

SHORT TERM SCIENTIFIC MISSION (STSM) SCIENTIFIC REPORT

This report is submitted for approval by the STSM applicant to the STSM coordinator

Action number: CM1404

STSM title: CHEMISTRY OF SMART ENERGY CARRIERS AND TECHNOLOGIES

STSM start and end date: 16/02/2019 to 24/02/2019

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PURPOSE OF THE STSM:

This one week long STSM had following objectives:

- Develop design ideas to fabricate state of the art facilities for species profile measurement.
- Implement optimized sampling system for a single pulse shock tube at NUIG.

An existing shock tube facility at NUIG was converted to single-pulse mode and coupled to a gas chromatograph/mass spectrometry (GC-MS) system to facilitate gas-phase chemical kinetic experiments. Temperatures of up to 2000 K can be achieved. The test pressures are in the range of 1–3 atm.

PCFC at RWTH Aachen recently developed a sampling system for their rapid compression machine and the main purpose of the visit was to engage in brainstorming to develop such a facility for our shock tube using their expertise and discuss regarding collaborative projects for detailed chemistry mechanism validation covering a wide range of pressures and temperatures.

AGENDA:

- Day 1 : Understanding the working of a rapid compression machine (RCM) and the sampling system
- Day 2: Chromatogram and Mass spectrum analysis
- Day 3: Discussion with Prof Heufer regarding optimizing facilities at NUIG and collaboration
- Day 4: Visit to the shock wave laboratory and also observe RCM sampling experiments
- Day 5: Visit to University of Duisburg and discuss regarding future collaborations and gave a presentation on work carried out at NUIG

DESCRIPTION OF WORK CARRIED OUT DURING THE STSM

The rapid compression facility (RCM) at PCFC is described in article by C.Lee et al. [1]. This high pressure, single piston RCM has variable compression ratio. The facility utilizes a pneumatic driving and hydraulic stopping mechanism. During this STSM, sampling experiments were carried out on this facility. An in-house program based on LabView was developed by researchers at PCFC for mixture preparation calculation and controlling the pneumatic driving and hydraulic stopping mechanism. A fast sampling system was developed for intermediate species sampling and quantification. During sampling experiments, a small amount of mixture was withdrawn from adiabatic core through a sampling probe into a pre-evacuated stainless steel volume. Parker fast acting solenoid valves triggered by Parker IOTA driver was used as sampling valve. The analyte was then extracted from the sampling volume using a syringe and injected into a GC-MS system. The sample is analyzed using appropriate method in a Porabond and Alumina/KCl column. MS is used for identification and FID is used for quantification. Experiments were carried out on

propane and butane oxidation by researchers at PCFC during this one week STSM and I observed the sampling system design and implementation.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The sampling system connected to our recently recommissioned shock tube at NUIG was optimized based on part of what was learned at PCFC, Aachen. In our sampling system, a 1/16th inch tube protrudes 8 mm into the shock tube from the end-wall and is connected to a Festo MHE4 solenoid valve which is, in turn, connected to an Agilent 6890/5975 GC-MS system through a series of six-port gas sampling valves which can be configured for various functions. The dead volume is minimal due to the smaller diameter of the sampling tube and therefore it is assumed that the effect of the unreacted mixture is negligible. This design allows online sampling, reducing dilution.

Validation of this newly recommissioned system is essential and a standard chemical thermometer, cyclohexene was chosen for this. Cyclohexene (C_6H_{10}) undergoes decomposition to ethylene and 1,3-butadiene at approximately 1000 K. There have been studies performed by Tsang et al. [2], Skinner et al. [3] and Stranic et al. [4] which have reported the rate constant of this single step reverse Diels-Alder reaction. Mixtures containing 1% and 2% C_6H_{10} were prepared on the basis of partial pressures in a 40 L mixing vessel and shock tube experiments were performed and the results are shown below:

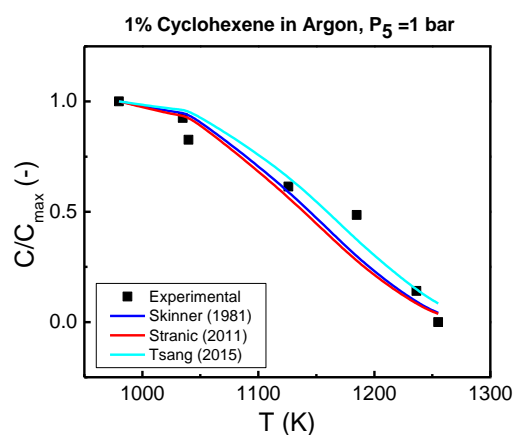


Figure 1: Cyclohexene concentration profiles at reflected pressures of 1 bar and 1% initial concentration.

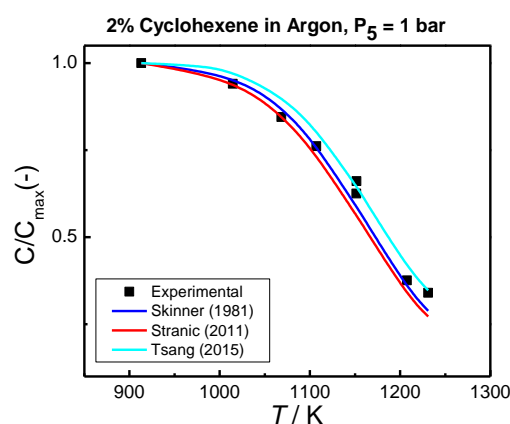


Figure 2: Cyclohexene concentration profiles at reflected pressures of 1 bar and 2% initial concentration.

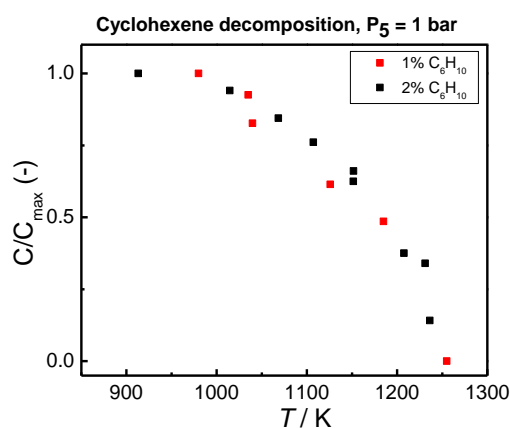


Figure 3: The experimental data showing the decomposition of cyclohexene for both concentrations.

From these results, it is evident that the new shock tube facility gives promising results at 1 bar in the temperature range 900–1300 K. At higher temperatures, cyclohexene decomposition produces multiple products including benzene, 1,3-cyclohexadiene, 1,3-butadiyne, 1-buten-3-yne, acetylene and ethylene. Therefore, the rate constants cannot be used under these conditions. This STSM helped me to optimize our sampling system to obtain these results.

REFERENCES

- [1] C. Lee, S. Vranckx, K.A. Heufer, S. V. Khomik, Y. Uygun, H. Olivier, R.X. Fernandez, On the chemical kinetics of ethanol oxidation: shock tube, rapid compression machine and detailed modeling study, *Zeitschrift Für Phys. Chemie.* 226 (2012) 1–28.
- [2] W. Tsang, C.M. Rosado-Reyes, Unimolecular rate expression for cyclohexene decomposition and its use in chemical thermometry under shock tube conditions, *J. Phys. Chem. A.* 119 (2015) 7155–7162.
- [3] G.B. Skinner, D. Rogers, K.B. Patel, Consistency of theory and experiment in the ethane–methyl radical system, *Int. J. Chem. Kinet.* 13 (1981) 481–495.
- [4] I. Stranic, D.F. Davidson, R.K. Hanson, Shock tube measurements of the rate constant for the reaction cyclohexene → ethylene + 1, 3-butadiene, *Chem. Phys. Lett.* 584 (2013) 18–23.