

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: Ultan Burke

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. As an example, the determination of $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$ is strongly influenced by a correct definition of $\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$. Similarly, HCO depletion typically used to determine $\text{HCO} + \text{O}_2$ does not only occur via the $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$ reaction, but for instance also through $\text{HCO} + \text{O}_2 = \text{CO}_2 + \text{OH}$. The results obtained for the above reaction ($\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$) are reported in the next Section.

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 LOG₁₀(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) HCO+O₂=CO+HO₂
- 2) H+H₂O₂=H₂O+OH
- 3) H+H₂O₂=H₂+HO₂
- 4) H₂+OH=H₂O+H

The next Section reports the final document for reaction 1.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

HCO+O₂=CO+HO₂

Conventions:

A; cm³ mol⁻¹ 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.

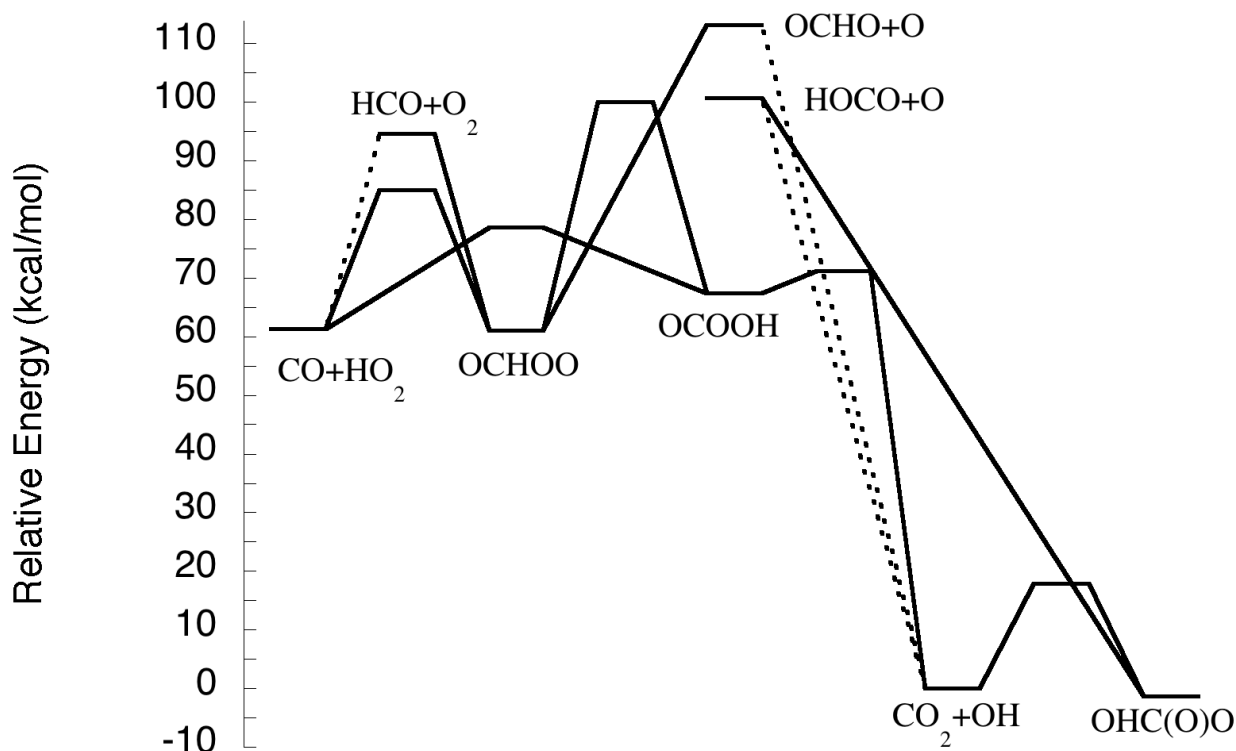


Figure 1: Potential energy surface for R31.

Figure 1 presents the potential energy surface for HCO_3 . Considering $\text{HCO}+\text{O}_2$ as reactants the most commonly considered products are $\text{CO}+\text{HO}_2$, either *via* direct H-atom abstraction or through the addition-elimination reaction sequence. In the later case pressure-dependence will be present. Generally, the experimental measurements for R31j are at <1 atm, therefore chemical activation dominates meaning the measurement of the rate constant is typically the total of the direct abstraction and the chemically activated reaction.

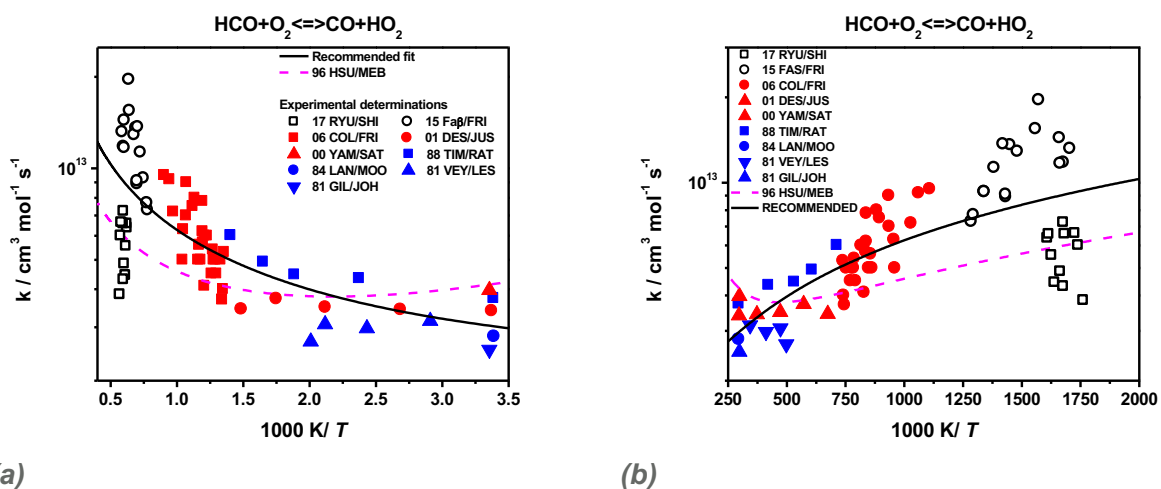


Figure 2: Rate constant for $\text{HCO}+\text{O}_2\rightleftharpoons\text{HO}_2+\text{CO}$. Measurements are denoted as points, while our recommended fit and any available theoretical calculations are presented as lines. (a) – Arrhenius representation of available data, (b) – Rate constant vs. temperature plot.

Figure 2 presents the available rate constant measurements and theoretical calculations for

reaction 31j. Additionally, the recommended fit as proposed in *this study* is shown in this figure. The experimental investigations are consistently complicated by the influence of secondary reactions, particularly the reaction $\text{HCO} + \text{M} \rightleftharpoons \text{H} + \text{CO} + \text{M}$. There also exists a somewhat semi-empirical theoretical study from Bozzelli and Dean (93 BOZ/DEA). This QRRK study relied on an estimated high-pressure limiting reaction rate constant as input for their QRRK investigation. While this study qualitatively provides an indication of the pressure dependence of the reaction and primary product distribution over temperature and pressure, we have chosen to omit it from our subsequent analysis. This decision is made based on the advancement in the field of *ab-initio* and master equation calculation methods. Additionally, it significantly differs in magnitude from the range of literature data available for this reaction. The publication lacks the required details regarding Lennard-Jones parameters and assumptions made to fit the ΔE_{down} parameter and therefore, we deem it unsuitable to include in our current recommendation for this reaction rate constant.

The theoretical study of 96 HSU/MEB have provided information regarding the pressure-dependence of the reaction rate constant, a summary of this is shown in Fig. 3. It is clear that the only range of temperature and pressure where the stabilization pathway becomes measurably competitive with the chemically activated pathway is at temperatures < 1000 K and at a pressure of 200 atm. This work did not provide information on the pressure-dependence of the rate constant between 1 atm and 200 atm, it is therefore difficult to accurately determine the impact of pressure on the rate constant at pressures in between these. However, for the majority of the experimental determinations of this rate constant the experimental pressures were 1 atm and below. This indicates that, at least in the experimental measurements the stabilization pathway was unlikely to measurably effect the rate constant measurement.

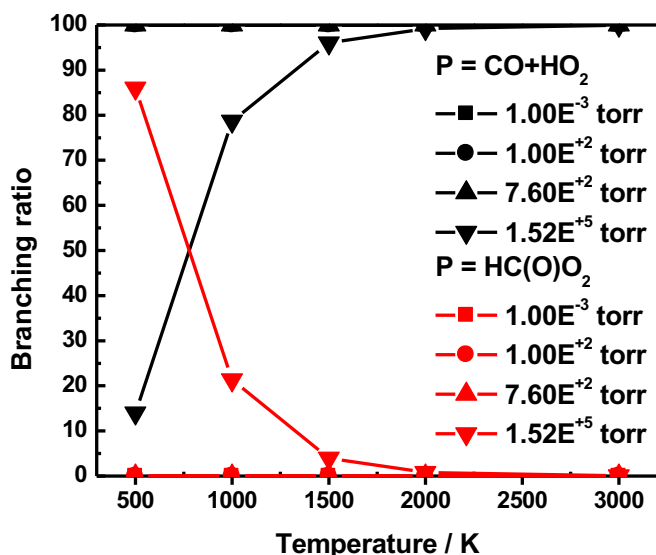


Figure 3: Branching ratio stabilization and chemical activation as per the calculations of 96 HSU/MEB.

In the temperature range of 1250–1750 K, two studies are available in the literature and seem to contradict one another. The study of 15 FAS/FRI measure a rate constant of approximately $1.05\text{E}13$ at 1625 K, while 17 RYU/SHI measure approximately $5\text{E}12$ at the same temperature. The precursors for formyl radical production in the two studies are, glyoxal in 15 FAS/FRI and methane in 17 RYU/SHI. The species detected and used to fit the final rate constant for both studies are formyl radical in 15 FAS/FRI and hydroxyl radical in 17 RYU/SHI. Both studies use detailed models in order to simulate their species-time measurements and subsequently fit their measured rate constants, which makes both studies somewhat indirect and open to scrutiny

depending on the fidelity of the models implemented. Our interpretation of the two studies concludes that, 15 FAS/FRI is certainly more direct, as the reaction pathway from glyoxal to formyl radical is more direct than methane to hydroxyl radical and the measurement of a reactant/product species should be considered best practice, as opposed to the measurement of hydroxyl radical profiles which is not directly involved in the reaction. However, this does not necessarily motivate us to neglect the measurement of 17 RYU/SHI completely, and we estimate that temperatures >1250 K the recommended rate constant has an uncertainty of approximately 2.5. This uncertainty takes into account the fitting of the measurements in the two available studies in this temperature regime *via* two different detailed kinetic models and the specific numerical differences in the final rate constant measurements in this temperature regime.

This uncertainty should not be considered as temperature independent. In Fig. 4 the percentage difference of experimental and theoretical determinations of R31j from the current recommended fit is presented. It is clear that as the temperature increases the differences between the recommended fit and the measurements/calculations markedly increases. We therefore estimate a more modest uncertainty of approximately 30% for lower temperatures, based also on the fact that there are more independent determinations of R31j in the lower temperature regime <750 K.

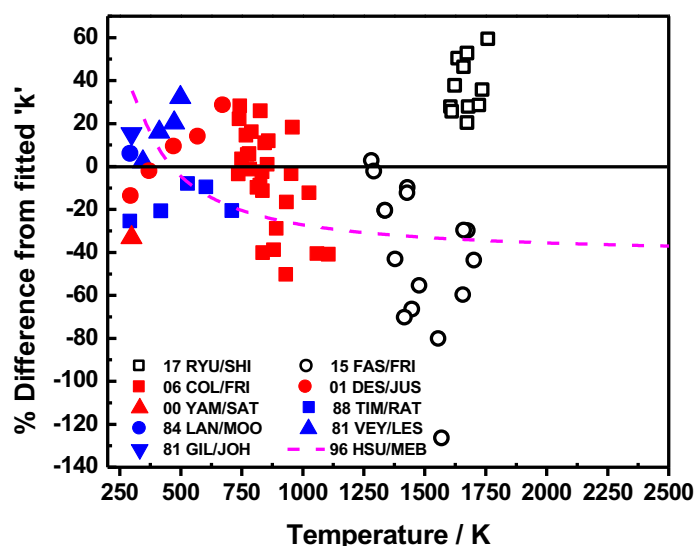


Figure 4: The percentage difference of experimental and theoretical determinations of reaction R31j from the current recommended fit.

The importance of this reaction in terms of the prediction of indirect kinetic data such as, ignition delay times and laminar burning velocities is considered well-known. In fact, it is the competition of the formyl radical's reaction with molecular oxygen and the unimolecular decomposition of the formyl radical which is of greatest importance for hydrocarbon oxidation models, as opposed to the absolute rate constant of either reaction. This link in the consumption of the formyl radical, trickles into the difficulty in selectively measuring the bimolecular reaction consuming formyl radical or the unimolecular reaction pathway. This is one of the major challenges when interpreting the available experimental measurements for R31j. If a study assumes a rate constant for the unimolecular decomposition of the formyl radical this will impact on the fitted rate constant for R31j. Therefore caution is required when one compares the measured rate constant from different studies which both use different kinetic models in their fitting process. A further complication is the potential for non-thermal decomposition of formyl radicals, which is not conventionally considered in chemical kinetic models. The inclusion of this type of reaction may impact upon the experimental rate constant measurements, which are based on sensitivity analysis using a chemical kinetic model, showing that the experimental conditions are primarily sensitive to reaction R31j and/or R15 for example. These complications lead us to recommend that if further experimental work are to be pursued on R31j the focus of the measurements should be towards the selective measurement of product species such as, CO and HO₂ as opposed to the measurement of formyl radical. Additionally, experiments above 1 atm are all but absent currently and given the pressure dependence tentatively proposed through the

calculations of 96 HSU/MEB, experimental determinations at increased pressures would be of interest in further elucidating the rate constant for R31j. If these rate constant measurements were accompanied with *ab-initio* calculations coupled with master equation calculations, this would improve significantly the existing uncertainty in the recommendation for this rate constant. For the purposes of the current study we provide a three parameter modified Arrhenius fit which accurately represents our recommendation.

- $\text{HCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{HO}_2$, $A = 2.57441\text{E}10$, $n = 0.78266$, $E_a = -174.57035$

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FUTURE COLLABORATIONS (if applicable)

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

- R2: $\text{H} + \text{H} + \text{M} \Rightarrow \text{H}_2 + \text{M}$
 R9: $\text{H} + \text{O} + \text{M} \Rightarrow \text{OH} + \text{M}$
 R10a: $\text{H} + \text{OH} (+\text{M}) \Rightarrow \text{H}_2\text{O} (+\text{M})$
 R10b: $\text{H}_2 + \text{O} \Rightarrow \text{H} + \text{OH}$
 R11: $\text{H}_2 + \text{OH} \Rightarrow \text{H}_2\text{O} + \text{H}$
 R15: $\text{HCO} (+\text{M}) \Rightarrow \text{CO} + \text{H} (+\text{M})$
 R16: $\text{HCO} + \text{H} \Rightarrow \text{CO} + \text{H}_2$
 R16p: $\text{O} + \text{O} + \text{M} \Rightarrow \text{O}_2 + \text{M}$
 R17a: $\text{H} + \text{O}_2 (+\text{M}) \Rightarrow \text{HO}_2 (+\text{M})$
 R17b: $\text{H} + \text{O}_2 \Rightarrow \text{O} + \text{OH}$
 R-17b: $\text{O} + \text{OH} \Rightarrow \text{H} + \text{O}_2$
 R18a: $\text{OH} + \text{OH} (+\text{M}) \Rightarrow \text{H}_2\text{O}_2$
 R18b: $\text{OH} + \text{OH} \Rightarrow \text{O} + \text{H}_2\text{O}$
 R18c: $\text{H} + \text{HO}_2 \Rightarrow \text{H}_2 + \text{O}_2$
 R18d: $\text{H} + \text{HO}_2 \Rightarrow \text{OH} + \text{OH}$
 R18e: $\text{H} + \text{H} + \text{O}_2 \Rightarrow \text{H}_2 + \text{O}_2$
 R18f: $\text{H} + \text{H} + \text{O}_2 \Rightarrow \text{OH} + \text{OH}$
 R22: $\text{CO} + \text{O} (+\text{M}) \Rightarrow \text{CO}_2 (+\text{M})$
 R23a: $\text{CO}_2 + \text{H} \Rightarrow \text{HOCO}$
 R23b: $\text{CO} + \text{OH} \Rightarrow \text{HOCO}$
 R23c: $\text{CO} + \text{OH} \Rightarrow \text{CO}_2 + \text{H}$

R23d: HCO + O => CO2 + H
R23e: HCO + O => CO + OH
R24: O2 + O (+M) => O3 (+M)
R24pa: HCO + OH => CO2 + H2
R24pb: HCO + OH => CO + H2O
R25a: O + HO2 => O2 + OH
R25b: H + O + O2 => OH + O2
R26a: OH + HO2 => H2O + O2
R26b: H2O2 + O => H2O + O2
R26c: H + OH + O2 => H2O + O2
R27: H2O2 + OH => H2O + HO2
R30a: HCO + HCO => OCHCHO
R30b: HCO + HCO => CO + H2CO
R30c: HCO + HCO => CO + CO + H2
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.