SHORT TERM SCIENTIFIC MISSION (STSM)
SCIENTIFIC REPORT

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

Action number: CM1404 - Chemistry of Smart Energy Carriers and Technologies (SMARTCATS)
STSM title: Kinetics and thermochemistry of 2-methyallyl and methyl-substituted amine radicals with molecular oxygen: experiments and theory
STSM start and end date: 25/03/2019 to 29/04/2019
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PURPOSE OF THE STSM:

(max.200 words)
The purpose of the STSM was to calculate the rate coefficients of two reactions (2-methylallyl radical + O_2 and dimethyl-aminyl + O_2) as a function of temperature and pressure. The first reaction is particularly important in the combustion of isobutene and soot formation, while the second reaction is relevant in both combustion and atmospheric chemistry. The atmospheric fate of amines will be of particular interest if amine scrubbing of post-combustion carbon dioxide becomes widespread. Amines are also present in some alternative fuels such as biomass.

We have measured in Helsinki the rate coefficients of these reactions as a function of temperature and pressure and intend to combine the experimental results with kinetic calculations. The kinetic calculations planned for the STSM consist of both high-level electronic structure calculations as well as master equation simulations. The experimental results are vital in fixing key parameters, such as collisional energy transfer parameters, in the master equation models. After the master equation simulations are made to reproduce our experimental results with sufficient accuracy, we intend to extend the master equation modeling to pressures and temperatures relevant in atmospheric and combustion chemistry

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

(max.500 words)
2-methylallyl radical + O_2
We have calculated the potential energy profile for this reaction (12 wells and 15 transition structures). Geometry optimizations were performed at the MN15/Def2TZVP level of theory. Single-point energies were calculated with the ROHF-CCSD(T), UHF-CCSD(T), G4 and ROHF-DLPNO-CCSD(T) methods using cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets. One cyclic transition state had significant multireference character so its single-point energy was calculated at the NEVPT2/CBS level of theory using a 7-electron and 5-orbital active space.

The relevant parts of the potential energy profile were input into a master equation program

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(MESMER). The low-temperature and low-pressure experimental data was used to optimise the exponential-down energy transfer parameter used in the master equation model. The experimental equilibrium constant data was used to evaluate the reliability of the computed well-depth of the initial addition reaction.

Particular focus was put into evaluating the reliability the partition functions as calculated by MESMER. This is done because the reaction intermediates can have up to three hindered rotors that are coupled to each other. Although MESMER cannot explicitly take into account the potential coupling between hindered rotors, it allowed us to use angle-dependent moments of inertia and relaxed one-dimensional hindered rotor potentials, which allows us to account for some of the coupling.

The initial addition reaction with O_2 is barrierless, and MESMER cannot explicitly calculate the microcanonical rate coefficients for such reactions. However, if the canonical (high pressure) Arrhenius parameters of a barrierless reaction are known, MESMER can use the Inverse Laplace Transform approach to calculate microcanonical rate coefficients for such a reaction. Since experimental data was available for our reaction, we performed a fitting exercise to obtain optimal values for the canonical Arrhenius parameters.

Dimethylaminyl + O_2
We have also started the computations for this reaction and they are in progress. The calculations address the determination of the potential energy profile of this reaction at the MN15/Def2TZVP // ROHF-CCSD(T) level of theory. To model this reaction, however, we need to calculate the canonical rate coefficient of the initial addition step, $C_2H_6N + O_2 \rightarrow C_2H_6NO_2$, as a function of temperature. This requires us to determine the transition state of this reaction variationally. To do this, we have started performing high-level multireference calculations. It seems that an active space of seven electrons and five orbitals (p orbitals of oxygen and the p orbital of the carbon atom that is the radical center) is satisfactory to capture the multireference behaviour of the system. Currently we are testing what is the difference between using DFT geometries with multireference single-point energies and using multireference geometries and energies.

DESCRIPTION OF THE MAIN RESULTS OBTAINED
The 2-methylallyl radical + O_2 reaction
The geometries of the stationary points on the potential energy surface of the *2*-methylallyl radical + O_2 were determined at the MN15/DefTZVP level of theory. The thermodynamic contributions to the thermochemistry were also calculated at this level. Single-point energies were calculated with the ROHF-CCSD(T), UHF-CCSD(T), G4 and ROHF-DLPNO-CCSD(T) methods using cc-pVDZ, cc-pVTZ and cc-pVQZ basis sets. The ROHF-CCSD(T) energies were found to be the most reliable, as many of the transition structures, as well as the 2-methylallyl radical, were found to have significant spin contamination in the unrestricted calculations. Of the other approximate methods (ROHF-DLPNO-CCSD(T) and G4), DLPNO was found to perform slightly better. We believe that the relative energies of all intermediates and most transition structures are within chemical accuracy (4 kJ/mol). This is based on the good agreement with the computed and experimental equilibrium constant. A few transition structures had a T1 diagnostic between 0.03–0.04, so for these species the uncertainty in the calculated relative energy is somewhat higher. One transition structure had a T1 diagnostic of 0.07 and the energy of this structure was calculated at the NEVPT2/CBS level of theory.

We used MESMER's Marquardt fitting algorithm and our experimental data to optimise the values of key parameters in the master equation model. We obtained a value of 160 cm^{-1} for the exponential down parameter of the peroxyl radical at 300 K. According to our fitting, the temperature dependence of the exponential down parameter is very weak, having an *n* value of about 0.1. For the canonical Arrhenius parameters of the initial addition reaction, we obtained the values $A = 1.85 \cdot 10^{-}$

^{12} cm^3 s^{-1}, E_a = 0 and m = -0.85.

The electronic structure calculations show that lowest-energy isomerisation pathway (21.0 kJ/mol) of the formed peroxy radical is the intramolecular abstraction of an allylic hydrogen from the methyl group. The QOOH species can then react with O_2 again to form OOQOOH (this step is presumably barrierless) or form a cyclic C_4H_6O species and kick out OH (68.2 kJ/mol). Other isomerization pathways of the initial peroxyl radical are the formation of four- or five-membered rings (through barriers of 40.0 and 33.8 kJ/mol, respectively) that can dissociate to C_3H_5O and C_4H_6O products through transition states that are over 50 kJ/mol in energy. At high temperatures (T > 1000 K), the master equation simulations show that the direct dissociation of the 2-methylallyl radical to methyl and allene becomes significant.

The partition function investigations indicate that errors arising from multi-structural and coupling effects should cause no more than a 50 % error in the single-structure, uncoupled hindered rotor partition function used by MESMER.

The dimethylaminyl + O_2 reaction

A part of the potential energy profile calculations for this reaction have been completed. The time-consuming multireference calculations are under way.

The results collected during the STSM will be organized for publication in the coming weeks.

FUTURE COLLABORATIONS (if applicable)

We plan to continue the collaboration according to the scheme set up in connection with this mission: The Helsinki group will continue the experimental investigations of the reactions of amine radicals and the theoretical modelling will be performed together with the theoreticians in Budapest.