Accurate Determination of Rate Coefficients Under Combustion-Relevant Conditions: Photoionization Mass Spectrometry and Master Equation Simulations

Timo Pekkanen,[a] Raimo Timonen,[a] Satya P. Joshi,[a] and Arkke Eskola.[a]
[a] University of Helsinki, Department of Chemistry

IX Liekkipäivä

23.10.2018

HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

Rate Coefficient

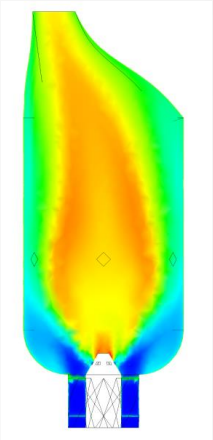
- Under constant-volume conditions, the rate of a chemical reaction can often be expressed in the following form:

$$r = \frac{1}{\nu_\mathrm{A}}\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{1}{\nu_\mathrm{B}}\frac{\mathrm{d}[\mathrm{B}]}{\mathrm{d}t} = \ldots = k_\mathrm{r}(p,T)[\mathrm{A}]^{c_\mathrm{A}}[\mathrm{B}]^{c_\mathrm{B}}\ldots$$

rate coefficient

- Rate coefficients almost always depend on temperature and in many cases also on pressure.

Combustion Models



Require the coupling of fluid dynamics with chemical kinetics.

Problems:

- The number of chemical reactions that need to be considered grows exponentially with fuel size.
- The rate coefficients need to be known over large temperature and pressure ranges.

$$\mathrm{CH_4} \xrightarrow[-\mathrm{H_2O}]{\mathrm{OH^\bullet}} \mathrm{CH_3^\bullet} \xrightarrow{\mathrm{O_2}} \mathrm{CH_3O_2^\bullet} \xrightarrow[-\mathrm{NO_2}]{\mathrm{NO}}$$

$$\mathrm{CH_3O^\bullet} \xrightarrow[-\mathrm{HO_2^\bullet}]{\mathrm{O_2}} \mathrm{H_2CO} \xrightarrow[-\mathrm{H^\bullet}]{h\nu} \mathrm{HCO^\bullet} \xrightarrow[-\mathrm{HO_2^\bullet}]{\mathrm{O_2}}$$

$$\mathrm{CO} \xrightarrow[-\mathrm{H^\bullet}]{\mathrm{OH^\bullet}} \mathrm{CO_2}$$

...

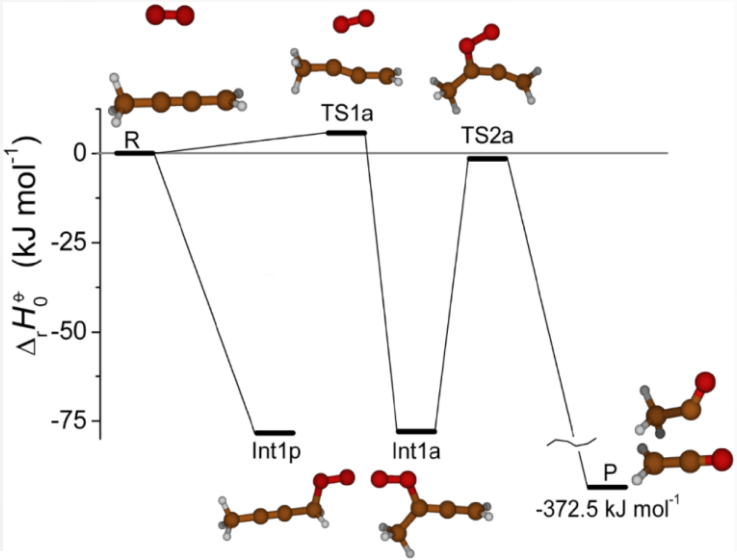
Two possible solutions.

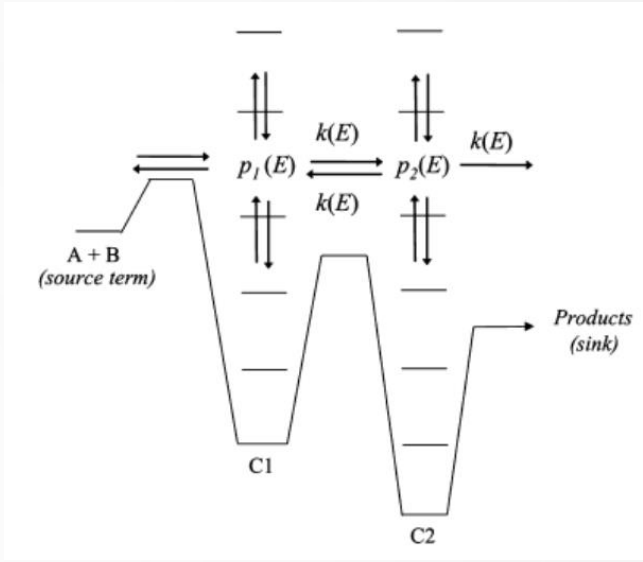
1. Measure the rate coefficients for all relevant reactions. Not a realistic solution if the model contains thousands of reactions. Also, experiments are difficult to perform at temperatures and pressures relevant for combustion.

2. Develop computational methods that are able accurately capture the temperature and pressure dependence of reaction rate coefficients. These methods then need to automated and coupled to combustion models.

Master Equation Modeling

Master equation modeling can be used compute reaction rate coefficients as a function of temperature and pressure.





-Master equation models require as input the potential energy surface of the reaction.
-Knowledge about collisional energy transfer is also required.

Master Equation Modeling: Problems

1. Even small errors (few kJ mol^{-1}) in the energies of the stationary points have a huge impact on the computed rate coefficient.

2. Collisional energy transfer parameters often have to be estimated.

3. Barrierless reactions require sophisticated treatment. This treatment is currently possible only for relatively small systems (< 8 heavy atoms).

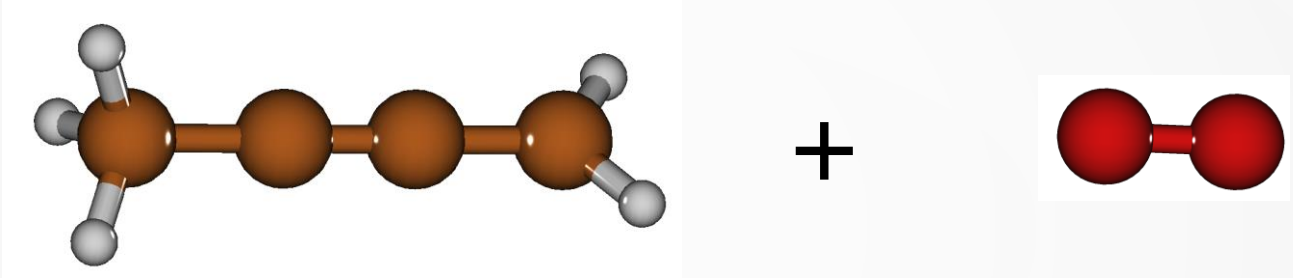
Solution: Combine Master Equation Calculations with Experiments

Idea:

- Measure rate coefficients at relatively low temperatures and pressures.
- Construct a master equation model and use the experimental data to constrain key parameters in the master equation model (energies of stationary points and collisional energy transfer parameters).
- Use at temperatures and pressures relevant to combustion.

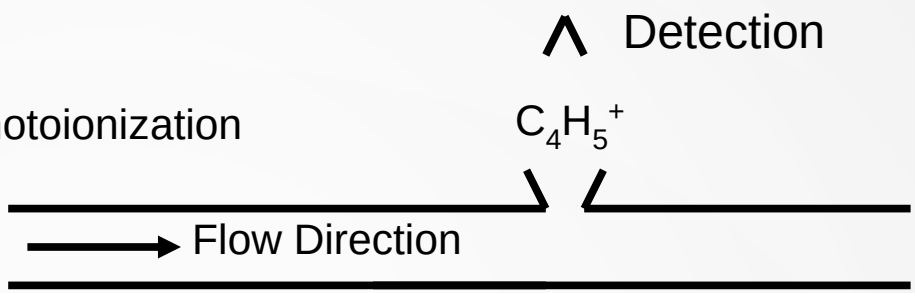
the experimentally adjusted master equation model to calculate rate coefficients

Example: The Reaction of 3-Methylpropargyl Radical With Molecular Oxygen



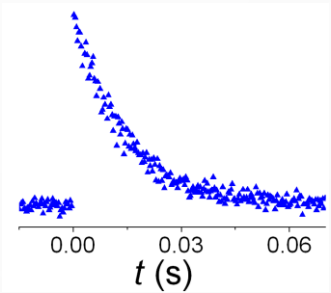
Experimental

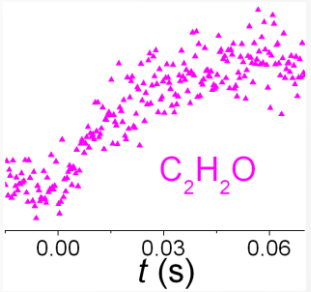
- We performed experiments in a laminar flow reactor coupled to a photoionization mass spectrometer. Pulsed laser photolysis was used for radical production. Reactions were performed under pseudo-first-order conditions ([O_2] >> [C_4H_5]).



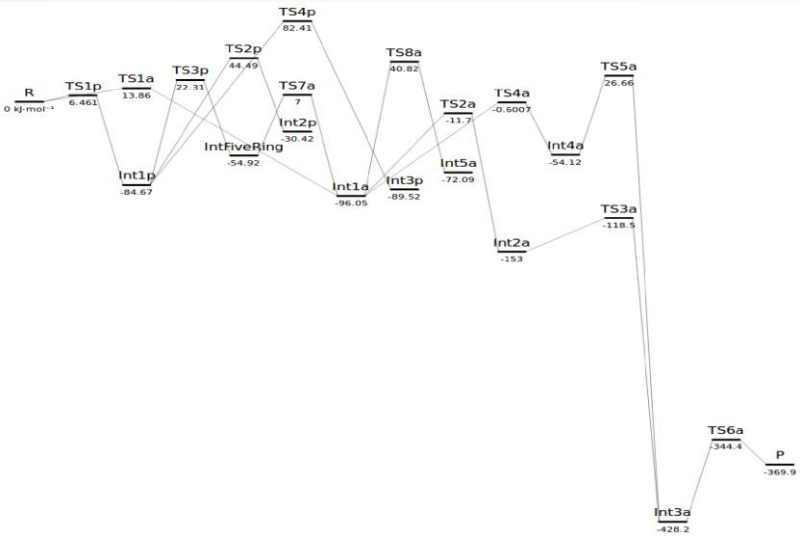
Photolysis along reactor:
$C_4H_5Br + h\nu(248\ nm) \rightarrow C_4H_5 + Br$

C_4H_5 then reacts with oxygen. The concentration of C_4H_5 is monitored as a function of time.

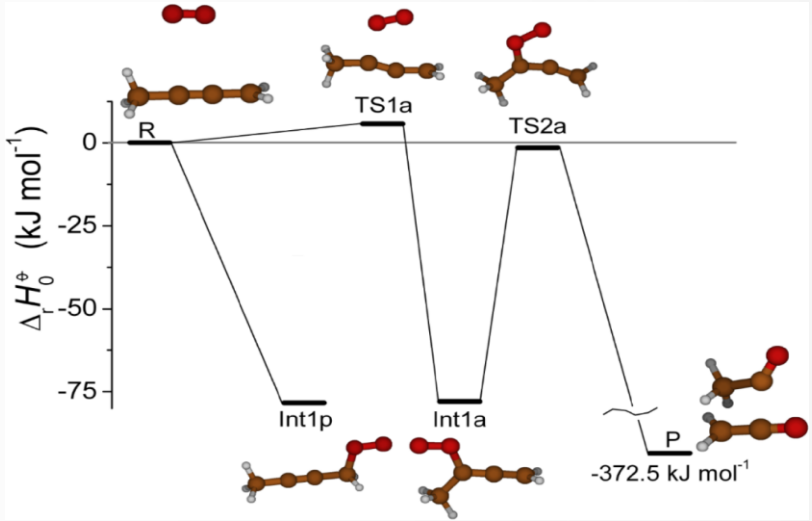




Potential Energy Surface

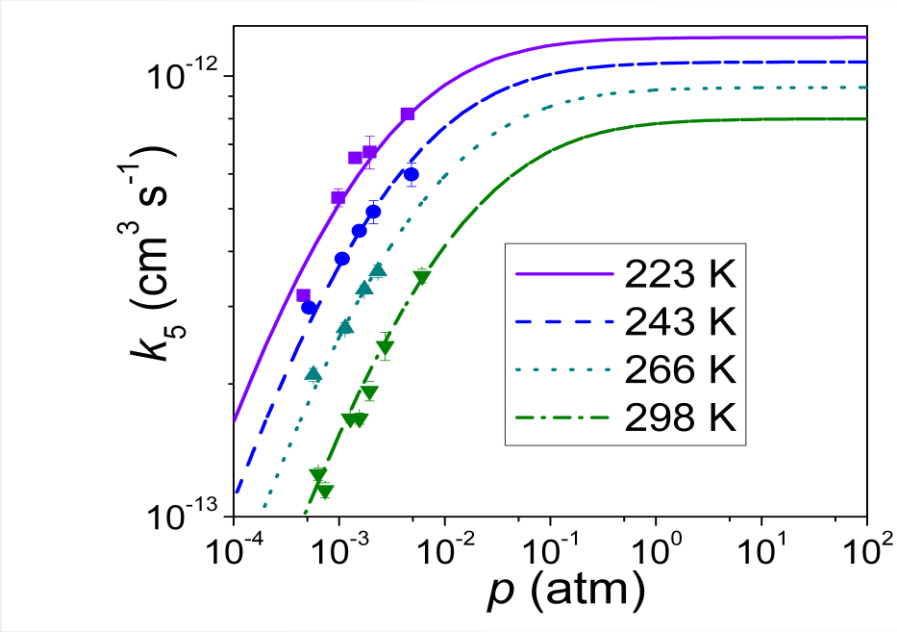


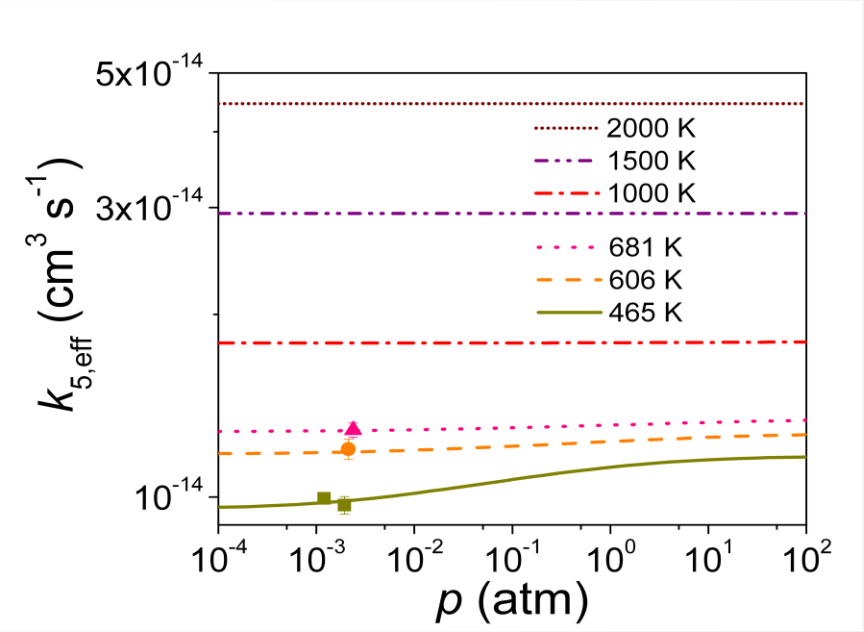
MN15/Def2ZVP



ROHF-CCSD(T)/CBS

Results


10^{-12}
10^{-13}
k_5 (cm^3 s^{-1})
223 K
243 K
266 K
298 K
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}
p (atm)


5x10^{-14}
3x10^{-14}
10^{-14}
$k_{5,eff}$ (cm^3 s^{-1})
2000 K
1500 K
1000 K
681 K
606 K
465 K
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2}
p (atm)

Conclusions

- The master equation approach can be used to calculate the rate coefficients of chemical reactions as a function of temperature and pressure. The rate coefficient can be determined at conditions inaccessible to experiments.
- Experimental data is still needed in the development of Master equation simulations.
- The final goal is to have fully automated approach to compute the rate coefficient of an arbitrary reaction.

Thank you for listening.

Acknowledgements: T. T. P. Acknowledges support from the doctoral programme in chemistry and molecular sciences of the university of Helsinki.

A. J. E. Acknowledges support from the academy of Finland, grant numbers 288377 and 294042 .

The authors also acknowledge COST action CM1401 for support as well as CSC IT center for science in Finland for computational resources.