

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: Ultan Burke

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 in order to garner relevant insight into the statistical evaluation of large sets of data. In particular, the statistical methods was a key goal for this researcher to learn during the STSM. The host institution has specific insight into these methods as illustrated through their recent publication by Vom Lehn and co-workers (Proc. Combust. Inst. 28 (2018) doi.org/10.1016/j.proci.2018.06.188). A main focus for this researcher was the critical review of $H+O_2 \rightleftharpoons O+OH$. This reaction is of particular importance in the prediction of combustion processes and therefore, a large quantity of experimental and theoretical data exists on this elementary reaction. In order for the current researcher to effectively assess and assign a realistic uncertainty and recommendation for a rate constant it was important to apply some form of statistical analyses as per the uncertainty quantification methods applied in the work of Vom Lehn and co-workers. Furthermore, the continued collaboration of COST partners National University of Ireland Galway (NUIG), Politecnico di Milano (PoliMi), RWTH Aachen, Argonne National Laboratory (ANL), Denmark Technical University (DTU) and ELTE Budapest, in order to collect, collate, evaluate and reconcile conflicting results for the existing data within the literature for the detailed chemical kinetic hydrogen/syngas oxidation mechanism. Ultimately, the goal of this collaboration is for the aforementioned institution to compile the results of the review into recommendations for each of the elementary reactions and produce a kinetic model which is an accurate reflection of our most up to date understanding of the chemical kinetics for hydrogen/syngas oxidation, while also ensuring that the final model can also predict the indirect data of interest for more practical application such as, ignition delay times and laminar burning velocities. The reaction focused on by this researcher is arguably the most important reaction under consideration for this system. It is therefore of the utmost importance to collect all the relevant data and consider all the data when building the basis for our recommendation. In order to provide those who wish to reduce or automatically optimize these detailed chemical kinetic mechanisms, with realistic uncertainties for this rate constant and others, the knowledge of Prof. Pitsch and Dr. Cai of RWTH Aachen was sought. The current researcher aimed to provide his hosts and collaborators with an overview of the data collected so far, and learn to treat these data correctly when attempting to statistically determine mean, standard deviations, uncertainties, systematic outliers, random outliers and potential methods to fit the data while retaining accurately the absolute rate constant values both measured and calculated. This researcher could also offer exchange of his experience in the performing of shock tube and rapid compression machine experiments and development of detailed chemical kinetic models in order to promote the open

dissemination of research work between collaborating institutions within the COST framework.

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 and users of kinetic models
- 5) Provide a recommendation for the reactions within the hydrogen/syngas model, specific to this researcher $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$

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. Namely, a weighted fit was applied to the procedure for coming to the final recommendation for a given elementary process. This method change, allows our fitting procedure to not be biased towards one experimental campaign which may have reported a larger number of datapoints than an equally relevant but sparser experimental campaign. Additionally, population distribution about the mean and standard deviation and means for data samples of the population was performed in order to get a more robust picture of the data and potentially identify numeric outliers. This analysis allowed the researcher to come to a much better representation of the literature on the rate constant for $\text{H} + \text{O}_2 \rightleftharpoons \text{O} + \text{OH}$, as can be seen in the figure below.

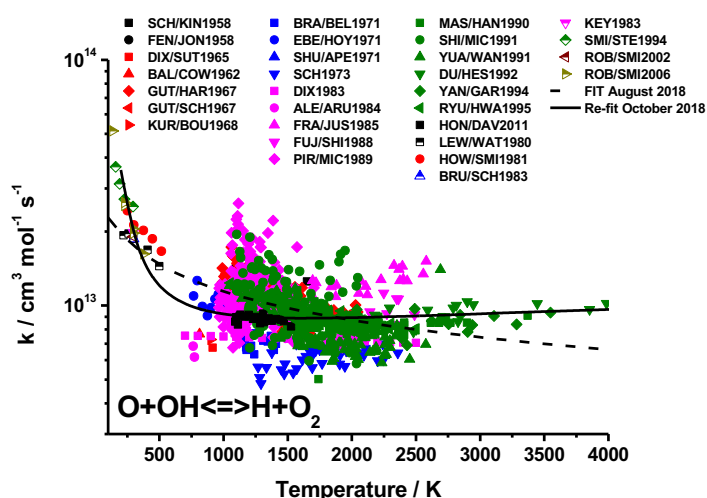


Figure 1: Rate constants for the reaction $\text{O} + \text{OH} \rightleftharpoons \text{H} + \text{O}_2$.

The weighting in the fit yields a much better description of the data as a function of temperature, in particular at the high and low temperature extremes.

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 $\ln(k)$ or $\log_{10}(k)$.

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

The next Section reports the final document for reaction 1.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

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

Initially, 80 experimental and 22 theoretical papers were collected relevant to this reaction. After expert reviews from collaborators, Dr. Kieran Somers (NUIG) and Dr. Stephen Klippenstein (ANL) the theoretical investigations were ruled out due to the lack of adequate accuracy in considering the chemical physics of this reaction. After review of the experimental paper 35 papers were identified as appropriate to use in order to inform the initial recommendation. This recommendation was arrived at *via* at fit to the forward direction of the above mentioned reaction without consideration of any weighting to the data. This fit is shown in Fig. 2.

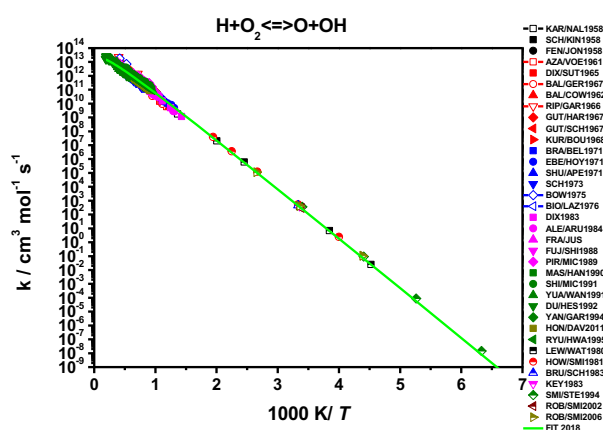


Figure 2: Rate constants for the reaction $\text{O} + \text{OH} \rightleftharpoons \text{H} + \text{O}_2$.

This initial fit was unsatisfactory as it does not adequately replicate the data at the extremes of temperature and due to the strong temperature dependence when considering the rate constant in the forward direction is it difficult to assess the data and the fit. For these reasons it was decided to perform the subsequent fits for any reaction in the exothermic direction of the elementary reaction. This STSM in Aachen allowed us as a team to pool the knowledge of the collaborators effectively and decide to limit the temperature range for our fit to 200–3000 K, remove indirect data from our fitting process due to the indirect nature of the determination and weight the fit to remove bias to datasets with more data than others by division of the error by the number a datapoints in the dataset. This yields a fit as shown in Fig. 3.

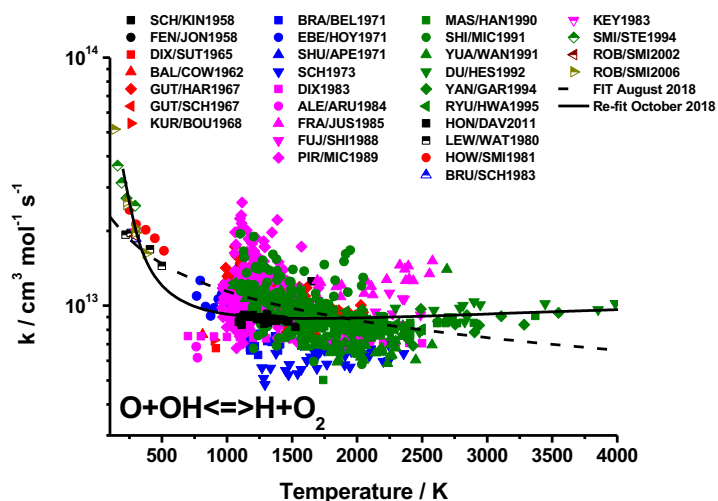


Figure 3: Rate constants for the reaction $O+OH\rightleftharpoons H+O_2$.

The basic qualitative agreement between the fit and the experimental data is clearly improved. The next consideration is to look at the residual differences from the fit for each individual datapoint and all the data considered. This is shown in Fig. 4.

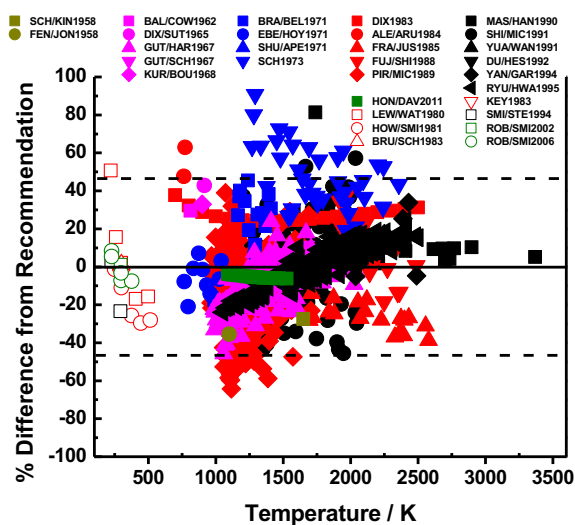


Figure 4: Rate constants for the reaction $O+OH\rightleftharpoons H+O_2$.

The two standard deviations of the populations yields a statistical uncertainty of $\pm 45\%$. Looking at the data further we can see that the data adhere to a Boltzmann distribution around the fit, Fig.5.

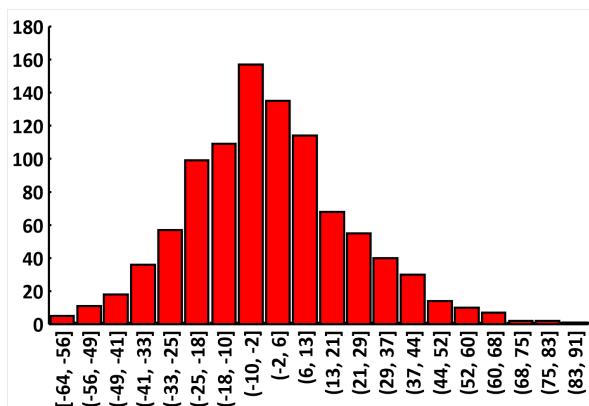


Figure 5: Population distribution around the recommended fit.

The datasets were also analysed based on each sample set. The mean error and standard deviation were plotted for each dataset, as shown in Fig. 6.

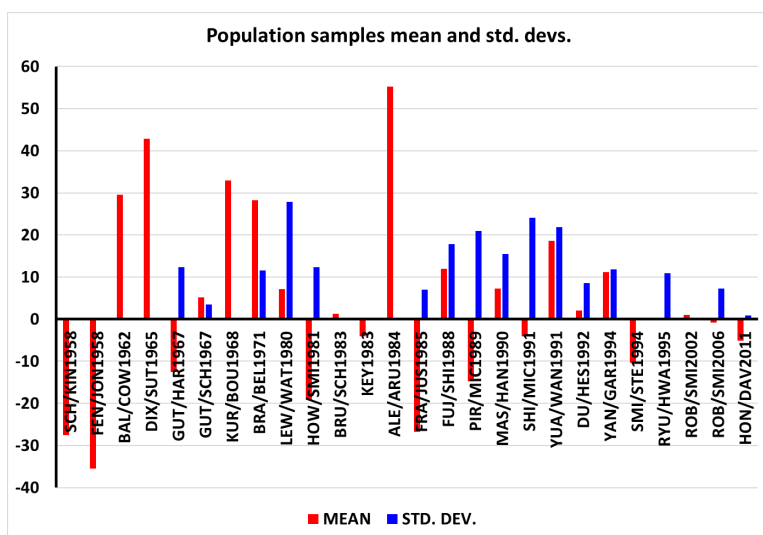


Figure 6: Mean and standard deviations of the individual sample sets.

What is evident from the data in Fig. 6 is 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 expected when the review began. The conclusion on this observation is that to reduce this uncertainty there are a number of potential ways:

1. Direct measurement of rate constant by numerous future experimental studies.
2. Consideration of the indirect data used for validation of detailed chemical kinetic models. Essentially, using the ignition delay times, laminar burning velocities and species measurements available to further constrain the fit and thereby increase the population size and potentially decrease the standard deviation in the overall data.
3. Perform *a priori* theoretical calculations to further constrain the fit and thereby potentially reduce the current statistical uncertainty.

One or all of the above would help to reduce the statistical uncertainty in the future. It is a key component of this review and STSM that these future work suggestions are communicated. The final modified Arrhenius fitting parameters for the reaction $O+OH \rightleftharpoons H+O_2$ are, $A=8.966E+11$, $n=0.273$ and $E_a=-888.38$. The units related to the rate constant for the fitting parameters are $cm^3 mol^{-1} s^{-1}$. The overall review and conclusions of this STSM represent the most comprehensive analysis of this reaction available to date in the literature. This is significant when one considers the importance of this reaction in prediction the

oxidation of hydrocarbon by detailed chemical kinetic models.

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: $H_2 + O \Rightarrow H + OH$
 R11: $H_2 + OH \Rightarrow H_2O + H$
 R15: $HCO (+M) \Rightarrow CO + H (+M)$
 R16: $HCO + H \Rightarrow CO + H_2$
 R16p: $O + O + M \Rightarrow O_2 + M$
 R17a: $H + O_2 (+M) \Rightarrow HO_2 (+M)$
 R18a: $OH + OH (+M) \Rightarrow H_2O_2$
 R18c: $H + HO_2 \Rightarrow H_2 + O_2$
 R18d: $H + HO_2 \Rightarrow OH + OH$
 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: $CO + O_2 \Rightarrow CO_2 + O$
 R31a: $OHC(O)O (+M) \Rightarrow OHOCO (+M)$
 R31b: $CO_2 + OH (+M) \Rightarrow OHC(O)O (+M)$
 R31c: $CO_2 + OH (+M) \Rightarrow OHOCO (+M)$
 R31d: $CO + HO_2 \Rightarrow OHC(O)O (+M)$
 R31e: $CO + HO_2 (+M) \Rightarrow OHOCO (+M)$
 R31f: $CO + HO_2 \Rightarrow CO_2 + OH$
 R31g: $HCO + O_2 (+M) \Rightarrow OHC(O)O (+M)$
 R31h: $HCO + O_2 (+M) \Rightarrow OHOCO (+M)$
 R31i: $HCO + O_2 \Rightarrow CO_2 + OH$
 R32: $HCO + HO_2 \Rightarrow CO + O_2 + H_2$
 R34: $HO_2 + HO_2 \Rightarrow H_2O_2 + O_2$

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.