SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

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

Action number: CM1404
STSM title: Uncertainties in chemical kinetic models of flame inhibition
STSM start and end date: 05/03/2018 to 20/04/2018
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PURPOSE OF THE STSM/

The STSM was aimed at investigation of key uncertainties of chemical kinetic models relevant to flame inhibition, which is important from both practical and theoretical point of view. The chemical kinetic scheme of the ($H_2/O_2/Br_2$) system was selected as a prototype to be studied with the purpose of global sensitivity analysis and further mechanism optimization.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

Chemical kinetics of hydrogen halides has long been studied, motivated by various reasons ranging from fundamental aspects of reaction dynamics and atmospheric chemistry to fire protection engineering or nuclear safety. During this STSM we studied selected reactions of HBr and HI at flame temperatures. Important updates on high-temperature bromine and iodine chemistry as well as appropriate thermochemical data became recently available in the literature, which together with some additional information allows one to quantify uncertainties relevant to model predictions of laminar flame structure (i.e. species profiles). Our work was mostly focused on the following set of bimolecular elementary reactions (R1 – R6, where X is a halogen atom, i.e. Br or I) involved in inhibition of H_2/O_2 combustion:

$H + HX \leftrightarrow H_2 + X$ (R1)

$O + HX \leftrightarrow OH + X$ (R2)

$OH + HX \leftrightarrow H_2O + X$ (R3)

$HO_2 + HX \leftrightarrow H_2O_2 + X$ (R4)

$HO_2 + X \leftrightarrow HX + O_2$ (R5)

$H + X_2 \leftrightarrow HX + X$ (R6)

Bibliographic records reporting their reaction rate coefficients were collected and reviewed. Methods of determination (both theoretical and experimental) were discussed in order to estimate their uncertainty factors.

Extensive bibliographic search was also conducted focusing on more general aspects of fire suppression chemistry, recent development and testing of perspective halon replacement agents, their atmospheric fate, etc. On the basis of the information gained, iodine chemistry relevant to inhibition of H_2/O_2 flames was finally also taken into consideration because of analogy to bromine reactions and due to practical importance regarding an extinguishing effect of trifluoromethyl iodode (CF_3I) as a perspective halon replacement for fires of oxygenated fuels.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

Uncertainties of the given system were investigated in relevance to scientific objectives of the CM1404 Action (mainly Secondary objective 4).

Extinguishing efficiency corresponding to flames of more complex oxygenated fuels is not usually considered in development and validation of chemical kinetic schemes for perspective fire suppression agents. Model performance and sensitivity of the well-established NIST (National Institute of Standards and Technology) HFC mechanism (and its modified versions) was partly investigated for methanol flames inhibited by CF_3Br and CF_3I. However, it is desirable to update former mechanisms in a hierarchical way employing recently optimized chemical kinetic schemes in order to reduce uncertainties of predictions (propensity to error propagation) and keep a model consistency for future practical use as well as further development.

As a first step in this direction, core sub-mechanisms of available chemical kinetic schemes describing flame inhibitory effects for bromine-/iodine- containing fire suppression agents were compared and their relative differences were identified. Kinetics data of elementary reaction steps being of particular importance for inhibition cycle were reviewed with the purpose of global sensitivity analysis and further mechanism optimization (within Optima++ framework). Documentation of theoretical rate determinations including the results of both direct and indirect measurements following the ReSpecTh Kinetic Data Format specification (v2.0) is in progress.

An abstract reporting this work was submitted as a contribution to Work-In-Progress Poster session of the 37th Symposium on Combustion held in Dublin (29th July – 3rd August 2018).

FUTURE COLLABORATIONS (if applicable)

Future collaboration is planned to be focused on determination of rate coefficients and temperature dependence for key reactions, which will be proposed based on results of sensitivity analysis. Another common interest was identified concerning spectroscopically based diagnostics in relevance to a given task. Minor species profiles measured in laminar flame doped by halogenated species are important Quantities of Interest (QoI) showing sensitivity to rate of reactions involved in flame inhibition chemistry. Diagnostics of hydroxyl radical concentrations (e.g. based on 2*f*-WMS measurement) is therefore an important issue to be further investigated in the given context. Close cooperation of the participating institutions with the groups of the host as welll as of profs. Turányi and Császar at Eötvös Loránd University (ELTE) is highly advantageous when utilizing optimized datasets and computational tools recently available from the ReSpecTh database. Such cooperation could also potentially foster cross-disciplinary exchange of knowledge and experience among scientific communities of combustion modellers and theoreticians/experimentalists in molecular spectroscopy.