

SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: CM1404

STSM title: SMARTCATS

STSM start and end date: 08/07/2018 to 13/07/2018

Grantee name: Matteo Pelucchi

PURPOSE OF THE STSM/

Since the pioneering studies of Tsang and Hampson (Journal of Physical and Chemical Reference Data 15.3 (1986): 1087-1279.), and of Baulch and co-workers (Journal of Physical and Chemical Reference Data 21.3 (1992): 411-734., Journal of physical and chemical reference data 34.3 (2005): 757-1397.) the knowledge of elementary combustion kinetics has increased, largely due to more accurate theories, advanced computing facilities and progresses in experimental measurements. However, no effort has been devoted to the collection and reinterpretation of this knowledge. In the last 16 months we have collected and interpreted a large number of direct and indirect rate constant measurements from the literature, as well as every state of the art theoretical calculation available for ~40 elementary reaction steps involved in H₂/CO pyrolysis and combustion. From this analysis the need for reconciling rate constant measurements and theory has emerged. 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 down to the need for reconciliation of data and theory, reinterpreting the raw signals of the measurements with more accurate and better constrained models according to an additional iterative procedure. The joint effort of COST partners such as, Politecnico di Milano, National University of Ireland Galway and ELTE Budapest, together with Argonne National Laboratory (USA), RWTH Aachen University (GE) and Denmark Technical University (DK), 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. This goal perfectly fits into WG1 aims 1) extending the experimental databases of reaction rate constant determination also over unconventional conditions, for example characterizing and better defining the effect of bath gases in terms of collisional efficiencies for pressure dependent rate constants. As implicit in the hierarchical nature of combustion, a precise assessment of syngas kinetics will increase the robustness of higher molecular weight fuel's kinetics. Moreover, the adoption of a common base mechanism will increase the fidelity of models that are continuously developed for many fossil and bio-based fuels, by fixing a high accuracy core mechanism. This activity also provides uncertainty bounds to the recommended model parameters, facilitating physically meaningful optimization within those bounds.

The detail of the objectives of this STSM are listed below:

- 1) Consistently format the data collected over the previous 16 months to facilitate dissemination and interpretation
- 2) Discuss the most suitable methods to perform mathematical fitting of rate constants based on theoretical and experimental determinations

- 3) Discuss and provide meaningful methods to define uncertainties
- 4) Provide an outline for the treatment of every elementary reaction that is suitable for publication and easy use by kinetic modelers
- 5) Provide case studies to serve as a basis to investigate all of the reactions involved in syngas combustion

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

Reactions have been ordered and numbered according to the number of electrons (increasing) involved. Reactions occurring on the same potential energy surface (PES) have been grouped, aiming at treating them in a concerted manner. It is worth noticing, that many of the secondary reactions occurring during an experimental test aimed at defining one specific reaction rate constant are non-negligible, as they are accessible from the same entrance channel on the potential energy surface. The rigorous approach applied here involves the iterative assessment of interdependent rate constants. In the following we report rules concerning format and methods on which we agreed during the STSM:

Format and method:

Plots to appear for each reaction:

Fit from “best” experimental data and theoretical determinations. This implies a deep investigation of the accuracy of experimental and theoretical methods involved.

Residuals (k/k_{rec} %) plots drive the definition of uncertainty bounds

Duplicates should be defined as the residuals highlight remarkable non-Arrhenius behaviours

Mathematical fitting not always preferable: for example residuals plots should help in optimizing the recommended rate (e.g. lowering/increasing recommended rate to have a “symmetric” uncertainty*)

Residuals for rate constants currently adopted in existing kinetic models should be provided to guide the user in the implementation of the recommended values

Pressure dependent rate constants will have the same plots as above together with a detailed definition of branching ratios to different products within the same PES (if information are available). If information are not enough ab initio transition state based master equation calculation will be performed to better define model parameters.

An exhaustive collection of data in different bath gases will serve the goal to provide more accurate collisional efficiencies.

Plogs format are preferable to Troe formalism.

Reverse reactions: convert theoretical and experimental values to forward rate constants using our standard thermochemistry (ATCT).

Mathematical fits should always be performed on $\text{LN}(k)$ or $\text{LOG}_{10}(k)$.

All the collected information, both experimental and theoretical, will be collected in excel spreadsheets to be attached to the final publication. This will facilitate re-interpretation by the users and increase the reliability of the recommended values providing an exhaustive documentation.

Experimental measurement spreadsheet will be structured as: YEAR, AUTHOR(S), JOURNAL, VOLUME, PAGES, TITLE, FITTING METHOD, REACTOR, DILUENT, T, p, UNCERTAINTY (if available), DETECTION, DETECTION II, PRECURSOR, SECONDARY REACTIONS, RAW PROFILES, MEASUREMENT (direct, semi-direct or indirect)

Theoretical determination spreadsheet will be structured as: YEAR, AUTHOR(S), JOURNAL, VOLUME, PAGES, TITLE, FITTING, ROVIB. ENERGIES, TST, P DEP., DILUENT, T, p, UNCERTAINTY.

Spreadsheets will also contain the detail of the fit, the residuals, the (x,y) values of collected data from which the plots were obtained.

Overall for every reaction the review will report:

1. ID (Number or NIST reference)
2. Dictionary Experiments
3. Dictionary Theory
4. Rate Data/Recommendation/Residuals
5. Rate constants from mechanisms and their residuals
6. Discussion document

All of the above have been applied to the following reactions:

- 1) $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$
- 2) $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{OH}$
- 3) $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2 + \text{HO}_2$
- 4) **$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$**

For sake of brevity, the next Section reports results obtained for reaction 4 (Part 1) and an application of this activity to collider efficiencies determination (Part 2).

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Conventions:

A; $\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for bimolecular

E_a ; cal/mol

T Range; K

Values obtained indirectly through modeling are not considered. Some earlier values that have clearly been superseded are not presented; this is particularly true for theory, where it can be clear that some calculation is performed at an inferior level of accuracy.

1) **$\text{H}_2 + \text{OH} = \text{H}_2\text{O} + \text{H}$**

- Recommended value: $A=3.880\text{E}+05$, $n=2.328$, $E_a=2312.0$

After a first evaluation of recommended parameters, the careful revision of the measurements and theoretical assessments available in the literature performed during the STSM led to a different suggestion. Such difference is reported in Figure 1. The two recommendation agree within a factor of 30%, which is comparable with the accuracy of theoretical methods available at present for such small molecules.

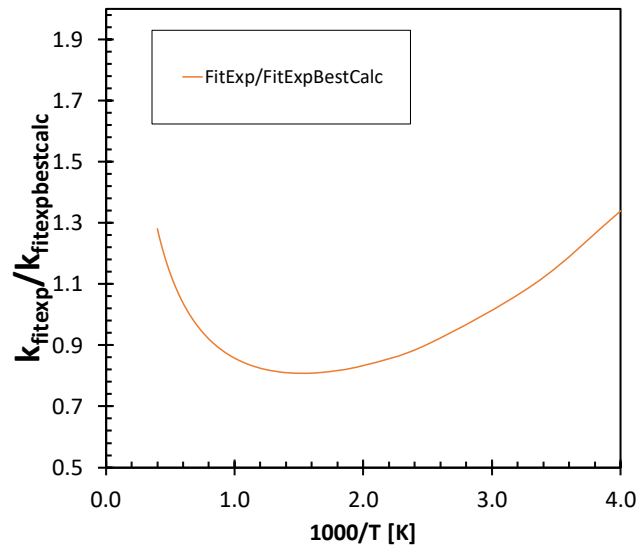


Figure 1: Ratio between first rate recommendation (FitExp) and that obtained after careful revision of the literature (FitExpBestCalc).

Figure 2 compares the recommended rate constant with selected experimental data and theoretical calculations, whose reliability was carefully checked throughout this activity.

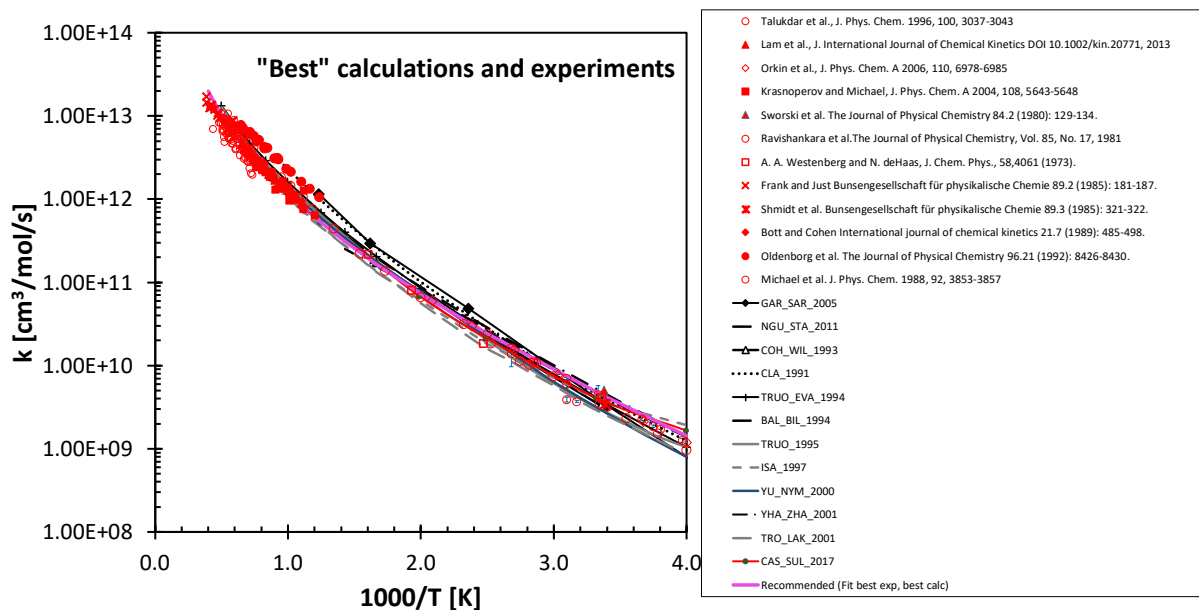


Figure 2: comparison between fitted rate constant "best" experimental measurements and theoretical calculations.

Residuals between the recommended rate constants and the values currently adopted in reference kinetic models such as Aramco2.0 (also implemented in POLIMI), DTU and ITV. In addition, also the optimized values by Varga et al. are considered. On one hand, this plot shows the dramatic difference existing between fundamental determinations and the modelling efforts. In the case of Aramco/POLIMI difference are as large as a factor of 10 at room temperature. Despite it could be claimed that 298 K is not a relevant condition for combustion applications, this comparison highlights the need of a structured collection and reinterpretation of literature information, aiming at the development of predictive models. The optimized values obtained at ELTE were obtained by means of comparison of model performances with a large database of macroscopic experimental data for syngas combustion and pyrolysis (e.g. laminar flame speeds, ignition delay times, species profile in ideal reactors). If one considers our suggestion as a "fundamentally" optimized rate constant (i.e. it considers all the fundamental rate measurements and theoretical determination to date), the

potential of a concerted optimization procedure involving firstly a microscopic revision and secondly a model optimization based on macroscopic experimental targets emerges clearly.

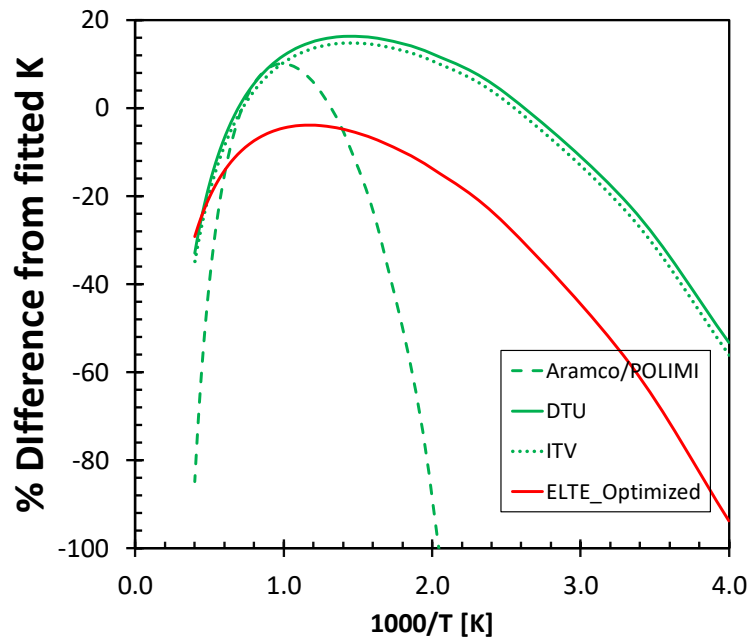


Figure 3: Residual plot of current model parameters for the investigated reaction and the recommendation.

The reverse reaction $\text{H}_2\text{O}+\text{H}=\text{H}_2+\text{OH}$ was measured by Davidson and co-workers at high temperature in shock tubes. Figure 4 compares the reverse rate constant obtained from our forward recommendation through equilibrium rate constant computed according to the thermochemistry parameters available in the Active Thermochemical Tables. The agreement is well within experimental uncertainty with maximum deviations not exceeding 30%.

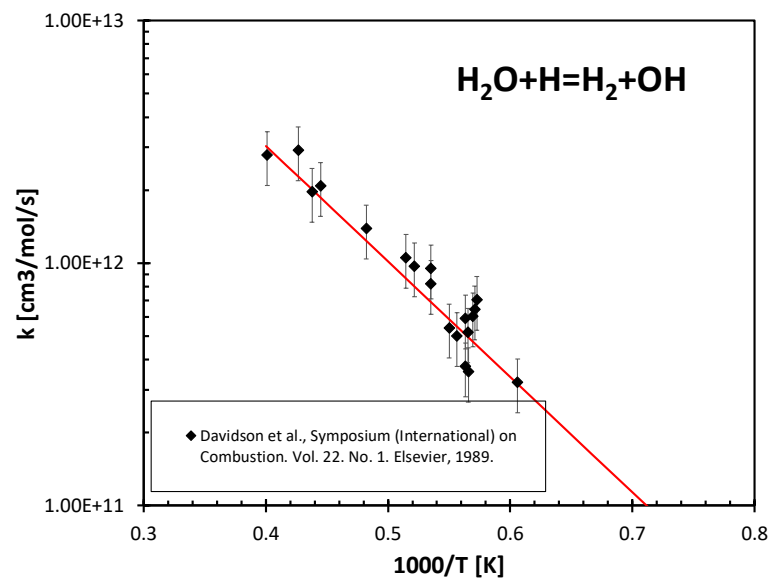


Figure 4: Reverse rate constant. Symbols are experimental data, lines is the recommended value from this work.

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2) Collider Efficiencies for $H+O_2 (+M)=HO_2 (+M)$:

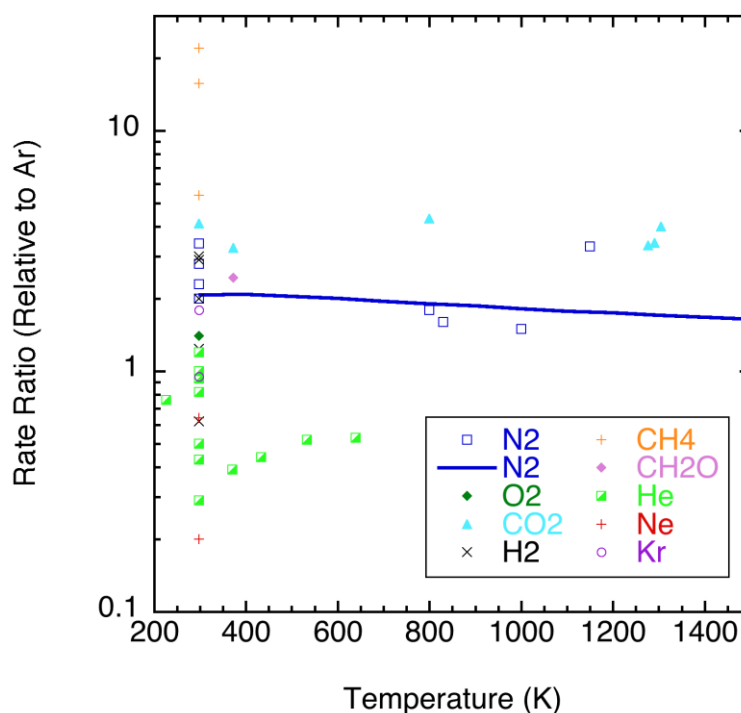


Figure 5: Plot of the collider efficiencies for $H + O_2 (+M) \rightarrow HO_2 (+M)$ for a variety of colliders, all relative to $M = Ar$. Where possible the experimentally measure collider efficiencies are plotted. Otherwise the collider efficiencies relative to our recommended values are plotted.

As shown in Figure 5, the dependence of the low pressure limit rate on collider has been measured for a variety of collider species. The numerical values for the direct measurements of the collider efficiencies are

summarized in Table 1.

Table 1: Collider Efficiencies for $H + O_2 (+M) \rightarrow HO_2 (+M)$

Ref.	N ₂	O ₂	H ₂ O	CO ₂	H ₂	CH ₄	CH ₂ O	He	Ne	Kr	T (K)	Reference
Ar	2.0	1.4	23					0.82	0.64	0.95	298	2002MIC/SU
Ar	3.3		20								1150	2001BAT/GOL
Ar	1.6										830	1998MUE/YET
Ar	1.8		18.9	4.3							800	1998ASH/HAY
Ar	2.3					5.4					298	1985COB/HIP
Ar	1.5										1000	1977SLA
Ar				4.1				1.0			300	1975VAS/MAK
Ar	2.8				3.0	22		0.93			298	1974WON/DAV
Ar					2.0			1.2	0.2	1.8	298	1972AHU/MIC
Ar	3.4					15.7		1.0			298	1972KUR
Ar					2.9						298	1971HIK/EYR
Ar					2.0						298	1970BIS/DOR
Ar			25								1259-1912	1969GET/BLA
N ₂								0.43			11	1989HSU/AND
								0.39			7.8	
								0.44			6.2	
								0.52			5.7	
								0.53			5.9	

Unfortunately, the data is not sufficient to make meaningful suggestions regarding the temperature dependence of the collider efficiencies. Here we recommend simple temperature independent collider efficiencies for N₂, O₂, CO₂, H₂, CH₄, CH₂O, He, Ne, and Kr relative to Ar, of 1.8, 1.4, 3.7, 2.5, 18, 0.8, 0.6, 1.0, respectively.

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FUTURE COLLABORATIONS (if applicable)

The same approach will be applied to all of the remaining reactions listed below:

R2: $H + H + M \Rightarrow H_2 + M$
 R9: $H + O + M \Rightarrow OH + M$
 R10a: $H + OH (+M) \Rightarrow H_2O (+M)$
 R10b: $H_2 + O \Rightarrow H + OH$
 R15: $HCO (+M) \Rightarrow CO + H (+M)$
 R16: $HCO + H \Rightarrow CO + H_2$
 R16p: $O + O + M \Rightarrow O_2 + M$
 R17a: $H + O_2 (+M) \Rightarrow HO_2 (+M)$
 R17b: $H + O_2 \Rightarrow O + OH$
 R-17b: $O + OH \Rightarrow H + O_2$
 R18a: $OH + OH (+M) \Rightarrow H_2O_2$
 R18b: $OH + OH \Rightarrow O + H_2O$
 R18e: $H + H + O_2 \Rightarrow H_2 + O_2$
 R18f: $H + H + O_2 \Rightarrow OH + OH$
 R22: $CO + O (+M) \Rightarrow CO_2 (+M)$
 R23a: $CO_2 + H \Rightarrow HOCO$
 R23b: $CO + OH \Rightarrow HOCO$
 R23c: $CO + OH \Rightarrow CO_2 + H$
 R23d: $HCO + O \Rightarrow CO_2 + H$
 R23e: $HCO + O \Rightarrow CO + OH$
 R24: $O_2 + O (+M) \Rightarrow O_3 (+M)$
 R24pa: $HCO + OH \Rightarrow CO_2 + H_2$
 R24pb: $HCO + OH \Rightarrow CO + H_2O$
 R25a: $O + HO_2 \Rightarrow O_2 + OH$
 R25b: $H + O + O_2 \Rightarrow OH + O_2$
 R26a: $OH + HO_2 \Rightarrow H_2O + O_2$
 R26b: $H_2O_2 + O \Rightarrow H_2O + O_2$
 R26c: $H + OH + O_2 \Rightarrow H_2O + O_2$
 R27: $H_2O_2 + OH \Rightarrow H_2O + HO_2$
 R30a: $HCO + HCO \Rightarrow OCHCHO$
 R30b: $HCO + HCO \Rightarrow CO + H_2CO$
 R30c: $HCO + HCO \Rightarrow CO + CO + H_2$

R30p: CO + O2 => CO2 + O
R31a: OHC(O)O (+M) => OHOCO (+M)
R31b: CO2 + OH (+M) => OHC(O)O (+M)
R31c: CO2 + OH (+M) => OHOCO (+M)
R31d: CO + HO2 => OHC(O)O (+M)
R31e: CO + HO2 (+M) => OHOCO (+M)
R31f: CO + HO2 => CO2 + OH
R31g: HCO + O2 (+M) => OHC(O)O (+M)
R31h: HCO + O2 (+M) => OHOCO (+M)
R31i: HCO + O2 => CO2 + OH
R32: HCO + HO2 => CO + O2 + H2
R34: HO2 + HO2 => H2O2 + O2

The working group has decided to meet on a 3 month basis. Matteo Pelucchi and Ultan Burke will apply for an additional STSM to be performed by the end of October. By then it is expected that half of the above reactions will be completed.

The advances in this investigation will be presented at the upcoming Laminar Flame International Workshop (http://www.princeton.edu/~yju/4th-flame-chemistry%20workshop-presentation-program/Workshop%20Program_final.htm).

A publication to be submitted to Progress in Energy and Combustion Science or, alternatively, to the Journal of Physical and Chemical Reference Data is expected by March 2019.