

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: 29/10/2018 to 02/11/2018

Grantee name: Matteo Pelucchi

PURPOSE OF THE STSM/

Following the successful STSM in Aachen in July, focusing on the collation, critical evaluation and design of a working process for efficient review, the current STSM expands upon the number of reactions under consideration and on the methods themselves, in order to garner relevant insight into the statistical evaluation of large sets of data. Ultimately, the goal of this collaboration between COST partners and external partners (National University of Ireland Galway (NUIG), Politecnico di Milano (PoliMi), RWTH Aachen, Argonne National Laboratory (ANL), Denmark Technical University (DTU) and ELTE Budapest) to collect, collate, evaluate and reconcile conflicting results for the existing data within the literature for hydrogen/syngas oxidation, is producing an outcome of outstanding relevance for the entire kinetic modelling community, by compiling the results of the review, into recommendations for each of the elementary reactions. The final outcome will be a kinetic model which is an accurate reflection of our most up to date understanding of the chemical kinetics for such system. This will also ensure that the obtained model can predict the indirect data of interest for more practical application such as, ignition delay times and laminar burning velocities.

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

- 1) Consistently format the data collected over the previous 21 months to facilitate dissemination and interpretation. Statistics on the number of data/paper collected are provided in the report of Kieran Somers.
- 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 and users of kinetic models
- 5) Discuss and provide appropriate treatments of pressure dependent reactions
- 6) Provide a recommendation for additional reactions within the hydrogen/syngas model ($\text{OH} + \text{OH} \rightleftharpoons \text{O} + \text{H}_2\text{O}$ was specific to this researcher, as well as the collection and organization of the large amount of information on $\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{O}_2$ that was useful to guide a proper treatment of pressure dependent reactions)

Together with these objectives, useful discussions allowed to further improve and extend the methods and approaches defined in the previous meeting.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The format and methods as described below from the previous STSM were acted upon for a wider array of reactions. There was however, improvements and extensions to these methods based on the information and training received as part of this STSM, details are discussed in the report from Ultan Burke.

In the following we report rules concerning format and methods on which we agreed during the STSM. Additional rules introduced during the last STSM are highlighted in **bold**.

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.

Pressure dependent rate constants fitting procedure: ad hoc master equation simulation will be performed on the temperature/pressure/bath gas space where experimental measurements are available, in a point by point fashion. The best fit will be produced by tuning the key parameter in master equation simulations (i.e., temperature dependent energy transfer for collisional deactivation

$$\Delta E_{down}(T) = \Delta E_{down}(300) \left(\frac{T}{300} \right)^{\beta}$$

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

Mathematical fits should always be performed on LN(k) or LOG₁₀(k).

Fits performed in the exothermic direction are preferable.

Fits should be limited to the temperature range of interest for combustion/atmospheric chemistry, i.e. 200-3000K.

Mathematical fits were performed according for weighting factors of two nature:

1) number of data points: one experimental campaign which may have reported a larger number of datapoints than an equally relevant but sparser experimental campaign,

2) To overcome issues related to the often superficial and badly documented assessment of uncertainty in the experimental and theoretical determination of rate constants, and to avoid weighting equally measurements that are clearly wrong/less accurate (i.e. measurements that ignore secondary chemistry, indirect measurements from the observation of macroscopic variables such as laminar flame speed, etc.) while still acknowledging all the efforts reported in the literature, we assigned a 3-point weight to the datasets. 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.

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

The next Section reports the final document for reaction 3.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

$\text{OH} + \text{OH} \rightleftharpoons \text{O} + \text{H}_2\text{O}$

Figure 1 shows the potential energy surface for the H_2O_2 system calculated at ANL1 level (*Klippenstein, Proc. Combust. Inst.*, 2017). Many different pathways exist for the unimolecular decomposition of H_2O_2 , the most important one being the decomposition to $\text{OH} + \text{OH}$, well known to govern the transition between low and high temperature oxidation regimes. The backward reaction, i.e. the recombination of two OH radicals not only can form H_2O_2 , but also, water and O^3P . Despite the barrierless channel leading to H_2O_2 is typically more relevant for ignition delay times, the reaction with atomic oxygen and water can contribute significantly to the reactivity in hydrogen-oxygen laminar flame propagation (*Varga et al., Int. J. Chem. Kin.* 2016).

Moreover, as stated in the previous STSM reports from Burke and Pelucchi, an accurate determination of recommended rate parameters strongly relies on the accurate determinations of secondary reactions and, even more, of the reactions occurring on the same potential energy surface. This allows not only to provide accurate absolute values, but also to provide accurate branching ratios whose importance equals, and often overcomes, the extremely accurate determination of the rate parameters for a single reaction channel.

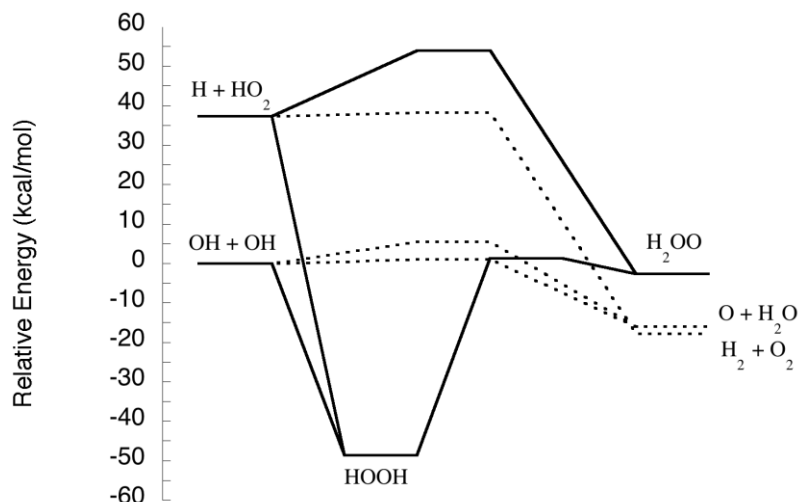


Figure 1: Potential Energy Surface of the H_2O_2 system.

After the collection of 24 datasets from the literature a first fit was performed for the reaction $\text{O} + \text{H}_2\text{O} = \text{OH} + \text{OH}$ according to the methods defined in the previous STSM. Results from this first fitting are reported in Figure 2 (black line).

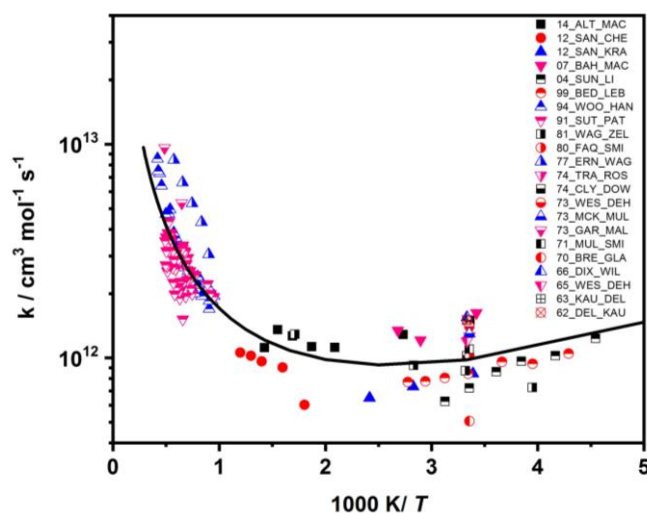


Figure 2: Rate constants for the reaction $\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH}$.

The corresponding residual plot is provided in Figure 3. This second plot also includes theoretical determinations (lines), in the attempt to provide guidelines for a better interpretation of the experimental measurements (points). As clear from Figure 3, at T relevant for combustion applications, the experimental and theoretical estimates can differ up to a factor > 3 , which is well above the state-of-the-art capabilities of theoretical and experimental methods.

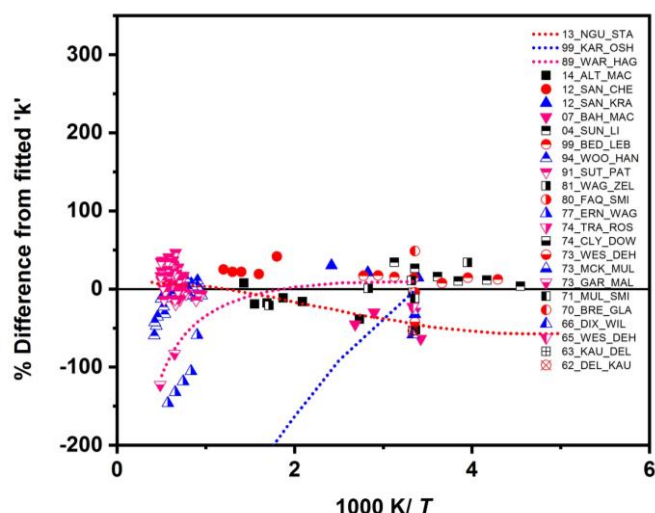


Figure 3: Residual plots for the reaction $O+H_2O \rightleftharpoons OH+OH$.

Stemming from this unsatisfactory comparison we firstly decided to limit the fitting temperature to the range 200-3000 K, to avoid specific issues and experimental/theoretical challenges related to extremely high or extremely low temperatures (improper treatment of tunnelling effects or anharmonicity effects, non idealities in experimental facilities etc.). Based on the treatment of $H+O_2=O+OH$ as explained in the report of Burke, weighting was applied according to the number of data points, to give the same importance to more or less populated datasets. Moreover a new fit was performed in the exothermic direction ($OH+OH \rightleftharpoons O+H_2O$) already providing lower residuals. A tool of use for the working group was obtained to convert forward/backward rate constants, by means of ATCT NASA polynomials provided by Branko Ruscic at ANL.

Careful evaluation of the experimental data led us to decision of excluding some dataset. In particular, as highlighted in Figure 4, the data from Ernst et al. (77_ERN_WAG, *Berichte der Bunsengesellschaft für physikalische Chemie*, 1977) were excluded as the measured OH concentration was based on equilibrium calculation of precursor decomposition. Most probably this led to the overestimation of a factor of about 3 clearly depicted in Figure 4. For the same reason the data of Gardiner et al. (73_GAR_MAL, *Symp. Int. Combust. Proc.*, 1973) were also excluded.

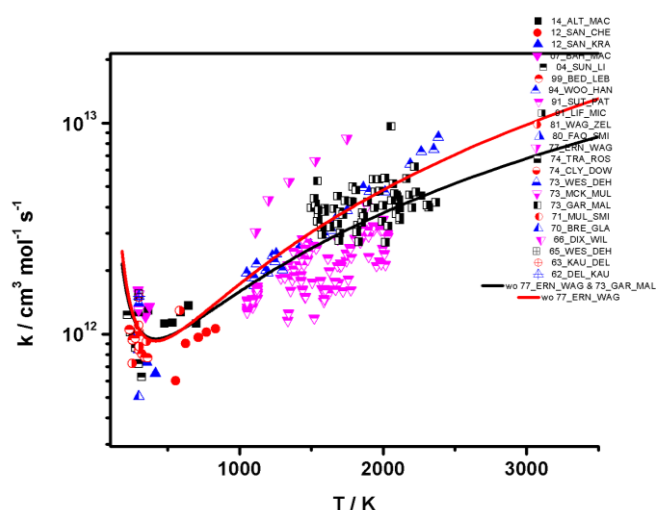


Figure 4: Rate constants for the reaction $OH+OH \rightleftharpoons O+H_2O$.

Figure 4 also shows the sensitivity of the fits to the exclusion of 77_ERN_WAG only, or of both 77_ERN_WAG and 73_GAR_MAL. Variations between the two fits vary from ~5% at 200 K, to about 50% at 2000 K. The final fit is that reported in the black line and the associated residual plots are given in Figure 5. It is also noticeable that the recommended fit agrees within a factor of 1.4 with the most accurate theoretical calculation available in the literature from Nguyen and co-workers (*J. Phys. Chem*, 2013).

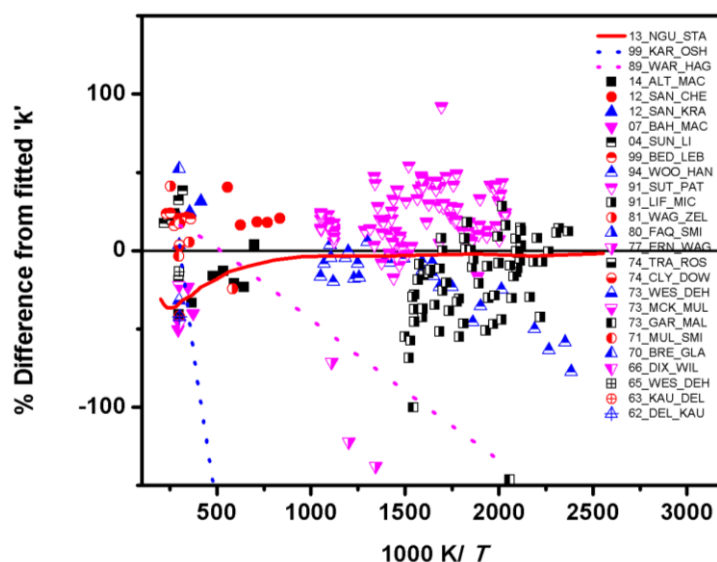


Figure 5: Residual plots for the reaction $\text{OH}+\text{OH}\rightleftharpoons\text{O}+\text{H}_2\text{O}$.

The final recommended value for the $\text{OH}+\text{OH}=\text{O}+\text{H}_2\text{O}$ reaction is $A=3.696\text{E}+06$, $n=1.771$, $E_a=-1468.332$.

Standard deviation σ is 35.5%, and $2\sigma=71.0\%$.

$\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$

37 experimental studies are available for this reaction, together with 4 theoretical studies. Many experimental investigations focused on very low pressure ($1\text{E}-3$ - $1\text{E}0$ bar) and low temperatures (298-500 K). The focus of the literature in the 70s and 80s has been clearly devoted to the interpretation of the chemically activated pathway ($\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_4=\text{H}_2\text{O}_2+\text{O}_2$) and of its competition with the direct H-abstraction channel. A large number of data are available for varying bath gases and varying pressures at ambient temperature. The following figures (Figure 6-8) report the variation of the rate constant as a function of pressure in different bath gases: Ar, He, N_2 .

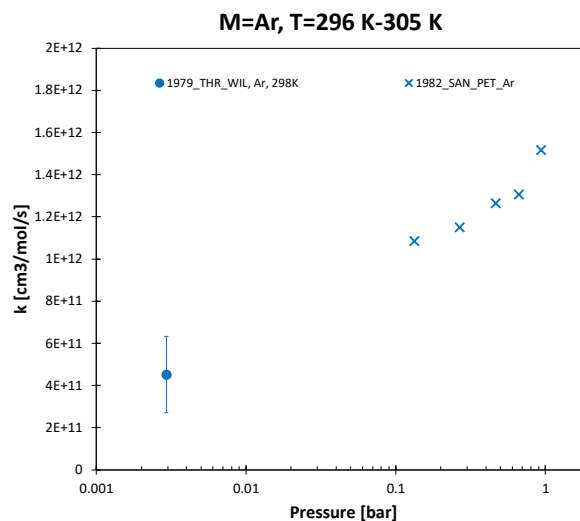


Figure 6: Experimental measurements of $\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$ at $T\sim 298\text{K}$, below atmospheric pressure in Ar.

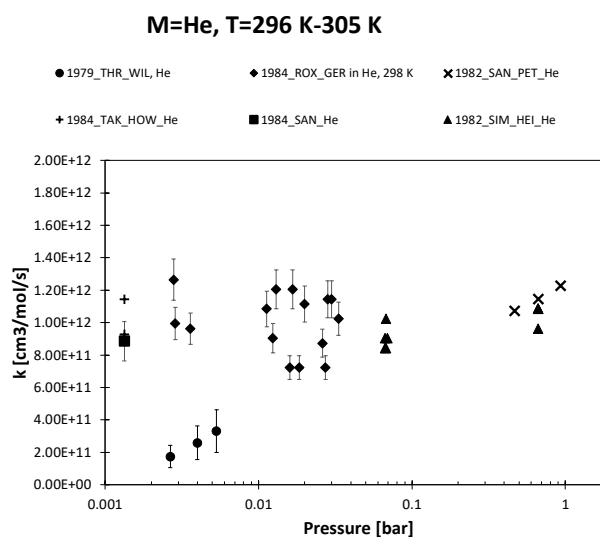


Figure 7: Experimental measurements of $\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$ at $T\sim 298\text{K}$, below atmospheric pressure in He.

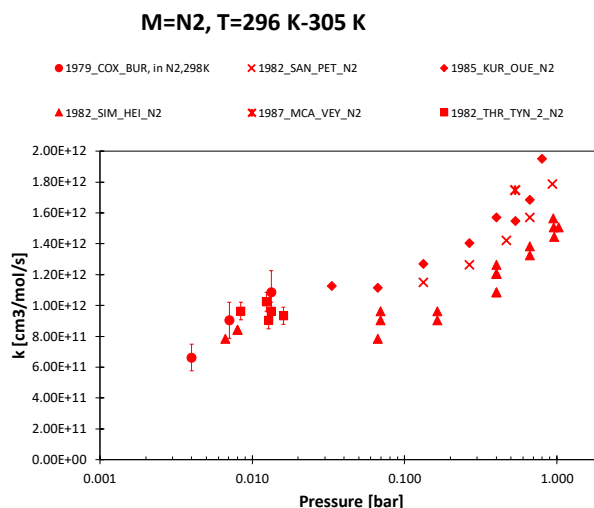
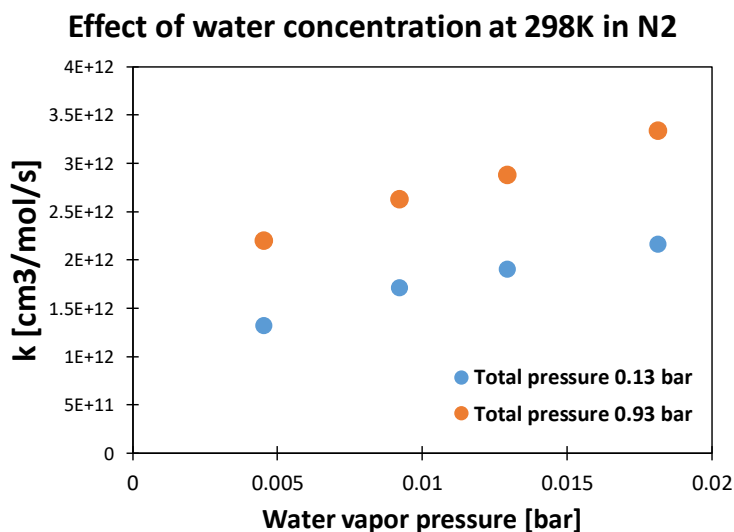


Figure 8: Experimental measurements of $\text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2$ at $T\sim 298\text{K}$, below atmospheric pressure in N_2 .

Many studies also focused on the influence of water vapour pressure on the rate constant. As an example the enhancing effect of both pressure and water concentration are reported in Figure 9. The experimental data are from Sander and co-workers (*J. Phys. Chem*, 1982), the rate constant was determined by means of flash photolysis and ultraviolet adsorption.



Due to the relevance of this reaction in both atmospheric chemistry and in combustion chemistry, many studies were devoted to its evaluation and to the assessment of its pressure and bath gas dependence. About 3000 data points have been collected from 37 experimental studies. The combination of different bath gases and of mixture of those (e.g. Ar, N_2 , He/ H_2O / NH_3) will also provide insights into mixture effects, whose investigations and relevance is starting to emerge in the combustion kinetics community (*Lei and Burke, Proc. Comb. Inst. 2018*). The data collected for this reaction provide a very wide test set for the implementation of the master equation based fitting for pressure dependent reactions discussed in the STSM report of Kieran Somers.

FUTURE COLLABORATIONS (if applicable)

The same approach will be applied to all of the remaining reactions listed below. The present status of the project for every single reaction will be displayed in the scientific report by Dr. Kieran Somers.

$R2_H+H+M \rightleftharpoons H_2+M$
 $R9_H+O+M \rightleftharpoons OH+M$
 $R10a_H+OH+M \rightleftharpoons H_2O$
 $R10b_H_2+O \rightleftharpoons OH+H$
 $R15_HCO+M \rightleftharpoons H+CO+M$
 $R16a_HCO+H \rightleftharpoons CH_2O$
 $R16b_HCO+H \rightleftharpoons CO+H_2$
 $R16p_O+O+M \rightleftharpoons O_2+M$
 $R18a_OH+OH+M \rightleftharpoons H_2O_2+M$
 $R18c_H+HO_2 \rightleftharpoons H_2+O_2$
 $R18d_H+HO_2 \rightleftharpoons OH+OH$
 $R18e_H+H+O_2 \rightleftharpoons H_2+O_2$
 $R18f_H+H+O_2 \rightleftharpoons OH+OH$
 $R19a_H_2O_2+H \rightleftharpoons H_2O+OH$
 $R19b_H_2O_2+H \rightleftharpoons HO_2+H_2$
 $R22_CO+O+M \rightleftharpoons CO_2+M$
 $R23a_H+CO_2+M \rightleftharpoons HOCO+M$
 $R23b_CO+OH+M \rightleftharpoons HOCO+M$
 $R23c_CO+OH \rightleftharpoons CO_2+H$
 $R23d_HCO+O \rightleftharpoons CO_2+H$
 $R23e_HCO+O \rightleftharpoons CO+OH$
 $R24a_HCO+OH \rightleftharpoons CO_2+H_2$
 $R24b_HCO+OH \rightleftharpoons CO+H_2O$
 $R24p_O_2+O+M \rightleftharpoons O_3+M$
 $R25a_O+HO_2 \rightleftharpoons O_2+OH$
 $R25b_H+O+O_2 \rightleftharpoons OH+O_2$
 $R26a_HO_2+OH \rightleftharpoons H_2O+O_2$
 $R26b_H_2O_2+O \rightleftharpoons OH+HO_2$
 $R26c_H+OH+O_2 \rightleftharpoons H_2O+O_2$
 $R27_H_2O_2+OH \rightleftharpoons HO_2+H_2O$
 $R30a_HCO+HCO \rightleftharpoons OCHCHO$
 $R30b_HCO+HCO \rightleftharpoons CO+CH_2O$
 $R30c_HCO+HCO \rightleftharpoons CO+CO+H_2$
 $R30p_CO+O_2 \rightleftharpoons CO_2+O$
 $R31a_OHC(O)O+M \rightleftharpoons OHOCO+M$
 $R31b_CO_2+OH+M \rightleftharpoons OHC(O)O+M$
 $R31c_CO_2+OH+M \rightleftharpoons OHOCO$
 $R32_HCO+HO_2 \rightleftharpoons CO+H_2+O_2$

The working group has decided to meet on bi-weekly telecons, in order to continue progress on the review of the above listed reactions.

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.

The progresses of this activity will be presented at the final SMARTCATs meeting and 1st International Conference on Smart Energy Carrier to be held in Naples on the 21st-23rd of January 2019.