

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Comments

R.A. Yetter, Penn State, USA. In your local sensitivity analysis of the H₂/O₂ flow reactor data with time shifting, what computational time was used to initiate the sensitivity calculations, i.e., was it $t = 0$ s from the model calculations or at the time of the first data point of the experiments? The choice would influence your overall uncertainties.

Reply. No local sensitivity or local uncertainty analysis was reported on the H₂/O₂ flow reactor data in either the paper or the lecture.

M. Frenklach, UC Berkeley, USA. Can you please provide a numerical comparison between local and global uncertainty values obtained in your study?

Reply. There was a good agreement between the local and global (Monte Carlo) uncertainty analysis results except at equivalence ratio 0.5, as shown in Table 1.

Frederick L. Dryer, Princeton University, USA. The mechanism that you tested does not compare favorably to our more extensive H₂/O₂ data [1] in either pre- or post-induction (flow reactor) profiles. Your

Table 1

Calculated percentage of the 1σ uncertainty of laminar flame velocity ($v_L/\text{cm s}^{-1}$), maximum temperature (T_{max}/K), and maximum molar concentrations of H, O, and OH ($c/\text{mol cm}^{-3}$) at equivalence ratios $\phi = 0.5, 1.0, 2.0,$ and 4.0 of freely propagating laminar flames of (95% CO + 5% H₂)/air mixtures

ϕ	0.5		1.0		2.0		4.0	
	Local (%)	Global (%)	Local (%)	Global (%)	Local (%)	Global (%)	Local (%)	Global (%)
v_L	7.71	5.48	4.98	4.68	5.26	5.04	8.27	8.78
T_{max}	0.11	0.09	0.09	0.08	0.06	0.06	0.06	0.06
c_{H}	21.39	7.97	9.14	7.68	7.53	7.95	10.07	10.24
c_{O}	13.16	5.57	6.33	6.07	7.12	7.94	14.30	14.30
c_{OH}	5.60	3.43	1.87	2.09	2.19	2.39	8.20	9.46

model actually requires positive, unrealistic time shifting as well. Comparison with our updated hydrogen/oxygen mechanism [2] gives more details on this problem and the mechanism therein compares much more favorably with a very wide range of experimental results including the above.

The techniques, which are conceptually the same as the local and global sensitivity methods in Scire et al. [3], are inappropriately applied here in terms of the method chosen to compare experiments and computations. Your results are a good demonstration of why our group has consistently recommended that flow reactor results should not be used to characterize induction chemistry [4–6]. Comparisons that use “zero time” (entry) matching conditions with flow reactors are subject to large uncertainties. For more complex reaction systems in which experimental perturbations occur in the early reaction time history, we have demonstrated and applied another means of constraining the input parameters such that global sensitivity methods can be more properly applied [6] by matching at some downstream extent of reaction.

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Reply. We have not tested our mechanism against the data of articles [1,2], but we will do it in the near future. Article [3] discussed the application of a Monte Carlo method in conjunction with parameter estimation. The methods used by us are substantially different and focused on the comparison of experimental and computational results. Similar methods have been used (Refs. [16–21] in paper) in atmospheric chemistry. We agree that flow reactor experiments are not appropriate for the characterization of the induction period.