

Computational Kinetics in Supercritical CO₂ Environment: Ethane Dissociation and Recombination Reactions C₂H₆ ⇌ CH₃ + CH₃

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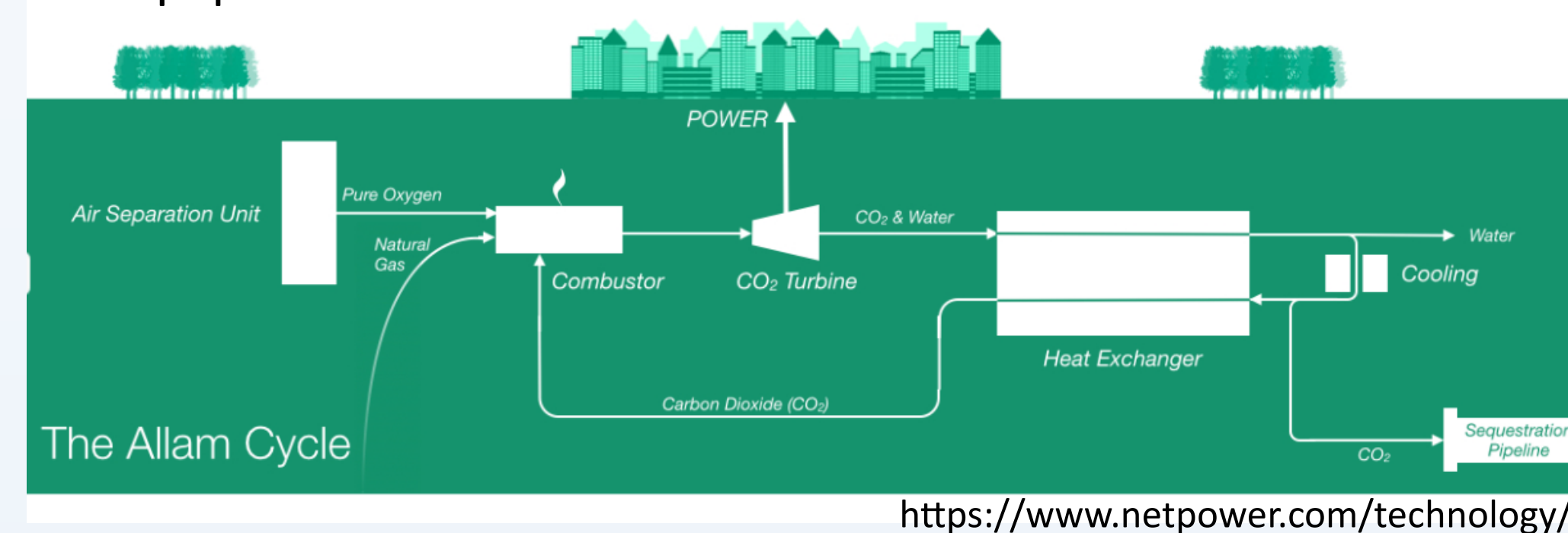
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Abstract

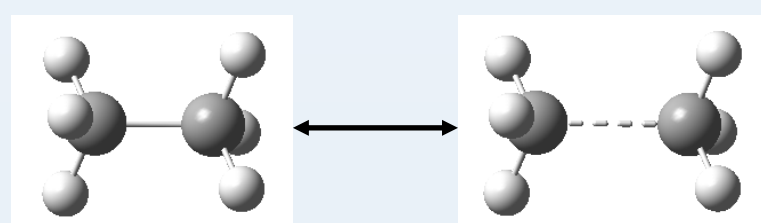
Fuel oxy-combustion is an emergent technology where habitual nitrogen diluent is replaced by high-pressure supercritical CO₂ (sCO₂), which increases the efficiency of energy conversion. In this study, the chemical kinetics of the reaction C₂H₆ ⇌ CH₃ + CH₃, important for combustion in sCO₂ environment is predicted at 30-1000 atm and 1000-2000 K. We adopt multiscale approach, where reactive complex is treated quantum mechanically in rigid rotor/harmonic oscillator approximation, while environment effects at different densities are taken into account by potential of mean force (PMF), produced with classical molecular dynamics (MD). Here we used boxed MD, where enhanced sampling of infrequent events of barrier crossing is accomplished without application of bias potential. Multi-state empirical valence bond (MS-EVB) model was applied to describe free radical formation accurately at the cost of classical force field. Predicted rates at low densities agree well with the literature data. Rate constants at 300 atm is $2.16 \times 10^{16} T^{-0.53} \exp(-77.04 \text{ kcal/mol}/RT)$ 1/s for ethane dissociation and $4.24 \times 10^{-13} T^{-0.0184} \exp(14.96 \text{ kcal/mol}/RT)$ cm³/molecule/s for methyl-methyl recombination.

Introduction

- Allam power cycle¹ has the advantage of capturing atmospheric emission CO₂ without external CO₂ capture equipment



- The optimized operating pressure for direct-fired supercritical CO₂ (sCO₂) combustion chamber can reach 300 bar and the percentage of CO₂ dilution is about 95 % by mass
- Ethane dissociation and its reverse reaction radical recombination are important reactions of oxy-fuel combustion

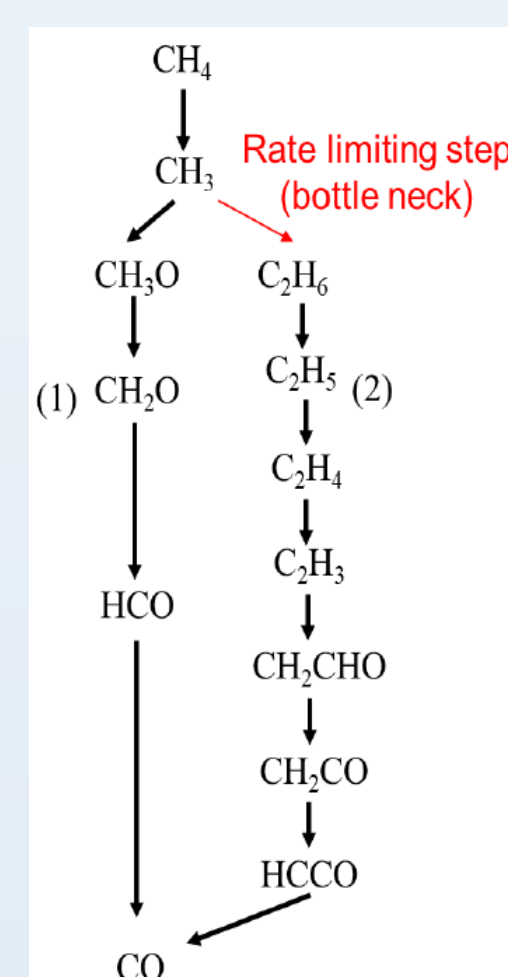


- Rate constant k is obtained from Eyring-Polanyi equation

$$k = \kappa \left(\frac{k_B T}{h} \right) \exp\left(-\frac{\Delta G^\ddagger}{RT}\right)$$

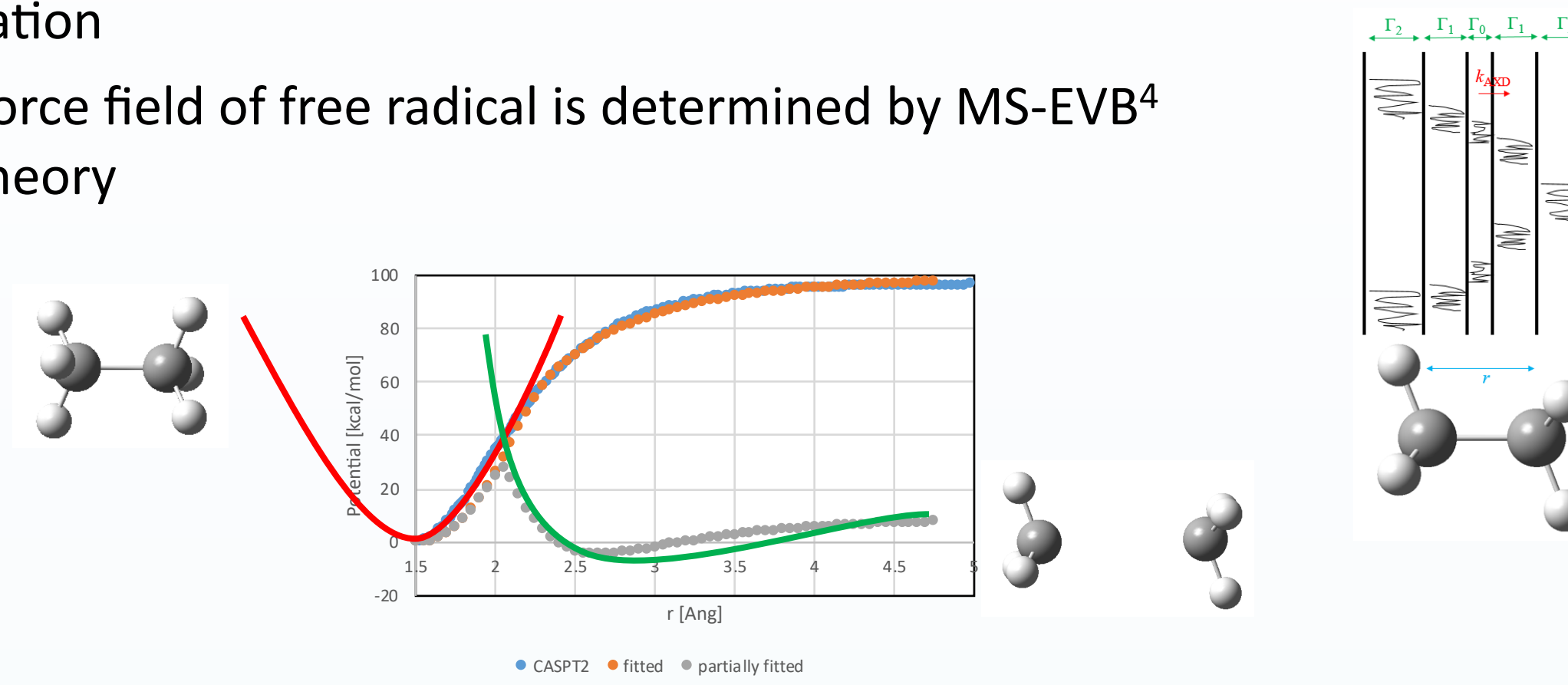
- Activation energy ΔG^\ddagger is evaluated both in gas phase and solvent sCO₂ phase²

$$\Delta G^\ddagger = \Delta G_{gas} + \Delta G_{sol}$$

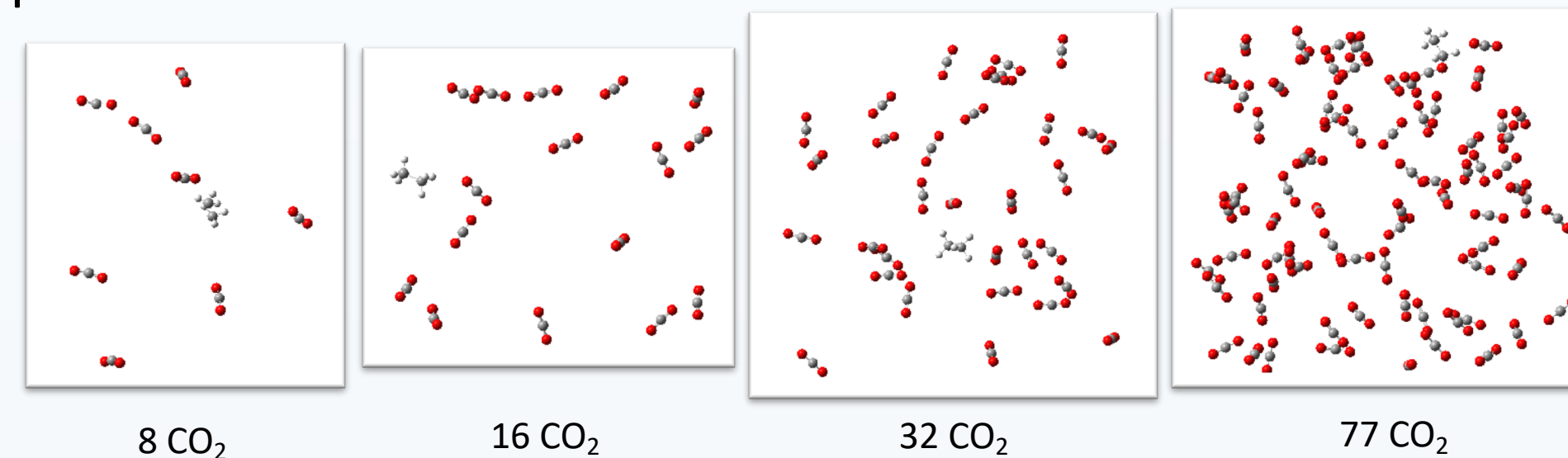


Computational Methods

- ΔG_{gas} is evaluated by canonical variational transition-state theory (CVTST) with CCSD/cc-pVDZ method
- ΔG_{sol} is evaluated by PMF with boxed molecular dynamics (BXD)³ simulation
 - Force field of free radical is determined by MS-EVB⁴ theory

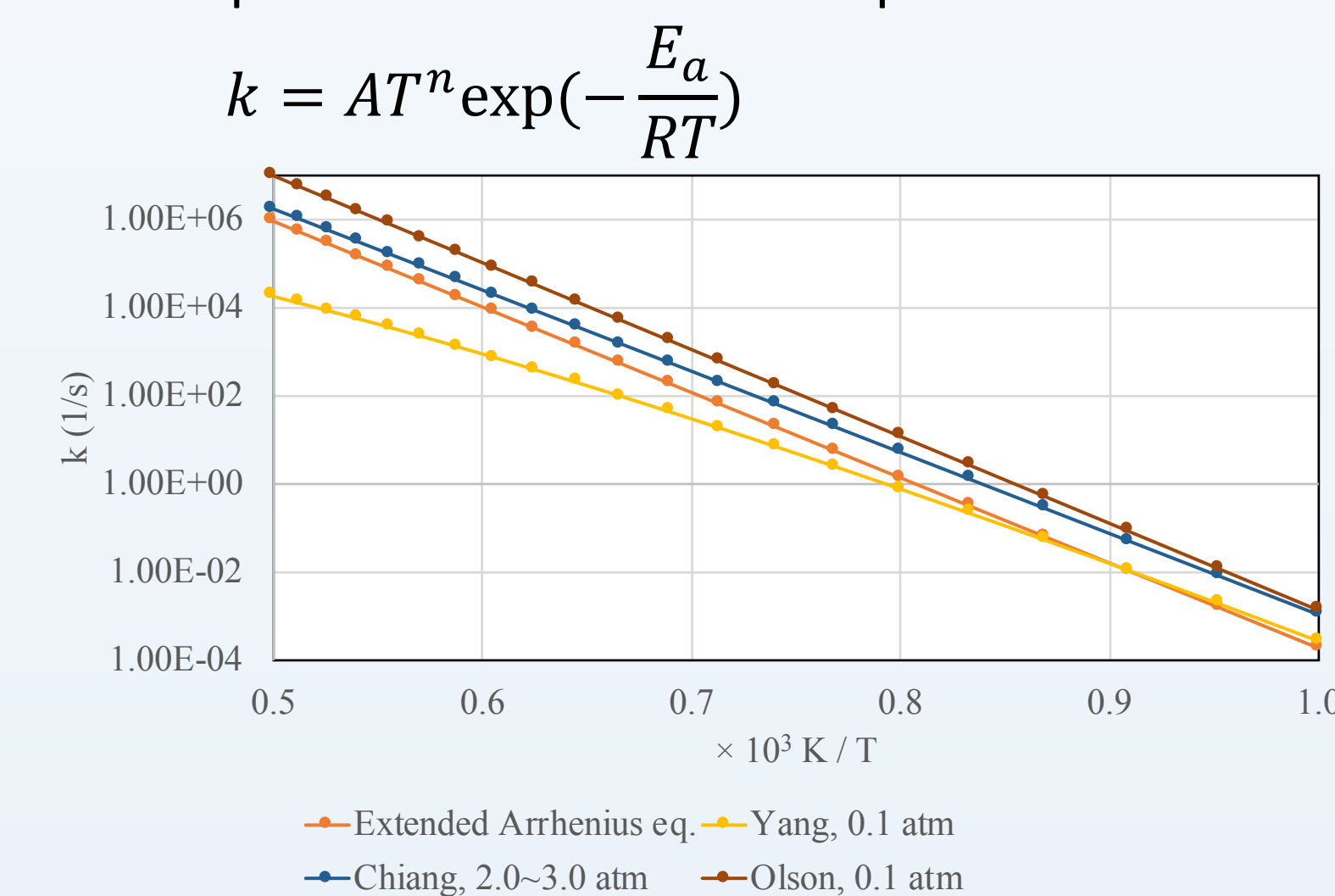


- As the number of CO₂ molecules increases, the pressure increases



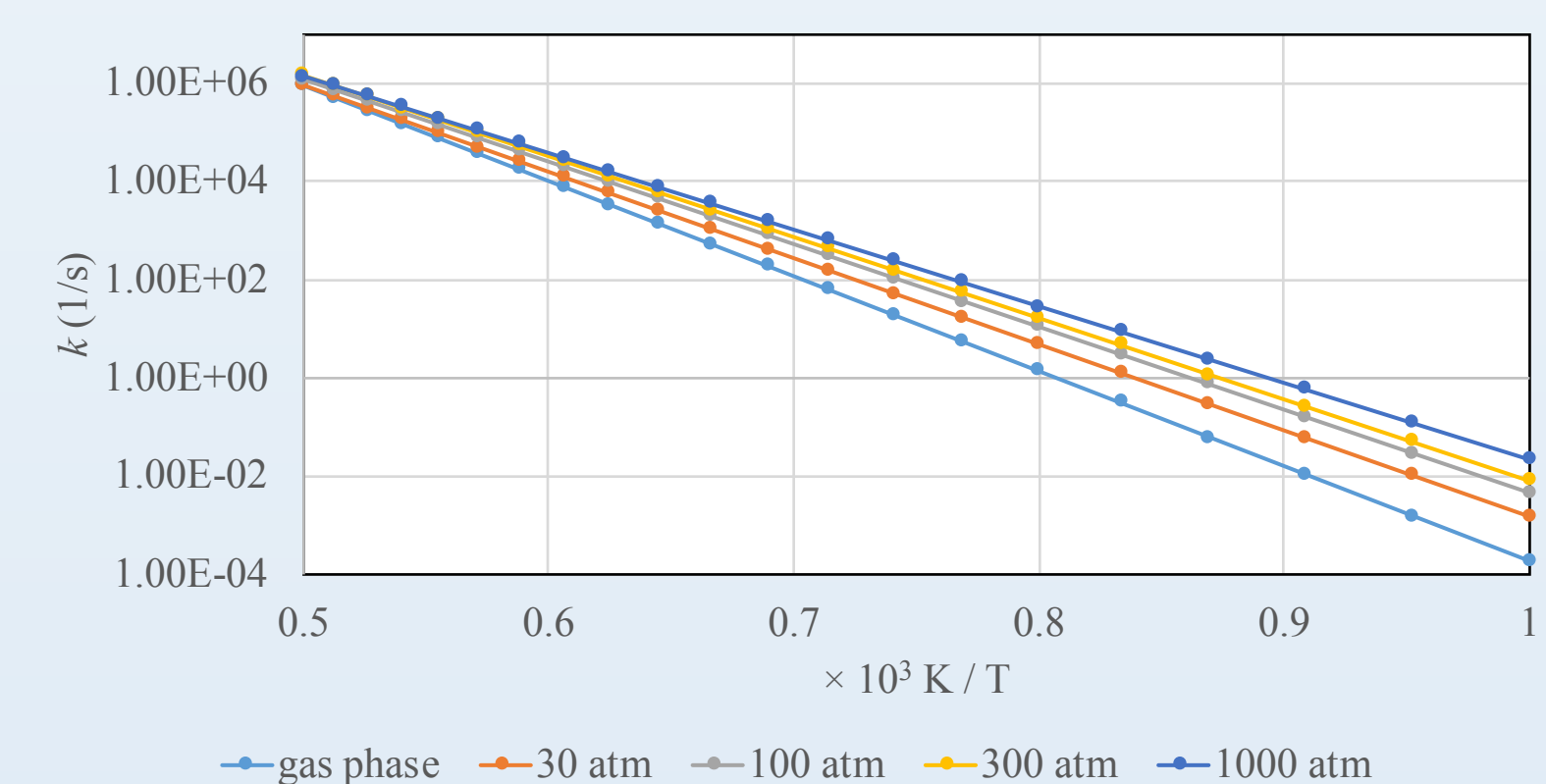
Results: C₂H₆ → CH₃ + CH₃

- Rate constant k in gas phase is fitted by extended Arrhenius equation and compared with shock tube experiments⁵⁻⁷



- The fitted k is located within other experimental results

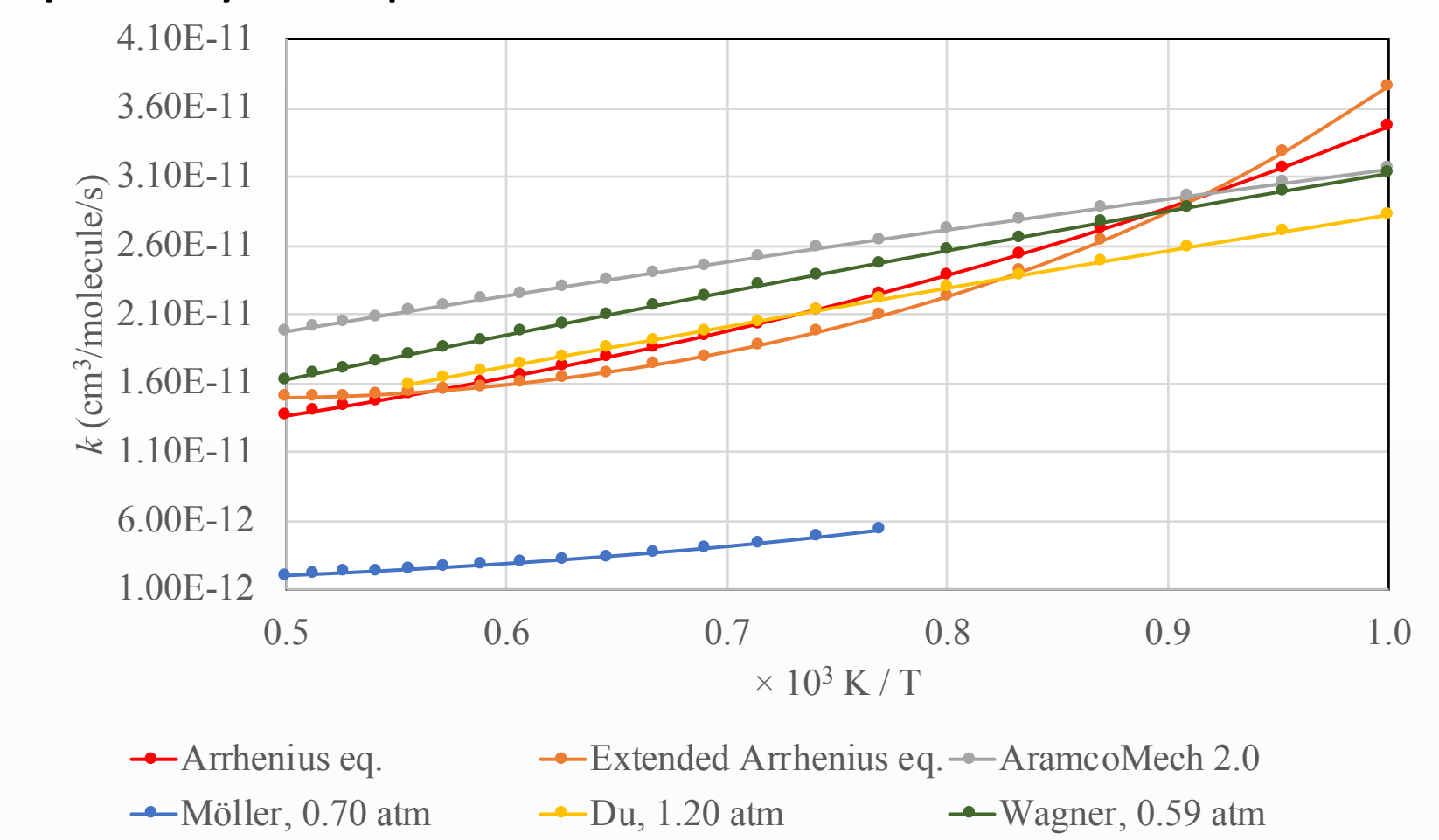
- k in solvent phase in various pressure. 300 atm is of our interests and the rate constant from Arrhenius expression is: $2.16 \times 10^{16} T^{-0.53} \exp(-77.04 \text{ kcal/mol}/RT)$ 1/s



- As the pressure increases, k increases
- The temperature increase reduce the influence of pressure increase

Results: CH₃ + CH₃ → C₂H₆

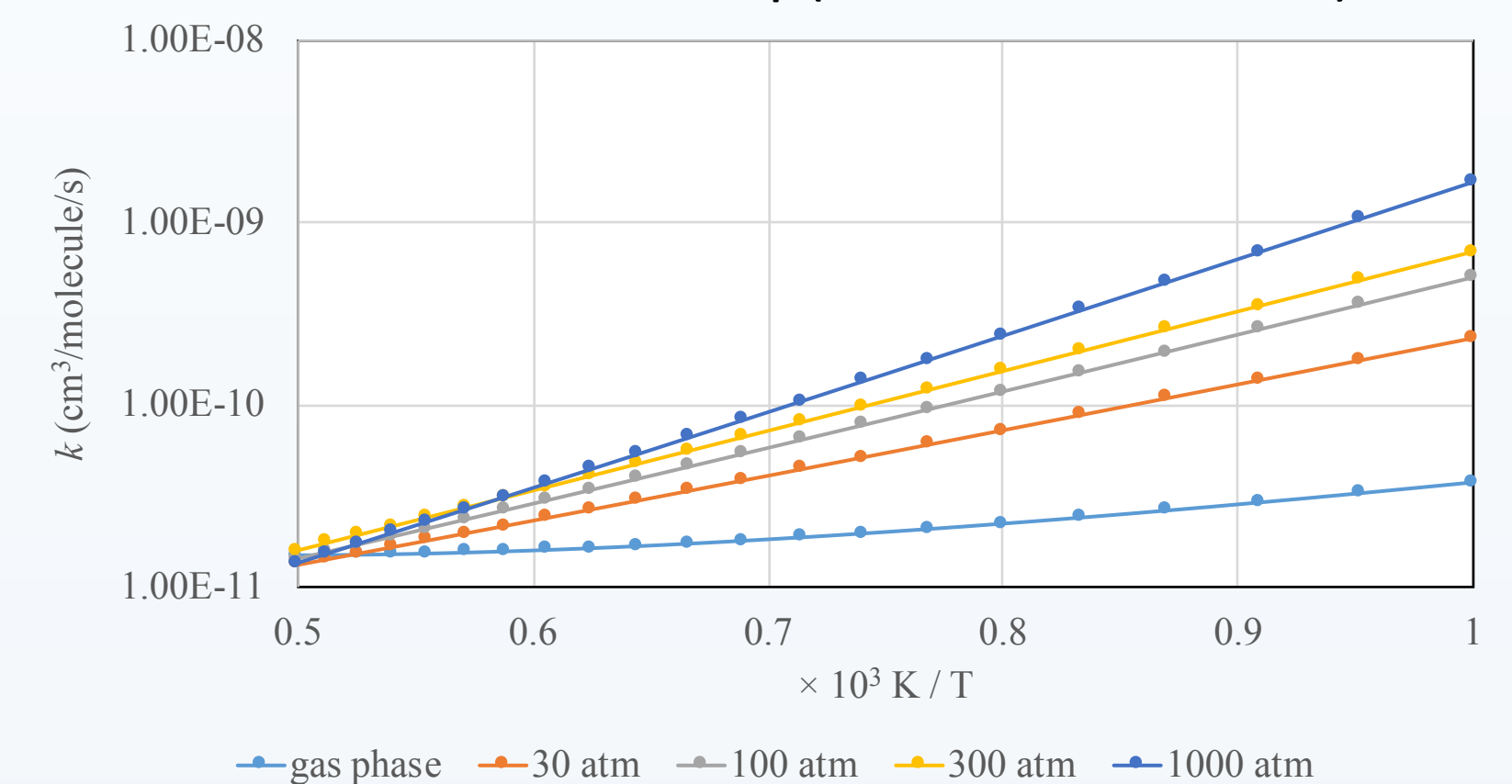
- k in gas phase is compared with AramcoMech 2.0, shock tube, and laser photolysis experiments⁸⁻¹¹



- The fitted k is located within other theoretical and experimental results

- k in solvent phase in various pressure. 300 atm is of our interests and the rate constant from Arrhenius expression is:

$$4.24 \times 10^{-13} T^{-0.0184} \exp(14.96 \text{ kcal/mol}/RT) \text{ cm}^3/\text{molecule/s}$$



- As the pressure increases, k increases
- The temperature increase reduce the influence of pressure increase

Conclusion and Future Work

- Successfully simulated reaction C₂H₆ ⇌ CH₃ + CH₃ in sCO₂ environment and evaluated the rate constant k in high temperature and pressure
- More combustion reactions regarding sCO₂ environment is studied underway

References

- Allam et al. *Energy Procedia* **2017**, *114*, 5948-5966
- Akiya et al. *J. Phys. Chem. A* **2000**, *104*, 4441-4448
- Glowacki et al. *J. Chem. Theory Comput.* **2011**, *7*, 1244-1252
- Glowacki et al. *J. Chem. Phys.* **2015**, *143*, 044120
- Yang et al. *J. Phys. Chem. A* **2009**, *113*, 8318-8326
- Chiang et al. *J. Phys. Chem.* **1981**, *85*, 3126-3129
- Olson et al. *J. Phys. Chem.* **1979**, *83*, 922-927
- Metcalfe et al. *Int. J. Chem. Kinet.* **2013**, *45*, 638-675
- Möller et al. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 854-861
- Du et al. *J. Phys. Chem.* **1996**, *100*, 974-983
- Wagner et al. *J. Phys. Chem.* **1988**, *92*, 2462-2471

Acknowledgements

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