Reduction of detailed kinetic mechanisms for pyrolysis, combustion, and detonation modeling

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Abstract. The values of ignition delay predicted for stoichiometric C₂H₂/O₂ and CH₄/O₂ mixtures by various detailed kinetic mechanisms presented in the literature are compared over the temperature range of 1000 < T < 2100 K and the pressure range of 0.02 < P < 1.1 MPa. The number of species in detailed kinetic mechanisms is reduced by a trial-and-error method while keeping the response of ignition delay within a relative error range of δ = 30%. The automatic computer code developed in this study has made it possible to reduce the number of species by a factor of more than 2 for the C₂H₂/O₂ mixture and a factor of 3 for the CH₄/O₂ mixture, respectively. A comparison of predictions based on the reduced mechanisms with experimental data presented in the literature shows good agreement.

1. Introduction

Ignition, combustion, and detonations in premixed gases are the focus of interest of various research groups. This is explained by the ubiquity of these processes in technologies, industrial and power-generating facilities, and propulsion systems. Since full-scale experiments involve huge costs, numerical simulation is widely applied at many stages of research [1] with a view to revealing the specifics of various physicochemical processes and optimizing experimental approaches [2]. It is a particularly valuable tool for studying the intermediate processes of transition from local ignition to combustion and detonation [3, 4]. Ignition delay τ is an important characteristic of these intermediate processes [5]. Its determination has been the subject of numerous experimental studies using a variety of techniques [5, 6]. Zero-dimensional analysis of ignition delay from a chemical kinetics perspective relies on the development of detailed kinetic mechanisms (DKMs) [7–12]. Based on experimental results obtained for ignition and oxidation of homogeneous hydrocarbon–oxygen mixtures, the use of different DKMs leads to different values of τ. This is due to considerable scatter in experimental data obtained by using different techniques under different conditions in terms of temperature, pressure, and mixture composition. Therefore, simulation of processes involving deflagration-to-detonation transition requires an analysis of the DKMs employed. Furthermore, modeling of ignition, combustion, and detonation requires numerical integration of complex sets of differential equations, which entails significant costs in terms of computing time and RAM usage. In particular, since reaction kinetics described by a DKM is governed by a stiff system of ODEs, whose Jacobian matrix has very different eigenvalues [13, 14], accurate solution of a direct problem requires very fine time-stepping, which leads to rapid error growth and increase in overall CPU time. Thus, the number of...
reactions and species in the DKM has to be reduced. As a result, one obtains a reduced kinetic mechanism (RKM) [1, 14] and/or a "global" kinetic mechanism (GKM) [15]. Most reduction methods are designed to reduce the number of reactions [1, 14]. However, the rank of the Jacobian matrix is determined by the number of species in the DKM. Whereas reaction rates are calculated by performing arithmetic operations on matrices, integration is performed in the composition space spanned by the large number of species concentrations. Therefore, it is reasonable to reduce the number of species as well as the number of reactions.

In this paper, we compare the values of $\tau$ for stoichiometric acetylene–oxygen and methane–oxygen mixtures predicted by various DKMs presented in the literature [7–12] and validate a method for reducing the number of species in a DKM. The choice of mixture compositions is made to demonstrate the universality of the proposed method. Acetylene has the highest energy content per unit mass and is the most explosive of all hydrocarbons, while methane is its antipode [5, 16]

2. Numerical simulations

All simulations are performed by using the CHEMKIN III package [17] under constant-volume conditions. Initial temperature is varied between 1000 and 2100 K for the mixture of $21.43\%\text{C}_2\text{H}_2 + 53.575\%\text{O}_2$ in Ar ($\phi = 1$) and between 1300 and 2000 K for $10\%\text{CH}_4 + 20\%\text{O}_2$ in Ar ($\phi = 1$). Initial pressure is set at 0.02, 0.1, and 1.1 MPa for the acetylene–oxygen mixture and 0.65 MPa for the methane–oxygen mixture. Since NASA format is required for thermodynamic data input in the CHEMKIN III module [17], the numerical simulations use only the DKMs represented in the literature [7–12] that contain the appropriate thermodynamic data files. The ignition delay $\tau$ is defined as the time corresponding to the highest rate of pressure rise [5].

Figure 1 presents graphs of $\tau$ obtained by using the DKMs of [7–12]. It is clear that the DKMs of [9, 11, 12] predict similar values of $\tau$ at $P = 0.02$ and 0.1 MPa over the entire temperature range, and only at $P = 1.1$ MPa the DKM of [9] predicts a longer $\tau$ for $T < 1200$ K. At the same time, the ignition delay times predicted by the DKM of [8] are the shortest at all pressures and temperatures, whereas those predicted by the DKM of [10] are the longest. Figure 1 illustrates characteristic changes in behavior of $\tau$ with pressure predicted by the DKMs of [8–12]. At lower temperatures, the increase in ignition delay with pressure is more pronounced. The change in $\tau$ with pressure at $T < 1200$ K is
weaker for the DKMs of [9, 11, 12] compared to the DKM of [10] and stronger compared to that predicted by the DKM of [8]. However, the curves of temperature-dependent \( \tau \) predicted for \( T > 1500 \) K by all DKMs of [8–12] have similar shapes. Variation in temperature dependence of \( \tau \) with pressure similar to the results based on [9–12] was predicted in [18] for pressures between 0.01 and 5 MPa over the same temperature range.

Overall, figure 1 demonstrates that simulations based on different DKMs yield different results, both qualitatively and in terms of absolute values of time-dependent ignition delay, for the acetylene–oxygen mixture. Note also that the difference in absolute values of \( \tau \) can exceed an order of magnitude. It is important to choose a particular DKM to be reduced. According to figure 1, the best agreement at the three pressures under study is achieved between the temperature-dependent curves of \( \tau \) predicted by the DKMs of [11, 12]. We have selected the DKM of [12] for further reduction.

The number of species in a detailed kinetic model is reduced by a trial-and-error method based on an analysis of the response of a target parameter to the removal of a species [14]. As such a parameter, we use the ignition delay for a hydrocarbon–oxygen mixture. The species considered as candidates for elimination include only the intermediate ones (molecules, radicals, and atoms) that play a minor role in branched chain propagation [5]. Therefore, the species not to be eliminated include the O and H atoms and the OH, HO\(_2\), and HCO radicals, as well as the original reactants. Also excluded from consideration as candidates for elimination are the molecules constituting the products of hydrocarbon combustion at quasi-equilibrium, such as CO, CO\(_2\), CH\(_2\)O, H\(_2\)O\(_2\), and H\(_2\)O.

| \( P \) (MPa) | \( T = 1000 \) K | \( T = 1200 \) K | \( T = 1500 \) K | \( T = 2100 \) K |
|--------------|-----------------|-----------------|-----------------|-----------------|
| DKM          | RKM             | DKM             | RKM             | DKM             | RKM             | DKM             | RKM             |
| 0.02         | 3.28E-4         | 3.25E-4         | 9.08E-5         | 9.07E-5         | 3.06E-5         | 3.06E-5         | 9.22E-6         | 9.53E-6         |
| 0.1          | 1.14E-4         | 1.11E-4         | 2.25E-5         | 2.24E-5         | 6.32E-6         | 6.33E-6         | 1.88E-6         | 1.91E-6         |
| 1.1          | 2.43E-4         | 2.19E-4         | 7.58E-6         | 7.29E-6         | 7.91E-7         | 7.88E-7         | 1.75E-7         | 1.78E-7         |

For acetylene, simulations are performed with each of the candidate species removed one at a time at 0.02, 0.1, and 1.1 MPa for the three temperatures of 1000, 1500 and 2100 K. The mechanism reduced is the DKM of [12], which consists of 405 reactions involving 57 species. To speed up the procedure, a FORTRAN-77 code has been developed that can automatically remove species one by one together with the reactions involving them. If the ignition delay obtained after removing a particular species differs from that predicted by the original DKM by less than \( \delta = 20\% \), then the species is eliminated. Finally, the procedure has reduced the DKM of [12] to an RKM of 25 species participating in 124 reactions. The table compares the temperature-dependent ignition delay times predicted by the DKM of [12] and the RKM. It demonstrates good agreement between the values of \( \tau \) obtained by using the DKM and RKM at the three pressures over the entire temperature range.

3. Results and discussion

Figures 2 and 3 compare the values of \( \tau \) predicted by the RKM with experimental data reported in [19–21]. Figure 2 demonstrates good agreement between the temperature-dependent ignition delay predicted by the RKM and experimental data from [19, 20]. Also plotted here are the values of \( \tau \) predicted by the DKMs of [7, 11, 22]. Even though the ignition delay times presented in figure 2 are obtained for a C\(_2\)H\(_2\)/O\(_2\) mixture highly diluted with argon, it is clear that the predictions of the DKM of [11] are close to those of the RKM, as under the conditions of the simulations represented in figure 1. However, the predictions of \( \tau \) by the DKMs of [7, 22] are less accurate. While the DKM of [7] is a relatively compact model, the DKM of [22] is the most comprehensive to date of the mechanisms presented in the literature. Figure 3 compares the temperature-dependent values of \( \tau \) predicted for
C$_2$H$_2$/O$_2$/Ar by the RKM and the DKMs of [11, 22] with those measured in [21]. It is clear that the RKM provides a good approximation of the experimental results of [21], and so does the DKM of [11], whereas the DKM of [22] is less accurate overall than the RKM and the DKM of [11] and predicts a somewhat different shape of time-dependent τ curves.

![Figure 2](image2.png)

**Figure 2.** Time-dependent ignition delay for 0.5%C$_2$H$_2$+1.25%O$_2$ in Ar at $P \approx 0.1$ MPa. Circles are experimental data points from [20]; triangles, those from [19]. Curves represent predictions by the RKM proposed in this work and by the DKMs of [7, 11, 22].

![Figure 3](image3.png)

**Figure 3.** Time-dependent ignition delay for 8.6%C$_2$H$_2$ + 21.4%O$_2$ in Ar at $P \approx 0.4$ MPa. Symbols are experimental data points from [21]. Curves represent predictions by the RKM proposed in this work and by the DKMs of [11, 22].

Besides validating the present DKM reduction method for C$_2$H$_2$/O$_2$/Ar mixtures, we reduced the DKM of [12] as applied to a CH$_4$/O$_2$/Ar mixture under the experimental conditions of [23] (see figure 4). Setting $\delta = 30\%$, we reduced the DKM of [12] for the CH$_4$/O$_2$/Ar mixture at $1300 < T < 2000$ K and $P = 0.65$ MPa to an RKM consisting of 60 reactions involving 16 species. It is clear from figure 4 that the values of $\tau$ predicted by the RKM and the DKM of [12] are almost equal for $\phi = 1$, and are
very close to those predicted by the DKM of [11]. The reduction was performed without considering the effect of $\phi$, because it had proved to be negligible despite variation of this parameter by a factor of 9 in experiments and simulations [23] (see figure 4). Thus, DKM reduction can be performed while keeping the value of $\phi$ constant at unity.

The degree of reduction can be varied by varying the value of $\delta$. In particular, by changing the value of $\delta$ to 10% for the $\text{C}_2\text{H}_2/\text{O}_2$, the DKM of [12] is reduced to a model consisting of 235 reactions involving 37 species. Since ignition delay is a gross parameter characterizing premixed combustion, the choice of $\delta$ strongly depends on the modeling problem at hand. An analysis of the comparisons between ignition delay times in figures 2–4, obtained by using the RKM and various DKMs, shows that of importance is not only the reduction method employed but also the choice of a DKM to be reduced. Different DKMs predict measured values of $\tau$ with different accuracies. At the same time, a measured ignition delay may vary within a factor of 2. Furthermore, the values of $\tau$ reported by different research groups are frequently widely different [5]. Therefore, there is some liberty in choosing both the DKM to be reduced and the value of $\delta$. The actual choice depends not only on the process to be simulated, including gas dynamics, but also on the approach to such problems used by a particular researcher.

![Figure 4](image_url)

**Figure 4.** Time-dependent ignition delay for 10%$\text{CH}_4$+20%$\text{O}_2$ in Ar. Symbols are experimental data points from [21]. Curves represent predictions by the RKM proposed in this work and by the DKMs of [11, 22] for $\phi = 1$.

While the DKM reduction performed in this work uses ignition delay as a target parameter, a variety of modeling problems focused on other ignition, combustion, and detonation characteristics can be formulated. Characteristics of interest may include laminar flame speed, concentration–time profiles of starting reactants and products, and total heat release. In simulations of hydrocarbon pyrolysis processes, the reduction targets can be experimental time profiles of products or their concentrations at the time when samples are taken for chemical analysis. In a study focused on emission by a reacting system or measurement of probe current, the targets may include excited electronic states of atoms, radicals, or molecules contributing to the process of interest.

### 4. Conclusions
The trial-and-error method proposed for reducing detailed mechanisms has been validated by applying it to autoignition of mixtures of acetylene and methane with oxygen. The number of species and reactions has been significantly reduced by using ignition delay as a target parameter. A comparison between predictions of the RKM developed in this work and experimental data on ignition delay presented in the literature has shown good agreement. Reduction of the number of species in a DKM could be further advanced by developing an algorithm for searching the minimums of a functional \( \Psi(P, T, \delta, \eta) \), where \( \eta \) is a target parameter. Success in DKM reduction would largely depend on the definition of \( \eta \) and the trade-off between degree of reduction and the accuracy determined by the value of \( \delta \). The present work has shown that DKM reduction can be performed efficiently by the trial-and-error method even without analyzing a functional \( \Psi \).

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**References**

[1] Frenklach M 1984 Modeling *Combustion Chemistry* ed W C Jr Gardiner (New York: Springer) chapter 7 pp 423–453
[2] Frolov S M, Dubrovskii A V and Ivanov V S 2013 *Russian J. Phys. Chem. B* 7 35
[3] Liberman M A, Kiverin A D and Ivanov M F 2012 *Physical review E* 85 056312
[4] Ivanov M F, Kiverin A D, Klumov B A and Fortov V E 2014 *Physics - Uspekhi* 184 247
[5] Zamanskii V M and Borisov A A 1989 The Mechanism and the Promotion of Self-Ignition of the Advanced Fuels *Achievements of Science and Engineering Ser. Kinet. Catal.* (Moscow: VINITI vol 19)
[6] Leschevich V V, Martynenko V V, Penyazkov O G, Sevrourk K L and Shabunya S I 2016 *Shock Waves* 26 657
[7] Smith G P, Golden D M, Frenklach M, Moriarty N W, Eiteneer B et al 1999 GRI-Mech 3.0 (http://combustion.berkeley.edu/gri-mech/version30/text30.html)
[8] Battin-Leclerc F 2008 *Progress in Energy Combust. Sci.* 34 440
[9] Fernandez-Galisteo D, Sanchez A L, Linan A and Williams F A 2009 *Combust. Theory Modelling* 13 74
[10] Smith G P, Tao Y and Wang H 2016 (FFCM-1) (http://nanoenergy.stanford.edu/ffcm1)
[11] Zhou C-W, Li Y, Burke U et al 2018 *Combust. Flame* 197 423
[12] Tereza A M, Medvedev S P and Smirnov V N 2019 *Acta Astronautica* 163 18
[13] Kalitkin N N 1978 *Numerical methods* (Moscow: Nauka)
[14] Turanyi T and Tomlin A S 2014 *Analysis of Kinetic Reaction Mechanisms* (Heidelberg: Springer)
[15] Basevich V Ya, Belyaev A A and Frolov S M 1998 *Chemical Physics Reports* 17 1895
[16] Tereza A M and Anderzhano E K 2019 *Russian J. Phys. Chem. B* 13 626
[17] Kee R J, Rupley F M, Meeks E and Miller J A 1996 CHEMKIN III *Preprint SAND96-8216*
[18] Varatharajan B and Williams F A 2001 *Combust. Flame* 125 624
[19] Rickard M J A, Hall J M and Petersen E L 2005 *Proc. Combust. Inst.* vol 30 ed Chen J H, Barlow R S, Colket M D and Yetter R A (Pittsburg, PA: Combustion Institute) pp 1915–23
[20] Smirnov V N, Tereza A M, Vlasov P A and Zhiltsova I V 2017 *Proc. Symp. Int. Shock Waves* vol 31 ed Sasoh A, Aoki T and Katayama M (Nagoya, Japan: Springer) pp 159–67
[21] Baranyschyn Y A, Krivosheyev P N, Penyazkov O G and Sevrourk K L 2020 *Shock Waves* (DOI:10.1007/s00193-020-00937-0)
[22] Ranzi E, Frassoldati A, Grana R et al 2012 *Progress Energy Combust. Sci.* 38 468
[23] Tereza A M, Severin E S and Slutskii V G 2003 *Khim. Fizika* 6 30