

Towards a common C₀-C₂ mechanism: a critical evaluation of rate constants for syngas combustion kinetics

M. Pelucchi^{1,*}, U. Burke², L. Cai³, K. P. Somers², P. Glarborg⁴, T. Turanyi⁵, H. Pitsch³, H. J. Curran², T. Faravelli¹, S. J. Klippenstein⁶

1. CRECK Modeling Lab - Politecnico di Milano, Milano - Italy

2. Combustion Chemistry Centre - National University of Ireland, Galway - Ireland

3. Institute for Combustion Technology - RWTH Aachen University, Aachen - Germany

4. Department of Chemical and Biochemical Engineering - Technical University of Denmark, Lyngby - Denmark

5. Institute of Chemistry - Eötvös Loránd University (ELTE), Budapest – Hungary

6. Chemical Sciences and Engineering Division – Argonne National Laboratory, Argonne – USA

1. Motivations and background

Since the pioneering studies of Tsang and Hampson [1], and of Baulch and co-workers [2, 3], the knowledge of elementary combustion kinetics has increased, largely due to more accurate theories, advanced computing facilities and progresses in experimental measurements [4]. However, no effort has been devoted to the collection and reinterpretation of this knowledge after the early 2000s.

Starting in February 2017, we have collected and interpreted a very large number of direct and indirect rate constant measurements from the literature, as well as every state of the art theoretical calculation available for 50 elementary reaction steps involved in H₂/CO pyrolysis and combustion. A strong need for reconciling rate constant measurements and theory has emerged from this analysis. A significant number of the indirect measurements of rate constants and theoretical determinations seem, in fact, to disagree beyond the expected accuracy of parameters in the syngas subset. This is mostly due to the need for reconciliation of data and theory and the reinterpretation of the raw signals of the measurements with more accurate and better constrained models according to a careful iterative procedure.

The joint effort of SMARTCAT partners at Politecnico di Milano, NUI Galway, ELTE Budapest and Denmark Technical University together with RWTH Aachen University (DE) and Argonne National Laboratory (USA), aims to propose a fundamentally based state of the art mechanism for syngas combustion, to serve as a reference for the entire combustion kinetics community. Due to many different reasons, models for real fuels available in the literature rely on more or less different C₀-C₂ subsets. These differences often do not have substantial impacts on the overall performances as different rates in the core mechanism are often counter-balanced by different rates in the model subset relating to heavier fuels. This leads to very similar radical distributions and therefore in similar macroscopic behavior. However, the adoption of a fundamentally based common core mechanism will constitute a substantial thrust to increase the robustness of higher molecular weight fuel's kinetics.

2. Project Overview: current status and general workflow

Table 1 below (Task Completion Summary) provides a synopsis of the current status of the project. Each reaction is classified based on the number of electrons in the system, which is appropriate when considering reactions that take place on a multi-channel or multiple-well potential energy surface (PES), where absolute rate constants may be sensitive to both pressure and temperature, and where relative rate constants (branching ratios) may also be of interest to kinetic modelers. For each reaction, lead investigator(s) are assigned, and a series of tasks must

be completed before a reaction data-sheet is written (RDS) and the data sheet is peer-reviewed (DSPR) by all collaborators before final recommendations are made. These tasks are non-trivial and labor-intensive (sourcing and mining data), and include exhaustive literature review to collate papers (PC), tabulation of experimental data (EDT), and tabulation of theoretical data (TDT) before the rate constant can be fitted (RCF) and a rate constant with appropriate uncertainties recommended for use in combustion modelling. Table 1 shows that approximately 37.5% of all tasks have been carried out when one analyses the set of 50 reactions of interest. The key tasks of PC, EDT, TBT, PES construction are ~50% complete. The total number of papers collected so far is 467, including experimental measurements (293), theoretical determinations (170), and detailed kinetic models (4).

Status	PC	ET	TT	PES	RRKM/ME	RCF	RDS	PR	Total %
Completed	52%	48%	42%	54%	0%	4%	14%	0%	26.75%
In Progress	0%	0	0%	0%	36%	34%	0%	16%	10.75%
To be Completed	48%	52%	58%	46%	64%	62%	86%	84%	62.5%
Completed/In Progress	52%	48%	42%	54%	36%	38%	14%	16%	37.5

Table 1: Task Completion Summary Statistics.

Of the 50 reactions considered as part of this work, 33 reactions (66%) involve bimolecular reactions proceeding through a single transition state forming bimolecular products, and 17 reactions (33%) involve an energized adduct, which can undergo non-reactive bimolecular collision which transfers ro-vibrational energy between the adduct and the collider. While the former 33 reactions tend to be only temperature-dependent, those 17 reactions which involve collisional energy transfer (CET) are both temperature- and pressure-dependent. Therefore, some form of a complex model (e.g. RRKM/Master Equation) is used to interpolate and extrapolate data so that rate constants can be cast in a form that is useful for chemical kinetic modeling studies, but also, a form which is based on a physically meaningful model. The approach to fitting the majority (66%) of reactions (i.e. bimolecular and only temperature-dependent) is described in the following Section referring to the $\text{H}+\text{O}_2=\text{O}+\text{OH}$ system. Due to space limitations, the approach for pressure dependent reactions is postponed to a more extended publication.

3. Results

3.1 $\text{H}+\text{O}_2=\text{O}+\text{OH}$ lessons learned for a proper fitting methodology

80 experimental and 22 theoretical papers were collected for this reaction. After careful reviews, the theoretical investigations were ruled out due to the lack of adequate treatment of multiple electronic states issues within all dynamical studies. After revision of all the experimental data available, 35 papers were identified as appropriate to use in order to inform the initial recommendation reported in Figure 2. This recommendation was arrived at via a fit to the forward direction of the abovementioned reaction without consideration of any weighting to the data. This initial fit was unsatisfactory, as it did not adequately replicate the data at the extremes of temperature (Figure 2) and, due to the strong temperature dependence when considering the rate constant in the forward direction, it is difficult to assess the data and the fit.

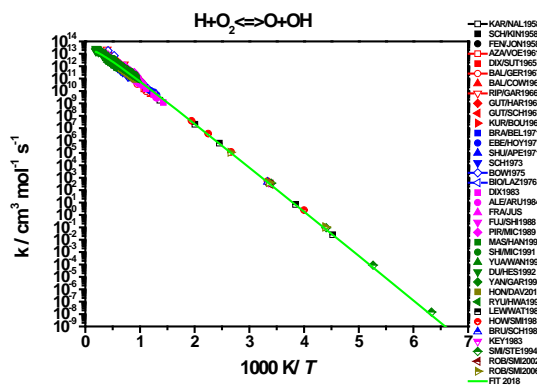


Figure 2: Rate constants for the reaction $H+O_2 \rightleftharpoons O+OH$.

For these reasons, the fits are always performed in the exothermic direction. Moreover, the temperature range is limited to 200–3000 K, and indirect data, i.e. those obtained through fitting to a detailed model targeting macroscopic measurements such as laminar flame speeds, are not considered. A weight is introduced to remove bias to datasets with more data than others dividing the error by the number of data points in the dataset.

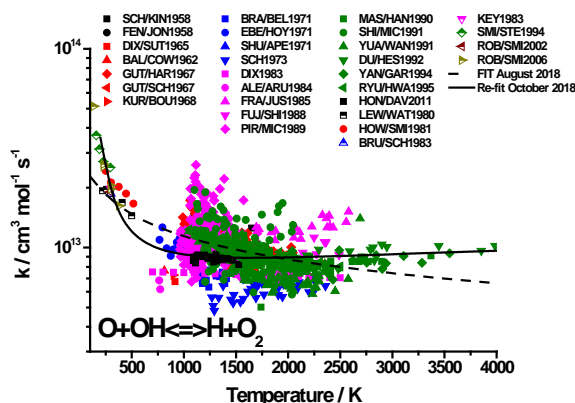


Figure 3: Rate constants for the reaction $O+OH \rightleftharpoons H+O_2$.

To overcome issues related to the often superficial assessment of uncertainty in the experimental and theoretical determination of rate constants, and to avoid weighting equally, measurements that are clearly less accurate while still acknowledging all the efforts reported in the literature, we assigned a 3-point weight to the datasets to account for the reliability of data. Namely, on a low/medium/high uncertainty (0.5/1.0/2.0) basis, we assign 0.5 to data we might want to reject or give a low weight (clear outliers); 1.0 to data we want to keep but weight less; 2.0: to data we consider as the most accurate. This yields the solid line fit shown in Figure 3, largely improving the agreement between the fit and the experimental data with respect to the dashed line.

3.2 $H+O_2=O+OH$ lessons learned for a proper definition of statistical uncertainty

Residual differences are also obtained in addition to recommended fits for every reaction investigated. Figure 4 shows the residual plot for the reaction $O+OH \rightleftharpoons H+O_2$ discussed above. The two standard deviations of the populations yield a statistical uncertainty of $\pm 45\%$ and the data adhere to a Boltzmann distribution around the fit.

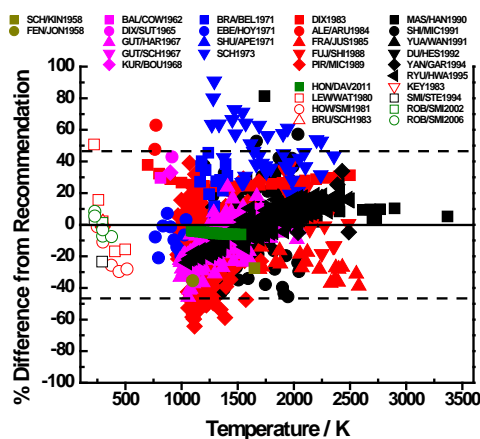


Figure 4: Residual plots for the reaction $O+OH \rightleftharpoons H+O_2$.

The datasets were also analyzed based on each sample set, for which mean error and standard deviation were also reported. What was evident from this investigation was the decrease in the mean error as the sample sets approach the present date. This observation may be attributed to the general improvement in the precision of the measurement techniques over time. Nonetheless, the statistical uncertainty obtained based on the data is higher than that expected when the review began (i.e. 5-10%).

4. Conclusions

This work presents a brief summary of the activity undertaken by different partners involved in the development of kinetic models for combustion. This activity aims at proposing a fundamentally based state of the art mechanism for syngas, open to the public, shared and adopted at least among the partners. Achieving this ultimate goal involves non-trivial and labor-intensive literature reviews and careful interpretation of experimental and theoretical data leading to rate constant recommendations as well as uncertainty assessment. At present, a third of the tasks involved in this complicated workflow has been completed providing recommendations for ~10 elementary reactions. Future steps involve the completion of all the tasks for all the reactions, the iterative revision of recommended values and the compilation of the final model to be tested against common macroscopic experimental targets (i.e. ignition delay times, laminar flames, speciation measurements).

References

- [1] Tsang et al., *Journal of Physical and Chemical Reference Data* 15.3 (1986): 1087-1279.
- [2] Baulch et al., *Journal of Physical and Chemical Reference Data* 21.3 (1992): 411-734.
- [3] Baulch et al., *Journal of Physical and Chemical Reference Data* 34.3 (2005): 757-1397.
- [4] Klippenstein, *Proceedings of the Combustion Institute* 36.1 (2017): 77-111.

Acknowledgements

Dr. M. Pelucchi, Dr. U. Burke and Dr. K.P. Somers acknowledge the financial support of COST CM1404 (SMARTCATs) through the Short Term Scientific Mission program. Dr. L. Cai and Prof. H. Pitsch acknowledge funding support from the Cluster of Excellence “Fuel Science Center”, which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. The contribution from Dr. S. Klippenstein is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences, under Contract No. DE-AC02-06CH11357 as part of the Argonne-Sandia Consortium High-Pressure Combustion Chemistry, (ANL FWP #59044).