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ORIGINAL PAPER

Structural analysis of combustion mechanisms

János Tóth · **Attila László Nagy** ·
István Gyula Zsély

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Abstract Thirty-nine detailed mechanisms for combustion of hydrogen, carbon monoxide and methanol are investigated using `ReactionKinetics`, a *Mathematica* based package published earlier. Our methods involved mainly structural and graph theoretical approaches as well as techniques which are related to the time evolution of the considered mechanisms. Our investigations support the view that the hydrogen mechanisms tend to take on a final form in these days. CO combustion mechanisms, however, showed a larger variety both in species and in reaction steps. There exist only a few mechanisms directly developed to describe methanol combustion (mechanisms developed for other purposes may contain a submechanism for methanol combustion); the big differences between them shows that the modeling community is only at the very beginning of exploring this process. Most of our results do not depend on the choice of reaction rate coefficients, the methods only use the underlying sets of reaction steps, hence they are robust and general. These investigations can be used before

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J. Tóth
Department of Mathematical Analysis, Budapest University of Technology and Economics,
Egry J. u. 1., Budapest 1111, Hungary
e-mail: jtoth@math.bme.hu

J. Tóth · I. G. Zsély
Laboratory for Chemical Kinetics of the Department of Physical Chemistry, Eötvös Loránd University,
Pázmány P. sétány 1/A, Budapest 1117, Hungary
e-mail: zsigy@chem.elte.hu

A. L. Nagy (✉)
Department of Stochastics, Budapest University of Technology and Economics, Egry J. u. 1.,
Budapest 1111, Hungary
e-mail: nagyal@math.bme.hu

or in parallel with usual numerical investigations, such as pathway analysis, sensitivity analysis, parameter estimation or simulation. The package and the methods may be useful for automatic mechanism generations, testing, comparing and reduction of mechanisms as well, especially in the case of large systems.

Keywords Combustion · Mathematical modeling · Graphs of reactions · Mathematica

Mathematics Subject Classification 92E10 · 80A30 · 80A25 · 34D

1 Introduction

The reaction steps of hydrogen and carbon monoxide combustion form a central part of the high temperature combustion of all hydrocarbons and oxygenates. Also, hydrogen is an important fuel itself in areas like carbon-free economy, safety issues, and rocket propulsion. In the recent years, there has been an increased interest in studying the combustion of fuel mixtures consisting of carbon monoxide and hydrogen, referred to as “wet CO” or syngas. These fuels can be produced from coal and biomass via gasification, and are considered to be a promising option towards cleaner combustion technologies for power generation. Oxygenated organic compounds have been proposed as alternative fuels in order to improve the fuel properties and reduce particulates and NOx emissions. Methanol is one of the most important oxygenated additives since it is the simplest alcohol, has high oxygen content and no C–C bonds.

In the present paper we investigate the combustion of hydrogen, carbon monoxide and methanol: three phenomena important both from theoretical and practical points of view in combustion.

The approach we use is absolutely structural in the sense that none of the results depend on the values of the rate coefficients (cf. [3]). We might say that we are going to discover possibilities instead of quantitatively dealing with individual mechanisms. To put it another way, we are going to raise questions to be answered by the chemist, rather than answering them.

In a previous paper we presented a *Mathematica* based program package called `ReactionKinetics` [27] aimed at symbolic and numerical treatment of chemical mechanisms. The package is especially useful when the numbers of species and reaction steps are larger than to allow manual investigations, i.e. if one has dozens or even thousands of species and reaction steps. After the publication of the previous version we made the package capable of reading CHEMKIN files by `CHEMKINImport`, added dozens of new functions and made the package compatible with Version 9 of *Mathematica*.

The structure of our paper is as follows. In Sect. 2 the mechanisms to be investigated are described. Results are shown in Sect. 3. The necessary mathematical background is relegated to the “Appendix”.

Finally, two electronic supplements are added. First, a *Mathematica* notebook showing all the details of the calculations which may be really useful for those interested in combustion modeling but of minor interest for the general audience. Some of the resulting figures are also given there. The calculations can be reproduced by using the package itself which can be downloaded from the following page:

http://www.math.bme.hu/~jtoth/Combustion2014.

The data can either be collected from the original authors, or from our database to be built in the near future. Second, we also attach the (very long) PDF version of our notebook which allows to passively follow what we have done, but this version does not need the *Mathematica* program.

2 Selected mechanisms of combustion of hydrogen, carbon monoxide and methanol

The simplest chain branching combustion reaction, the oxidation of hydrogen is already a much more complex system than the Mole and Robertson reactions discussed in the "Appendix". It is a common misconception that the chemistry of these low-order systems is well understood: Zsély et al. [45] showed recently in a comprehensive mechanism comparison paper that this is not the case. The description of the experimental data is still not satisfactory and some of the recently published reaction mechanisms perform worse than older ones. Similar comparison was done by Olm et al. [31] for the oxidation of carbon monoxide. In this work we utilize the mechanism collection of these papers, but focus on the structural differences of the mechanisms. By extending the investigations to some detailed methanol mechanisms we show that the suggested formal mathematical handling is still applicable for even larger kinetic systems. The phenomena are more and more complex as we proceed from hydrogen through carbon monoxide to methanol. Correspondingly, the mechanisms are larger and more and more diverse.

3 On the structure of the selected combustion mechanisms

Even the simplest mechanisms for combustion usually contain dozens of species and of reaction steps, therefore we can only show selected parts of the results here, e.g. Volpert graphs of the investigated reactions are not shown here as the figures themselves are not useful, they can only be used for calculating the Volpert indices. However, we have shown the Volpert graphs together with Volpert indices for two simple reactions in the "Appendix".

3.1 Hydrogen

As a starting point the basic data of the investigated mechanisms are presented in Table 1.

> *Number of species*, M All mechanisms contains the same (core) set of species: H, H_2, H_2O, OH, H_2O_2, HO_2, O_2, O. The Keromnes2013 mechanism, formally, contains $h\nu$ as a species, but this is only a description for the photoexcitation in a photochemical reaction step.

Table 1 Basic data of the investigated hydrogen combustion mechanisms

Mechanism	Reference	M	R	$\delta = N - L - S$
Ahmed2007	[1]	8	38	$29 - 11 - 6 = 12$
Burke2012	[7]	8	38	$31 - 12 - 6 = 13$
CRECK2012	[16]	8	37	$29 - 11 - 6 = 12$
Dagaut2003	[9]	8	42	$31 - 12 - 6 = 13$
Davis2005	[10]	8	40	$31 - 12 - 6 = 13$
GRI30	[36]	8	40	$31 - 12 - 6 = 13$
Hong2011	[17]	8	40	$31 - 12 - 6 = 13$
Keromnes2013	[18]	9	42	$32 - 12 - 7 = 13$
Konnov2008	[20]	8	42	$31 - 12 - 6 = 13$
Li2007	[23]	8	38	$31 - 12 - 6 = 13$
NUIG2010	[16]	8	38	$31 - 12 - 6 = 13$
OConaire2004	[30]	8	38	$31 - 12 - 6 = 13$
Rasmussen2008	[32]	8	40	$31 - 12 - 6 = 13$
SanDiego2011	[8]	8	42	$31 - 12 - 6 = 13$
SaxenaWilliams2006	[35]	8	42	$31 - 12 - 6 = 13$
Starik2009	[37]	9	52	$41 - 16 - 7 = 18$
Sun2007	[38]	8	40	$31 - 12 - 6 = 13$
USC2007	[43]	8	40	$31 - 12 - 6 = 13$
Zsely2005	[46]	8	42	$31 - 12 - 6 = 13$

This mechanism is the only one which contains the excited OH species (OHEX) to describe some ignition delay experiments better.

There is another mechanism (Starik2009) which contains an additional species, ozone. It is quite unique to include this species in a reaction mechanism intended to be used for the description of combustion processes.

Number of reaction steps, R The number of reaction steps, R, varies between 37 and 44, except Starik2009, where this number is 52. Thus—as Law [22] reported in his comprehensive review paper—the number of reactions is approximately 5 times larger than the number of species (except the mentioned case).

Deficiency, δ The number of complexes, N, varies between 29 and 32, except Starik2009, where this number is 41. The number of weakly connected components is either 11 or 12, except again Starik2009, where this number is 16. The preliminary data suggest that Starik2009 is structurally richer than the other mechanisms.

The deficiencies are large, neither the zero deficiency theorem, nor the one deficiency theory can be applied.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as all the reactions, except in CRECK2012, are fully reversible. Accordingly, all the reactions are weakly reversible, except again CRECK2012, which has a single **irreversible step**: $H_2O_2 + O \longrightarrow HO_2 + OH$.

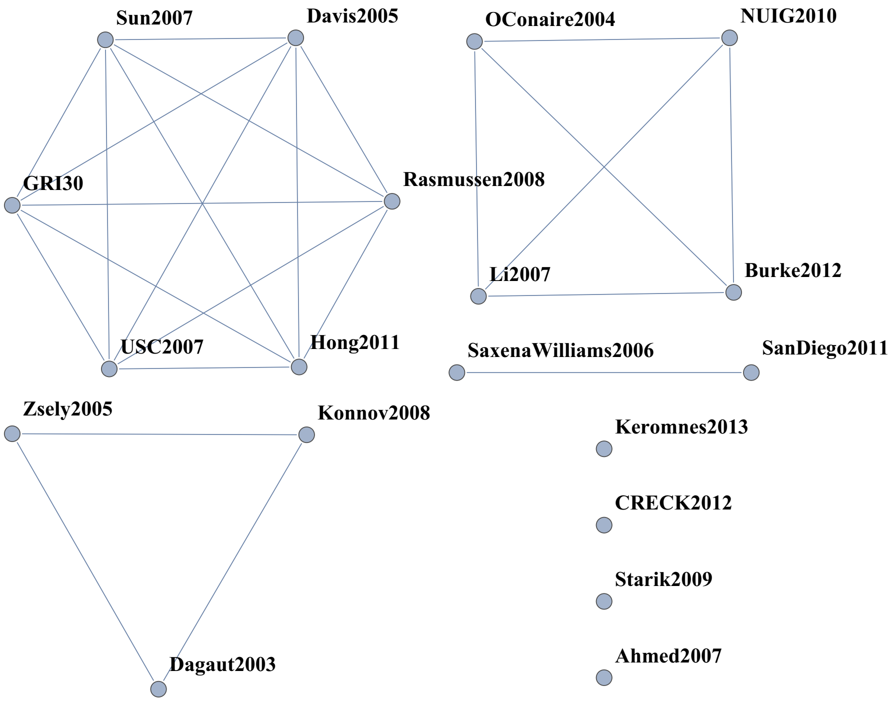

Fig. 1 Classes of hydrogen combustion mechanisms. Mechanisms with the same structure are connected with an edge of the graph

3.1.1 Representations of mechanism classes

From our—let us emphasize: structural—point of view not all the mechanisms in Table 1 are different, one has classes with exactly the same structure if the values of reaction rate coefficients are disregarded. (To put it another way: the underlying complex chemical reaction is the same.) The classes are shown in Fig. 1.

During mechanism development one of the first steps is the decision of which species should be included in the mechanism. After this, the reaction steps and the best possible (to the best knowledge of the authors) set of parameters are selected. This last step, the assignment of the rate parameters forms the largest part of a mechanism development work. However, we have to keep it in mind that the parameter set corresponds to the previously fixed structure of the model. Therefore, it is important to compare the mechanisms from the point of view of their structures. Figure 1 is a demonstrative example that the currently published hydrogen combustion mechanisms are different not at the level of the parameters, but already in their general structures (i.e. the reaction steps underlying in the mechanism). It is interesting to see that a significant number of reaction mechanisms in this collection kept the structure of the old GRI30. It is also interesting, that when the mechanisms are updated most of the authors do not modify their structures (see the reaction mechanisms coming from the same research group, e.g. SaxenaWilliams2006 and SanDiego2011, or Li2007

Table 2 Volpert indices of the species in Ahmed2007

Index	Species
0	H_2, O_2
1	H, HO_2, O
2	H_2O_2, H_2O, OH

Table 3 Volpert indices of the species in Burke2012

Index	Species
0	H_2, O_2
1	H, HO_2, O
2	H_2O_2, OH
3	H_2O

Table 4 Volpert indices of the reaction steps in Burke2012

Index	Reaction steps
0	$H_2 \longrightarrow 2H, H_2 + O_2 \longrightarrow H + HO_2, O_2 \longrightarrow 2O$
1	$HO_2 + O \longrightarrow O_2 + OH, H + O \longrightarrow OH, H + HO_2 \longrightarrow 2OH,$ $2O \longrightarrow O2, H + O_2 \longrightarrow HO_2, H + HO_2 \longrightarrow H_2 + O_2,$ $2\ HO_2 \longrightarrow H_2O_2 + O_2, 2\ H \longrightarrow H_2, HO_2 \longrightarrow H + O_2,$ $H + O_2 \longrightarrow O + OH, H_2 + O \longrightarrow H + OH, H_2 + HO_2 \longrightarrow H + H_2O2$
2	$HO_2 + OH \longrightarrow H_2O + O2, O + OH \longrightarrow H + O_2,$ $H + OH \longrightarrow H_2 + O, OH \longrightarrow H + O, 2\ OH \longrightarrow H + HO_2,$ $H_2 + OH \longrightarrow H + H_2O, H + OH \longrightarrow H_2O, 2\ OH \longrightarrow H_2O + O,$ $H + H_2O_2 \longrightarrow H_2 + HO_2, 2\ OH \longrightarrow H_2O_2, H_2O_2 \longrightarrow 2\ OH,$ $H + H_2O_2 \longrightarrow H_2O + OH, H_2O_2 + OH \longrightarrow H_2O + HO_2,$ $HO_2 + OH \longrightarrow H_2O_2 + O, H_2O_2 + O \longrightarrow HO_2 + OH,$ $O_2 + OH \longrightarrow HO_2 + O, H_2O_2 + O_2 \longrightarrow 2\ HO_2,$
3	$H_2O + O_2 \longrightarrow HO_2 + OH, H_2O + HO_2 \longrightarrow H_2O_2 + OH, H_2O + O \longrightarrow 2\ OH,$ $H_2O + OH \longrightarrow H + H_2O_2, H + H_2O \longrightarrow H_2 + OH, H_2O \longrightarrow H + OH$

and Burke2012, or OConaire2004 and NUIG2010). Clinging to potentially outdated structures can be one of the possible pitfalls in mechanism development. The structural relationship the OConaire2004, Li2007, NUIG2010 and Burke2012 is obvious, as they are based on some older reaction mechanisms of Dryer's group [26].

However, this finding allows us to choose a single mechanism from the classes, and we remind the reader that from now on Davis2005 also represents GRI30, Hong2011, Rasmussen2008, Sun2007, USC2007; Burke2012 also represents Li2007, NUIG2010, OConaire2004; and Dagaut2003 also represents Konnov2008 and Zsely2005. SanDiego2011 also represents SaxenaWilliams2006; whereas each of Ahmed2007, CRECK2012, Keromnes2013 and Starik2009 form a separate class. The representatives have been selected by the caprice of the alphabet.

Given that the initial species in the case of hydrogen combustion mechanisms are H_2 and O_2, the Volpert indices of the species are displayed in Tables 2, 3, 5, 7, 8 and 9. The Volpert indices of the reaction steps will only be given in the case of Burke2012 (Table 4).

Table 5 Volpert indices of the species in CRECK2012

Index	Species
0	H_2, O_2
1	H, HO_2, O
2	H_2O_2, OH
3	H_2O

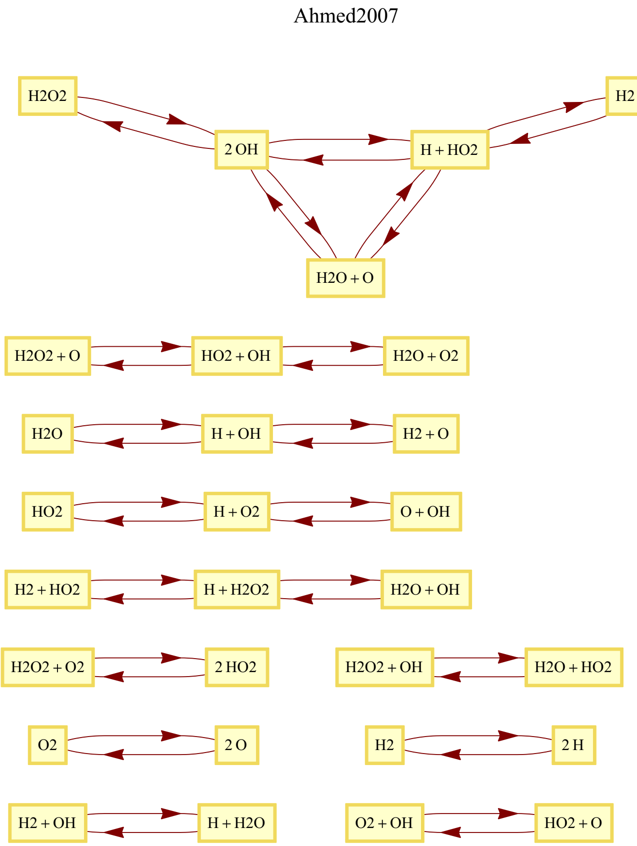

Fig. 2 The Feinberg–Horn–Jackson graph of Ahmed2007

3.1.2 Ahmed2007

As an illustration, the Feinberg–Horn–Jackson graph of the Ahmed2007 mechanism is shown in Fig. 2.

One can also investigate the maximal (weakly) connected components of the Feinberg–Horn–Jackson graph. It turned out that this substructure is rather stable: the maximal (weakly) connected components of Ahmed2007-, Davis2005-, SanDiego2011- and Starik2009-type mechanisms are the same. Also, in the case of Burke2012-, CRECK2012- and Keromnes2013-type mechanisms we get the same

Table 6 Volpert indices of the reaction steps in CRECK2012

Index	Reaction steps
0	$O_2 \longrightarrow 2\,O, H_2 + O_2 \longrightarrow H + HO_2, H_2 \longrightarrow 2H$
1	$HO_2 \longrightarrow H + O_2, H_2 + HO_2 \longrightarrow H + H_2O_2, 2\,H \longrightarrow H_2H + O \longrightarrow\ OH,$ $2\,O \longrightarrow O_2, H + HO_2 \longrightarrow 2\,OH,$ $H + O_2 \longrightarrow O + OH, HO_2 + O \longrightarrow O_2 + OH,$ $H_2 + O \longrightarrow H + OH, H + HO_2 \longrightarrow H_2 + O_2,$ $2\,HO_2 \longrightarrow H_2O_2 + O_2, H + O_2 \longrightarrow HO_2,$
2	$HO_2 + OH \longrightarrow H_2O + O_2, O + OH \longrightarrow H + O_2, O_2 + OH \longrightarrow HO_2 + O,$ $HO_2 + OH \longrightarrow H_2O_2 + O, H_2O_2 + O \longrightarrow HO_2 + OH,$ $2\,OH \longrightarrow H_2O + O, H + OH \longrightarrow H_2 + O, H_2O_2 + OH \longrightarrow H_2O + HO_2,$ $2\,OH \longrightarrow H + HO_2, H_2O_2 + O_2 \longrightarrow 2\,HO_2, 2\,OH \longrightarrow H_2O_2,$ $H + H_2O_2 \longrightarrow H_2O + OH, H + H_2O_2 \longrightarrow H_2 + HO_2, OH \longrightarrow H + O,$ $H_2O_2 \longrightarrow 2\,OH, H_2 + OH \longrightarrow H + H_2O, H + OH \longrightarrow H_2O$
3	$H_2O + O_2 \longrightarrow HO_2 + OH, H_2O + O \longrightarrow 2\,OH, H_2O + HO_2 \longrightarrow H_2O_2 + OH,$ $H_2O + OH \longrightarrow H + H_2O_2, H + H_2O \longrightarrow H_2 + OH, H_2O \longrightarrow H + OH$

component. And finally, the Dagaut2003-type mechanism is special, its Feinberg–Horn–Jackson graph is a kind of enlargement of the previous graphs. Chemically, OH has four different channels to be transformed as opposed to three in the other mechanisms. Let us mention that the three most important radicals in combustion: H, O and OH form a full triangle in most of the maximal connected components except the second series: Burke2012-, CRECK2012- and Keromnes2013-type mechanisms.

3.1.3 Burke2012

The Volpert indices of species and reaction steps in the Burke2012 mechanism can be seen in Tables 3 and 4, respectively. Let us note that water only appears at the third level. To use another terminology [40] one can say that it is only tertiary reactions steps which are able to produce water in this model.

This is the same with some mechanisms in other classes: CRECK2012 and Keromnes2013; and in all the other mechanisms it appears (together with all the other species and reaction steps) earlier, at level 2.

3.1.4 CRECK2012

CRECK2012 contains a single **irreversible step**: $H_2O_2 + O \longrightarrow HO_2 + OH$. Upon going through all the hydrogen combustion mechanisms it turns out that no other mechanism contains any irreversible steps. The Volpert indices of this mechanisms are shown in Tables 5 and 6.

3.1.5 Dagaut2003

The maximal connected component of the Feinberg–Horn–Jackson graph of Dagaut2003 is shown in Fig. 3 . Tables 7–9 show the Volpert indices in three different reactions.

Table 7 Volpert indices of the species in Dagaut2003

Index	Species
0	H_2, O_2
1	H, HO_2, O
2	OHEX, H_2O_2, OH
3	H_2O

Table 8 Volpert indices of the species in Keromnes2013

Index	Species
0	H_2, O_2
1	H, HO_2, O
2	H_2O_2, H_2O, OH

Table 9 Volpert indices of the species in Starik2009

Index	Species
0	H_2, O_2
1	H, HO_2, O_3, O
2	H_2O_2, H_{20}, OH

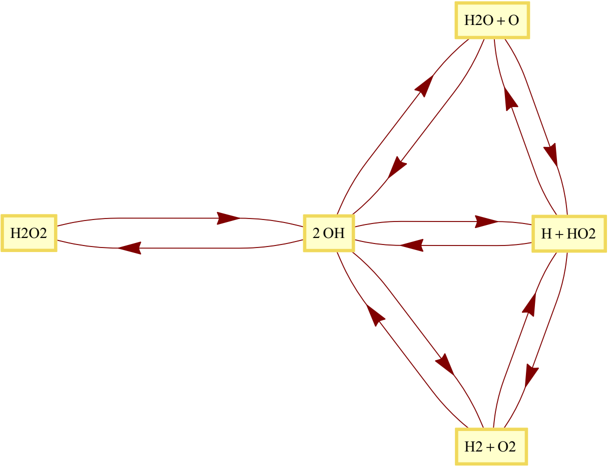

Fig. 3 The maximal connected component of the Feinberg–Horn–Jackson graph of Dagaut2003

3.1.6 Keromnes2013

The maximal connected component of the Feinberg–Horn–Jackson graph of Keromnes2013 is shown in Fig. 4.

Figure 4 well visualizes the foundation that the Keromnes2013 mechanism does not contain reaction $H + HO_2 = H_2O + O$. Absence of this reaction is a unique feature and can be questioned since the importance of this reaction was clearly demonstrated by Konnov [20, p. 523].

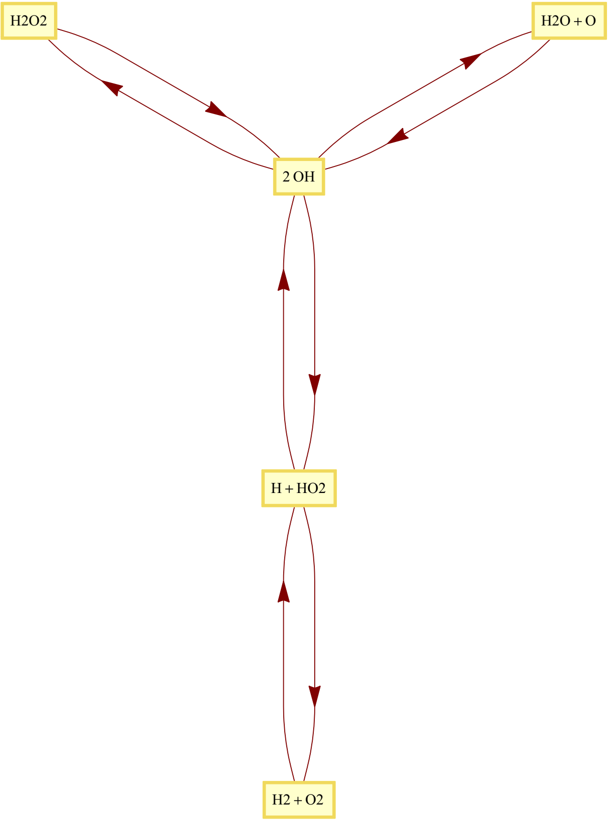

Fig. 4 The maximal connected component of the Feinberg–Horn–Jackson graph of Keromnes2013

Another interesting application can be found. Both from the point of view of thermodynamics and from the point of view of reducing the number of reaction rate coefficients one can require that a mechanism be detailed balanced, naturally, under the assumption that temperature and pressure are constant. Applying the pair of conditions formulated by Feinberg [14] (with an appropriate numbering of reaction steps, see the Electronic Supplementary Material) we get the following necessary and sufficient conditions in the case of Keromnes2013-type mechanisms:

$$\begin{aligned}
&k_{26}k_{27}k_{42} = k_{25}k_{28}k_{41},\ k_4k_{13}k_{39} = k_3k_{14}k_{40},\ k_2k_{14}k_{17} = k_1k_{13}k_{18},\\
&k_3k_8k_{11} = k_4k_7k_{12},\ k_2k_4k_5 = k_1k_3k_6,\ k_2k_4k_9k_{21} = k_1k_3k_{10}k_{22},\\
&k_2k_8k_9k_{19} = k_1k_7k_{10}k_{20},\ k_2k_9k_{14}k_{15} = k_1k_{10}k_{13}k_{16},\\
&k_2k_8k_9k_{13}k_{23}k_{37}^2 = k_1k_7k_{10}k_{14}k_{24}k_{38}^2,\ k_2k_8k_9k_{14}k_{24}k_{35}^2 = k_1k_7k_{10}k_{13}k_{23}k_{36}^2,\\
&k_1k_8k_{10}k_{13}k_{24}k_{33}^2 = k_2k_7k_9k_{14}k_{23}k_{34}^2,\ k_1k_8k_9k_{13}k_{24}k_{29}^2 = k_2k_7k_{10}k_{14}k_{23}k_{30}^2,\\
&k_2k_8k_9k_{13}k_{24}k_{25}^2 = k_1k_7k_{10}k_{14}k_{23}k_{26}^2,\ k_2k_4^2k_8k_9k_{13}k_{24}k_{31}^2 = k_1k_3^2k_7k_{10}k_{14}k_{23}k_{32}^2
\end{aligned}$$

Further investigations may also use the extended theory by [15].

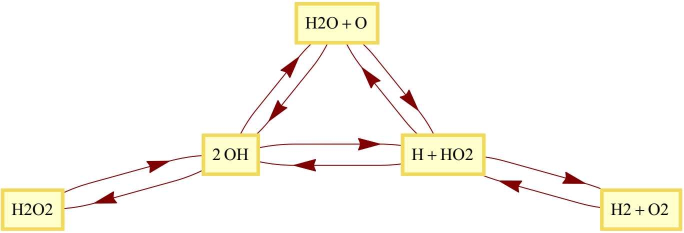

Fig. 5 The maximal connected component of the Feinberg–Horn–Jackson graph of Starik2009

Table 10 Number of different reaction steps in different mechanisms I

	Ahmed 2007	Burke 2012	CRECK 2012	Dagaut 2003
Ahmed2007	0	2	3	0
Burke2012	2	0	3	0
CRECK2012	2	2	0	2
Dagaut2003	4	4	7	0
Davis2005	2	2	5	0
Keromnes2013	6	4	7	4
SanDiego2011	4	4	5	2
Starik2009	14	14	17	12

3.1.7 Starik2009

The maximal connected component of the Feinberg–Horn–Jackson graph of Starik2009 is shown in Fig. 5, while the corresponding Volpert indices in Table 9.

3.1.8 Similarities and differences between the mechanisms of hydrogen

We can further analyse the similarities and differences between the class representatives of hydrogen combustion mechanisms. (Similarity of mechanisms is understood in the naïve way: the more common species and reaction steps two underlying reactions contain the more similar they are.) One can easily determine which are the reaction steps present in one mechanism and missing in the other. This generates a very huge table, a simpler one is obtained if one only counts the number of reaction steps (reversible counts 2) present in one mechanism and missing from the other.

Tables 10 and 11 shows the number of reaction steps missing in the respective "column" mechanism, but present in the "row" mechanism.

Let us look at a single example. The reaction steps included in Ahmed2007, but not in Burke2012, CRECK2012 and Keromnes2013 are $H + HO_2 \rightleftharpoons H_2O + O$ in all cases, and in the case of CRECK2012 $H_2O_2 + O \longleftarrow HO_2 + OH$, as well. Reaction steps contained in CRECK2012, but missing in Ahmed2007 are $HO_2 \rightleftharpoons O + OH$. This shows that in Tables 10 and 11 reaction steps may mean either an irreversible step, or a reversible pair. Furthermore, Table 11 shows again that Starik2009 and Keromnes2013 contain quite a few reaction steps missing in the other mechanisms.

Readers interested in detailed combustion chemistry are referred to the supplement.

Table 11 Number of different reaction steps in different mechanisms II

	Davis 2005	Keromnes 2013	SanDiego 2011	Starik 2009
Ahmed2007	0	2	0	0
Burke2012	0	0	0	0
CRECK2012	2	2	0	2
Dagaut2003	2	4	2	2
Davis2005	0	2	0	0
Keromnes2013	4	0	4	4
SanDiego2011	2	4	0	2
Starik2009	12	14	12	0

Table 12 Basic data of the investigated carbon monoxide combustion mechanisms

Mechanism	Reference	M	R	$\delta = N - L - S$
Ahmed2007	[1]	12	72	$57 - 23 - 9 = 25$
CRECK2012	[16]	11	60	$49 - 19 - 8 = 22$
Dagaut2003	[9]	12	68	$52 - 21 - 9 = 22$
Davis2005	[10]	11	60	$47 - 19 - 8 = 20$
GRI30	[36]	12	74	$57 - 23 - 9 = 25$
Keromnes2013	[18]	12	64	$52 - 21 - 9 = 22$
Li2007	[23]	12	78	$61 - 24 - 9 = 28$
NUIG2010	[16]	12	78	$61 - 24 - 9 = 28$
Rasmussen2008	[32]	13	88	$66 - 26 - 10 = 30$
SanDiego2011	[8]	12	74	$57 - 23 - 9 = 25$
SaxenaWilliams2006	[35]	11	60	$45 - 18 - 8 = 19$
Starik2009	[37]	13	88	$70 - 28 - 10 = 32$
Sun2007	[38]	12	66	$52 - 21 - 9 = 22$
USC2007	[43]	12	74	$57 - 23 - 9 = 25$
Zsely2005	[46]	11	62	$47 - 19 - 8 = 20$

3.2 Carbon monoxide

Let us now summarize the basic data of carbon monoxide combustion mechanisms in Table 12.

Since all CO and hydrocarbon mechanisms contain a subset of hydrogen reactions, they also appear in Table 1. Hydrogen-only mechanisms (OConaire2004, Konnov2008, Hong2011, Burke2012) were not used here. Although the references show a large overlap with those in Table 1, here we focus on the submechanism describing carbon monoxide combustion. Now let us start finding the reasons why we have different numbers in different mechanisms.

Species and their number, M Here, the values are much more diverse. The core species present in all the mechanisms are CO, CO_2, H, H_2, H_2O, HCO, HO_2, H_2O_2, O, O_2, OH. Additional species are listed in Table 13.

Table 13 Species present only in a given mechanism

Particular species	Mechanisms
CH_2O	Ahmed2007, Dagaut2003, GRI30, Li2007, NUIG2010, Rasmussen2008, SanDiego2011 Starik2009, Sun2007, USC2007
OHEX	Keromnes2013
HOCO	Rasmussen2008
O_3	Starik2009

Number of reaction steps, R The number of reaction steps, R, varies between 60 and 88. The law of Law [22] reported in his comprehensive review paper that the number of reactions is approximately 5 times larger than the number of species is fulfilled again.

Deficiency, δ The number of complexes, N, varies between 45 and 66. The number of weakly connected components is between 18 and 28. The deficiencies are large, neither the zero deficiency theorem, nor the one deficiency theory can be applied.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as all the reactions, except CRECK2012 and Keromnes2013, are fully reversible. Both the mentioned two mechanisms contain two irreversible steps:

$$\mathrm{HCO} + \mathrm{HO_2} \longrightarrow \mathrm{CO_2} + \mathrm{H} + \mathrm{OH},\ \mathrm{H_2O_2} + \mathrm{O} \longrightarrow \mathrm{HO_2} + \mathrm{OH}$$
$$\text{(CRECK2012);}$$
$$2\ \mathrm{HCO} \longrightarrow 2\ \mathrm{CO} + \mathrm{H_2},\ \mathrm{HCO} + \mathrm{HO_2} \longrightarrow \mathrm{CO_2} + \mathrm{H} + \mathrm{OH}$$
$$\text{(Keromnes2013).}$$

Although irreversible steps are acceptable modelling tools, there are at least two problems with them. If only one direction of the reaction is used the negligibility of the reverse reaction step may depend on the circumstances and it is possible that the mechanism will be used at such conditions where this simplification assumption will not be valid. In case both directions are present in a mechanism both of their values should change according to the thermodynamic equilibrium if they are re-parametrized.

3.2.1 Representations of mechanism classes

The situation is much simpler here, in the case of carbon monoxide combustion mechanisms. From the structural point of view USC2007 is identical to GRI30, while NUIG2010 is identical to Li2007, and all the other mechanisms are different. Hence we do not introduce classes of mechanisms in this case.

3.2.2 Similarities and differences between the mechanisms of carbon monoxide

Tables 14 and 15 shows the number of species missing in the respective "column" mechanism, but present in the "row" mechanism.

Table 14 Species present in one CO mechanism and missing in others I

Mechanism	Ahmed 2007	CRECK 2012	Dagaut 2003	Davis 2005	GRI 30	Kerom-nes 2013	Li 2007
Ahmed 2007	0	19	12	14	2	16	2
CRECK 2012	7	0	6	7	7	6	6
Dagaut 2003	8	14	0	8	8	8	4
Davis 2005	2	7	0	0	0	2	2
GRI 30	4	21	14	14	0	16	2
Keromnes 2013	8	10	4	6	6	0	4
Li 2007	8	24	14	20	6	18	0
Rasmussen 2008	16	34	24	28	14	29	12
SanDiego 2011	4	19	14	14	2	16	4
Saxena Williams 2006	4	7	2	2	2	4	4
Starik 2009	16	35	24	28	16	29	14
Sun 2007	6	12	0	6	6	6	2
Zsély 2005	4	9	0	2	2	4	4

Table 15 Species present in one CO mechanism and missing in others II

Mechanism	Rasmussen 2008	SanDiego 2011	Saxena Williams 2006	Starik 2009	Sun 2007	Zsely 2005
Ahmed2007	0	2	16	0	12	14
CRECK2012	6	5	7	7	6	7
Dagaut2003	4	8	10	4	2	6
Davis2005	0	0	2	0	0	0
GRI30	0	2	16	2	14	14
Keromnes2013	5	6	8	5	4	6
Li2007	2	8	22	4	14	20
Rasmussen2008	0	16	30	14	24	28
SanDiego2011	2	0	14	2	14	14
SaxenaWilliams2006	2	0	0	2	2	2
Starik2009	14	16	30	0	24	28
Sun2007	2	6	8	2	0	6
Zsely2005	2	2	4	2	2	0

As an illustration let us calculate the Volpert indices of Zsely2005 under the assumption that the species O_2, H_2 and CO are initially present (Table 16).

The maximal (weakly) connected components of the Feinberg–Horn–Jackson graphs are the same as those found in the case of hydrogen combustion mechanisms. The reason for this is that there are not enough carbon containing species in the mechanisms to form larger components, which is not the case with methanol mechanisms.

Table 16 Volpert indices of the species in Zsely2005

Index	Species
0	H_2, O_2, CO
1	$H, O, HO_2, OH, HCO, CO_2$
2	H_2O_2, H_2O

Table 17 Basic data of the investigated methanol combustion mechanisms

Mechanism	Reference	M	R	$\delta = N - L - S$
Aranda2013	[2]	76	1,063	$661 - 187 - 71 = 403$
Klippenstein2011	[19]	18	172	$122 - 42 - 15 = 65$
Li2007	[23]	18	170	$121 - 42 - 15 = 64$
Rasmussen2008	[33]	28	320	$222 - 75 - 24 = 123$
ZabettaHupa2008	[44]	58	724	$500 - 163 - 54 = 283$

3.3 Methanol

Let us start again with the basic data, see Table 17.

The analysis of these mechanisms is much harder.

Species, classes of mechanisms The number of reaction steps is around ten times that of the species here.

There is a striking similarity of Klippenstein2011 and Li2007 at the level of numbers. Really, they use the same set of species, and the only difference between their reaction steps is that Klippenstein2011 contains also the reversible reaction step

$$CH_3O + H_2O_2 \rightleftharpoons CH_3OH + HO_2$$

in addition to the common reaction steps. It is in accordance with the statement of the authors that they only made a small change on the structure of Li2007.

Otherwise, methanol mechanisms are so different that the question of classes and their representation does not even come up.

Number of reaction steps, R The number of reaction steps, R, ranges between 18 and 76.

Weak reversibility and acyclicity None of the reactions have an acyclic Volpert graph, as Li2007, Rasmussen2008 and ZabettaHupa2008 are fully reversible, and most of the reaction steps of the two other reactions are reversible. The exceptions are that Aranda2013 contains the irreversible reaction steps

$$\begin{aligned}
&CH_2OOH \longrightarrow CH_2O + OH,\\
&C_2H_4 + HOCH_2CH_2OO \longrightarrow CH_2O + CH_2OH + CH_3CHO,\\
&CH_2O + HOCH_2CH_2OO \longrightarrow CH_2OH + CH_2OOH + HCO,\\
&HO_2 + HOCH_2CH_2OO \longrightarrow CH_2OH + CH_2OOH + O_2,\\
&CH_2CHOH + O_2 \longrightarrow CH_2O + HCO + OH;
\end{aligned}$$

whereas Rasmussen2008 contains the irreversible reaction steps

$$\mathrm{NO_2} \longrightarrow \mathrm{NO_2\cdot},\ 2\ \mathrm{NO_2\cdot} \longrightarrow 2\ \mathrm{NO} + \mathrm{O_2},$$

and all the other reaction steps in all the other mechanisms are reversible.

Deficiency, δ As even the smallest Feinberg–Horn–Jackson graph is too large to be shown here, we shall again deal with the largest components of the Feinberg–Horn–Jackson graph of the individual mechanisms. Volpert graphs will only be used for indexing, and will show some interesting relationships.

3.3.1 Aranda2013

The maximal weakly connected components of the Feinberg–Horn–Jackson graph of Aranda2013 can be found in our supplementary document as these are too large to be displayed here.

Starting from CH_3OH, O_2 and N_2 as initial species all the reaction steps can finally take place and all the species will be produced except NH_2 and NH_3 and the largest finite Volpert index is now 4. These species appears at level four, or to put it another way: they can only be produced by quaternary reaction steps. However, to have finite indices for all the species either NH_2 or NH_3 is to be included initially.

There are 22 species containing two carbon atoms (or C–C bonds, as these expressions are synonymous in this case): $HOCH_2CH_2OO$, CH_3CHO, CH_2CHOH, H_2CC, CH_2CHO, CH_2CO, CH_3CO, CH_2CH_2OH, CH_2CH_2OOH, CH_3CH_2OO, CHCHOH, CH_2CHOO, CYCOOC, CH_2CHOOH, CH_3CH_2O, CH_3CH_2OH, CH_3CHOH, HCCO, CH_3CH_2OOH, CH_3CHOOH, HCCOH and OCHCHO. Beyond Aranda2013 it is only ZabettaHupa2008 where species with not less than two carbon atoms can be found.

3.3.2 Klippenstein2011 and Li2007

The maximal weakly connected components of the Feinberg–Horn–Jackson graph of Klippenstein2011 or Li2007 are shown in Fig. 6.

Starting from CH_3OH and O_2 as initial species all the reaction steps can finally take place and all the species will be produced and the largest Volpert index is now 4: that of CO_2. This species appears at level four, or to put it in another way: CO_2 can only be produced by quaternary reaction steps.

3.3.3 Rasmussen2008

The maximal weakly connected component of the Feinberg–Horn–Jackson graph of Rassmussen2008 is shown in Fig. 7.

Starting from CH_3OH and O_2 as initial species all the reaction steps can finally take place and all the species containing no N will be produced and the largest finite Volpert index is now 3: including that of CO_2. These species appears at level three, or to put it another way: they can only be produced by tertiary reaction steps. If e.g. either NO_2 or NO_3 is also added then all the species will have a finite Volpert index.

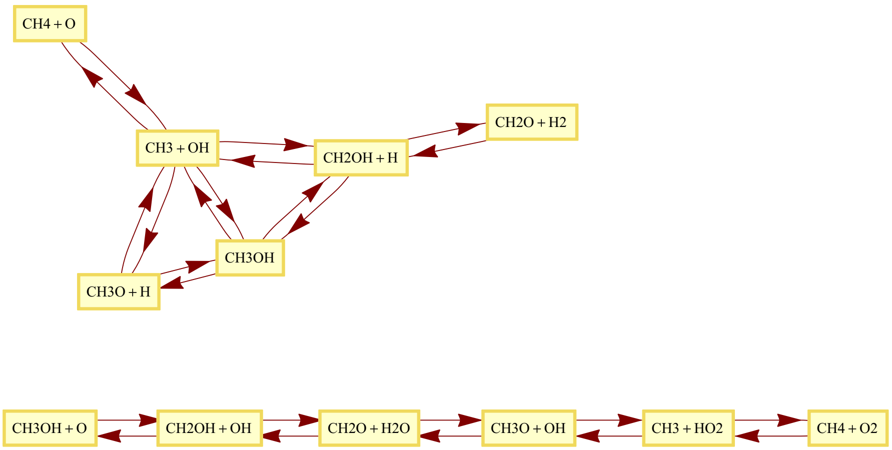

Fig. 6 The maximal weakly connected components of the Feinberg–Horn–Jackson graphs of Klippenstein2011 and Li2007

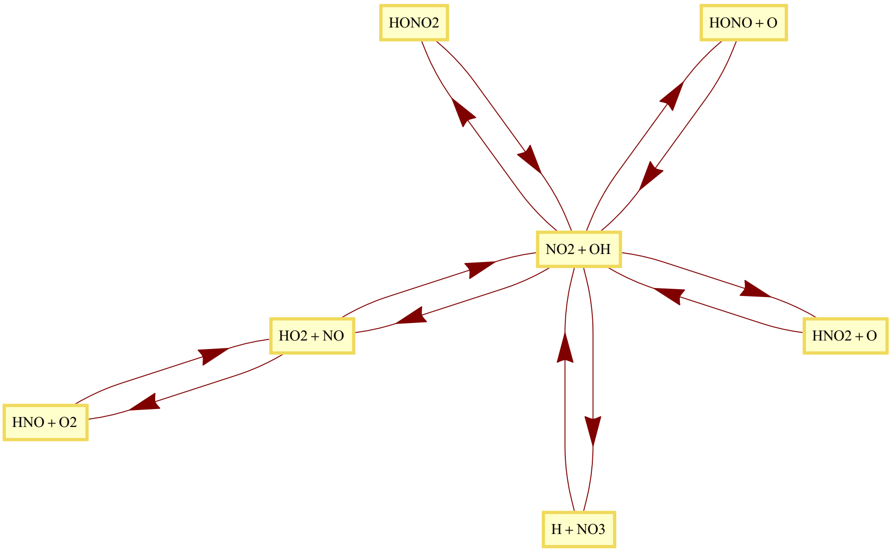

Fig. 7 The maximal weakly connected component of the Feinberg–Horn–Jackson graph of Rasmussen2008

Let us emphasize that the statements of this paragraph (and similar statements below) are independent from the values of the reaction rate coefficients.

3.3.4 *ZabettaHupa2008*

The maximal connected component of the Feinberg–Horn–Jackson graph of ZabettaHupa2008 is shown in Fig. 8.

Starting from CH_3OH, O_2 and N_2 as initial species all the reaction steps can finally take place and all the species will be produced and the largest Volpert index is now

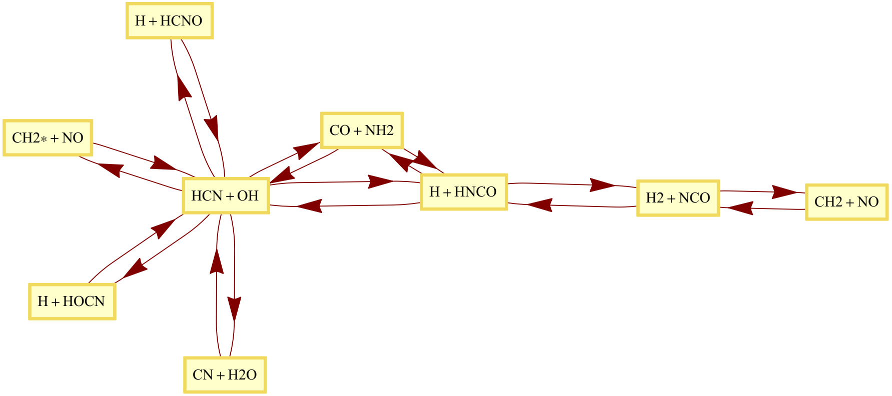

Fig. 8 The maximal connected component of the Feinberg–Horn–Jackson graph of ZabettaHupa2008

Table 18 The number of different reaction steps in the different mechanisms

Mechanism	Aranda2013	Klippenstein2011	Li2007	Rasmussen2008	ZabettaHupa2008
Aranda2013	0	897	899	759	737
Klippenstein2011	6	0	2	8	18
Li2007	6	0	0	6	16
Rasmussen2008	16	156	156	0	120
ZabettaHupa2008	398	570	570	524	0

5: that of C_2N_2 and C_4H_2. These species appears at level five, or to put it in another way: they can only be produced by fifth level reaction steps.

Species containing two carbon atoms are CH_2CO, HCCO.

3.3.5 Similarities and differences between the mechanisms of methanol

The mechanisms are too large (especially Aranda2013) to present all details here. However, it is possible to show the number of reaction steps present in the different mechanisms and missing in the others, see Table 18.

Thus, 897 in the first row, second column in Table 18 means that there are altogether 897 reaction steps enumerated in Aranda2013 but missing in Klippenstein2011. Note that the table is not symmetric, it should not be in general.

Let us look at a few examples in more detail. As Li2007 is a proper subset of Klippenstein2011, there is no reaction step present in the first one and missing in the second. The reaction steps present in Klippenstein2011 and missing in ZabettaHupa2008 are:

$$\begin{gathered}
2\,\mathrm{CH_2O} \rightleftharpoons \mathrm{CH_2OH} + \mathrm{HCO},\;\; \mathrm{CH_2O} + \mathrm{CO} \rightleftharpoons 2\mathrm{HCO},\\
\mathrm{CH_3O} + \mathrm{CO} \rightleftharpoons \mathrm{CH_3} + \mathrm{CO_2},\;\; \mathrm{CH_3O} + \mathrm{H} \rightleftharpoons \mathrm{CH_3} + \mathrm{OH},\\
2\,\mathrm{CO} + \mathrm{H_2} \rightleftharpoons 2\,\mathrm{HCO},\;\; \mathrm{CH_2O} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{CH_2OH} + \mathrm{HO_2},\\
\mathrm{CH_2O} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{CH_3O} + \mathrm{HO_2},\;\; \mathrm{CH_3O} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{CH_3OH} + \mathrm{HO_2},\\
\mathrm{HCO} + \mathrm{HO_2} \rightleftharpoons \mathrm{CO_2} + \mathrm{H} + \mathrm{OH}
\end{gathered}$$

Finally, Rasmussen2008 contains a few reaction steps among nitrogen compounds (including two irreversible steps) which are not present in the huge Aranda2013. These are as follows.

$$\begin{gathered}
CH_2O + H_2O_2 \rightleftharpoons CH_3O + HO_2,\ HNO_2 \rightleftharpoons H + NO_2,\\
HO_2 + NO_2 \rightleftharpoons NO_3 + OH,\ NO_3 \rightleftharpoons NO + O_2,\\
H + NO_3 \rightleftharpoons NO_2 + OH,\ HO_2 + NO_3 \rightleftharpoons NO_2 + O_2 + OH,\\
NO_3 + O \rightleftharpoons NO_2 + O_2,\ NO_2 \longrightarrow NO_2\cdot,\ 2\,NO_2\cdot \longrightarrow 2\,NO + O_2
\end{gathered}$$

3.3.6 Constructing new mechanisms

Once we have such (big) mechanisms as those above one can easily construct new ones by “tayloring”. Let us make a few experiments with Klippenstein2011, as this is the smallest mechanism. One can easily select those reaction steps which contain water on the left side of the reaction steps.

$$\begin{aligned}
&CH_2O + H_2O \longrightarrow CH_2OH + OH, \quad CH_2O + H_2O \longrightarrow CH_3O + OH,\\
&CH_2OH + H_2O \longrightarrow CH_3OH + OH, \quad CH_3 + H_2O \longrightarrow CH_4 + OH,\\
&CH_3O + H_2O \longrightarrow CH_3OH + OH, \quad CO + H_2O \longrightarrow HCO + OH,\\
&H_2O + HCO \longrightarrow CH_2O + OH
\end{aligned}$$

One can also consider such a submechanism of Klippenstein2011, which contains CH_2O on both of the sides of the reaction steps.

$$\begin{aligned}
&CH_2O \rightleftharpoons CO + H_2, \quad CH_2O \rightleftharpoons H + HCO,\\
&2\,CH_2O \rightleftharpoons CH_2OH + HCO, \quad CH_2OH \rightleftharpoons CH_2O + H\\
&2\,CH_2OH \rightleftharpoons CH_2O + CH_3OH, \quad CH_2O + CH_2OH \rightleftharpoons CH_3OH + HCO,\\
&CH_2O + CH_3 \rightleftharpoons CH_4 + HCO, \quad CH_3O \rightleftharpoons CH_2O + H,\\
&2\,CH_3O \rightleftharpoons CH_2O + CH_3OH, \quad CH_2OH + CH_3O \rightleftharpoons CH_2O + CH_3OH,\\
&CH_2O + CO \rightleftharpoons 2\,HCO, \quad CH_2O + H \rightleftharpoons H_2 + HCO,\\
&CH_2O + H \rightleftharpoons CH_3 + O, \quad CH_2OH + H \rightleftharpoons CH_2O + H_2,\\
&CH_2O + H_2O \rightleftharpoons CH_2OH + OH, \quad CH_2O + H_2O \rightleftharpoons CH_3O + OH,\\
&CH_2O + H_2O_2 \rightleftharpoons CH_2OH + HO_2, \quad CH_2O + H_2O_2 \rightleftharpoons CH_3O + HO_2,\\
&H_2O + HCO \rightleftharpoons CH_2O + OH, \quad H_2O_2 + HCO \rightleftharpoons CH_2O + HO_2,\\
&CH_2O + HO_2 \rightleftharpoons CH_2OH + O_2, \quad CH_2O + HO_2 \rightleftharpoons CH_3O + O_2,\\
&HCO + HO_2 \rightleftharpoons CH_2O + O_2, \quad CH_2O + O \rightleftharpoons HCO + OH,\\
&CH_2OH + O \rightleftharpoons CH_2O + OH, \quad CH_3O + O \rightleftharpoons CH_2O + OH,\\
&CH_3 + O_2 \rightleftharpoons CH_2O + OH
\end{aligned}$$

And the possibilities know no bounds.

4 Discussion and outlook

The major application of the methods outlined in the paper is a structural analysis of the selected mechanisms prior to a quantitative analysis including the evaluation of reaction rate constants.

A systematic use of Volpert indexing may also serve the selection of a minimal initial set of species: the least number of species which is enough for all the reaction steps in a given mechanism to occur and for all the species to be produced.

Another possible application is that one starts from a big mechanism and deletes reaction steps obeying some restrictions. E.g. one starts from a CO combustion mechanism and deletes reaction steps containing C, thus we should arrive at a hydrogen combustion mechanism etc. The results are only useful if they are exported to a CHEMKIN file, **`CHEMKINExport`** will serve for this purpose, which is a built-in function of our package **`ReactionKinetics`**.

Additional fields of application of our method are metabolism chemistry as well as atmospheric chemistry.

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Appendix

Fundamentals for formal kinetics

The basic notions can be found in textbooks such as [11–13,24,42] etc.

Let us consider the reaction

$$\sum_{m=1}^{M} \alpha(m,r)\mathrm{X}(m) \longrightarrow \sum_{m=1}^{M} \beta(m,r)\mathrm{X}(m) \quad (r=1,2,\ldots,R) \tag{1}$$

with $M \in \mathbb{N}$ chemical **species**: $\mathrm{X}(1), \mathrm{X}(2), \ldots, \mathrm{X}(M)$; $R \in \mathbb{N}$ **reaction steps**, $\alpha(m,r)$, $\beta(m,r) \in \mathbb{N}_0$, where $m = 1,2,\ldots,M$; $r = 1,2,\ldots,R$, **stoichiometric coefficients** or **molecularities**. Mind that we count a reversible reaction step as two reaction steps, although chemists count it as one, sometimes.
Furthermore, suppose the deterministic model of (1) is

$$\dot{c}_m(t) = f_m(\mathbf{c}(t)) := \sum_{r=1}^{R} (\beta(m,r) - \alpha(m,r)) w_r(\mathbf{c}(t)) \tag{2}$$

$$c_m(0) = c_m^0 \in \mathbb{R}_0^+ \quad (m = 1,2,\ldots,M), \tag{3}$$

describing the time evolution of the concentration vs. time functions $t \mapsto c_m(t) := [\mathrm{X}(m)](t)$ of the species, which is most often based on **mass action-type kinetics**:

$$w_r(\overline{\mathbf{c}}) := k_r \overline{\mathbf{c}}^{\alpha(.,r)} := k_r \prod_{p=1}^{M} \overline{\mathbf{c}}_p^{\alpha(p,r)} (r = 1, 2, \ldots, R),$$

where the constants $k_r \in \mathbb{R}$ are referred to as the **reaction rate coefficients**. (2) is also called the **(induced) kinetic differential equation** of the reaction (1) (see [11]).

When reaction (1) is **reversible** one can ask that whether the molecular process is **detailed balanced** or not at equilibrium. It means that a reaction step and its reverse occur, on the average, at the same rate. More formally, equations $k_r(\mathbf{c}_*)^{\alpha(\cdot,r)} = k_{-r}(\mathbf{c}_*)^{\beta(\cdot,r)}$ are required to be satisfied for equilibrium points $\mathbf{c}_*$ and for all the reversible reaction step pairs, where k_r, k_{-r} denote the corresponding reaction rate coefficients (see [28,29] and references therein).

The number of **complexes** N is the number of different **complex vectors** among $\alpha(\cdot, r)$ and $\beta(\cdot, r)$ $(r \in \{1, 2, \ldots, R\})$. The **Feinberg–Horn–Jackson graph** (or, FHJ graph, for short) of the reaction is a directed graph obtained if one writes down all the complex vectors (or simply the **complexes**) exactly once and connects two complexes with a directed edge (or two different edges pointing into opposite directions) if the first one is transformed into the second by a reaction step. We note that the FHJ graph is a useful tool to decide (together with the method proposed by Feinberg [14]) whether a reversible reaction is **detailed balanced** or not.

A subgraph H of the FHJ graph is called **(strongly) connected** if between any of its two vertices (complexes) there is a directed (reaction) path: a sequence of concatenated reaction steps. We say that a subgraph H of the FHJ graph is **weakly connected** if between any two vertices (complexes) of the undirected version of H there is a path. The maximal weakly (strongly) connected subgraphs of the FHJ graph are called the **weakly (strongly) connected components**. Notice that a strongly connected subgraph is automatically weakly connected as well, but the converse is not true in general. For reversible reactions the concepts coincide. Furthermore, the weakly connected components are also called as **linkage classes** in the literature. The number of weakly connected components of the FHJ graph is denoted by L. Finally, the **maximal weakly (strongly) connected component** of the FHJ graph is any of the weakly (strongly) connected components with the maximal number of vertices.

The **stoichiometric space** is the linear subspace of $\mathbb{R}^M$ generated by the **reaction vectors**: $\{\beta(\cdot, r) - \alpha(\cdot, r);\ r \in \{1, 2, \ldots, R\}\}$; its dimension is denoted by S. Finally, the nonnegative integer $\delta := N - (L + S)$ is the **deficiency** of the reaction (1).

The larger the deficiency is the more richer the mechanism is in complexes. We note that the notion of the deficiency plays an important role in characterizations and stability of the deterministic model of reaction (1) (see [11] and references therein, the papers by Feinberg [12,13] or the recent papers [4–6].

The **Volpert graph** of the reaction is a directed bipartite graph, its two vertex sets are the species set and the set of reaction steps, and an arrow is drawn from species $X(m)$ to the reaction step r if $\alpha(m, r) > 0$; (species $X(m)$ is needed to the reaction step r to take place) and an arrow goes from reaction r to species $X(m)$ if $\beta(m, r) > 0$

(species $X(m)$ is produced in the reaction step r). Sometimes it is worth labeling the edges with $\alpha(m, r)$ and $\beta(m, r)$, respectively.

It is very useful to assign indices to the vertices of the Volpert graph. This goes in the following way. A subset of species is selected, this will be the **initial set**. In real applications this will be the set of species with positive initial concentrations. The elements of the initial set receive index zero together with all the reaction steps which can proceed once the **initial species** are present. Next, species without an index which can be produced by the indexed reaction steps receive the index one, and reaction steps without index which can proceed receive also one, and so on. As the Volpert graph is finite, the procedure finishes in a finite number of steps. At the end either all the vertices receive an index, either a finite value κ or the infinite index ∞. One of the many possible interpretations of the meaning of a finite index κ is that the given species or reaction step can only appear in the κth step or at the κth level. In accordance with this, species with an infinite index cannot be produced, reaction steps with an infinite index cannot proceed with the prescribed initial species of the reaction. These statements and some others not less important ones can be found in a precise form e.g. in [42] or in the original paper [41]. An application of the Volpert index in the decomposition of overall reactions is given in [21].

Simple examples from combustion theory follow to illustrate the meaning of the definitions.

Example 1 (Mole reaction) The earliest combustion mechanism (which has been given a detailed treatment from the point of view of the qualitative theory of differential equations) is probably the Mole reaction ([25]), see also Fig. 9:

$$\mathrm{Y} \rightleftharpoons 0 \rightleftharpoons \mathrm{X} \quad \mathrm{X} + \mathrm{Y} \longrightarrow 2\mathrm{X} + 2\mathrm{Y}. \tag{4}$$

Example 2 (Robertson reaction) The reaction proposed in [34] contains three species, its Feinberg–Horn–Jackson graph is

$$\mathrm{A} \longrightarrow \mathrm{B} \quad 2\mathrm{B} \longrightarrow \mathrm{B} + \mathrm{C} \longrightarrow \mathrm{A} + \mathrm{C}, \tag{5}$$

the complexes are A, B, 2B, B + C, A + C, the deficiency is $N - L - S = 5 - 2 - 2 = 1$. The Volpert graph of this reaction is shown in Fig. 10.

Suppose one takes A as the only initial species, then A and the reaction step A $\longrightarrow$ B gets zero index, B and the reaction steps 2B $\longrightarrow$ B + C receives 1, finally C and the reaction step B + C $\longrightarrow$ A + C is assigned 2. Upon selecting B one gets a similar result. However, if one chooses C as the single initial species then all the other species and all the reaction steps will have an infinite index.

One may have the objection that the Robertson mechanism is not detailed balanced (as it is not even reversible). In some circumstances it may be required that only detailed balanced reactions be taken into consideration, however, as approximate models one often uses reactions not obeying this principle. Our view is presented in [28,29] in a detailed way.

We have done all the calculations of the characteristic quantities of reactions using the package `ReactionKinetics` developed in *Mathematica* and shown also at

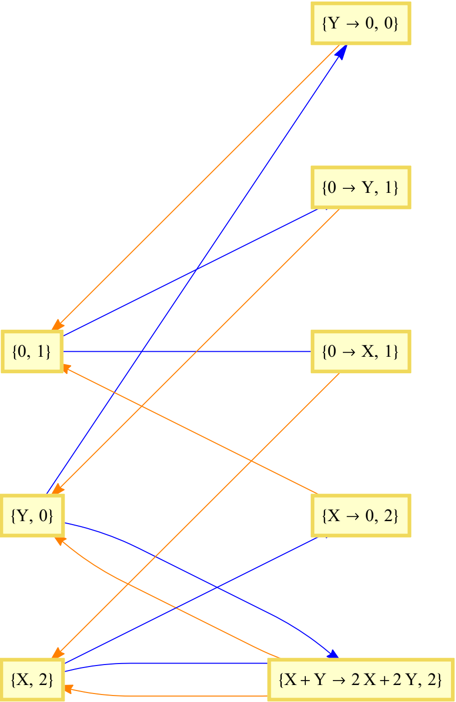

Fig. 9 The Volpert graph of the Mole reaction (4)

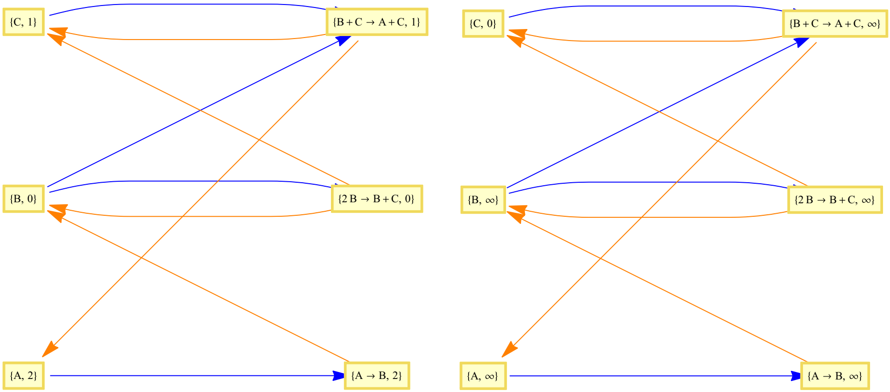

Fig. 10 The Volpert graphs of the Robertson reaction (5) with B and C as initial species

MaCKiE 2011 [27] and described in detail in [39]. Figures have also been drawn by the package.

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