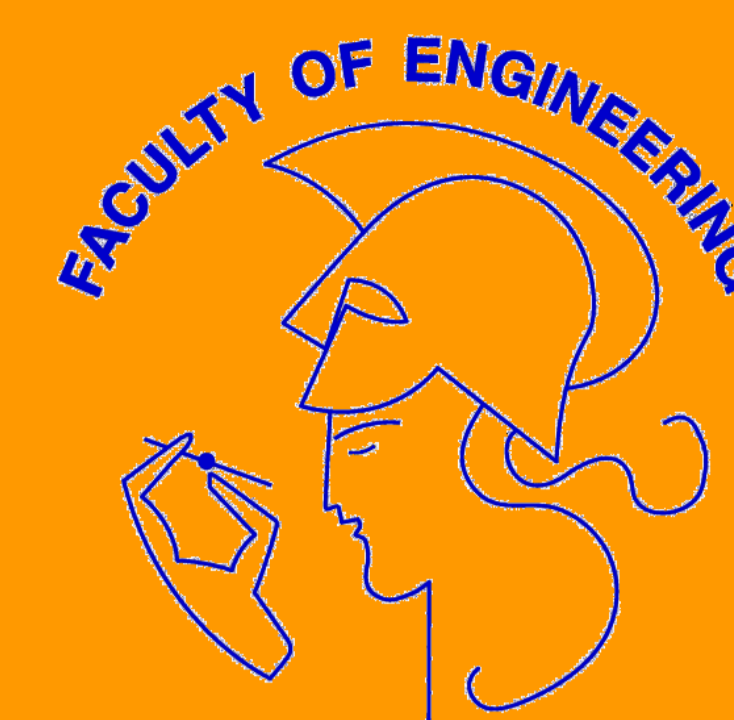


Ab initio modeling of the elementary reactions during thermal decomposition of polysulfides



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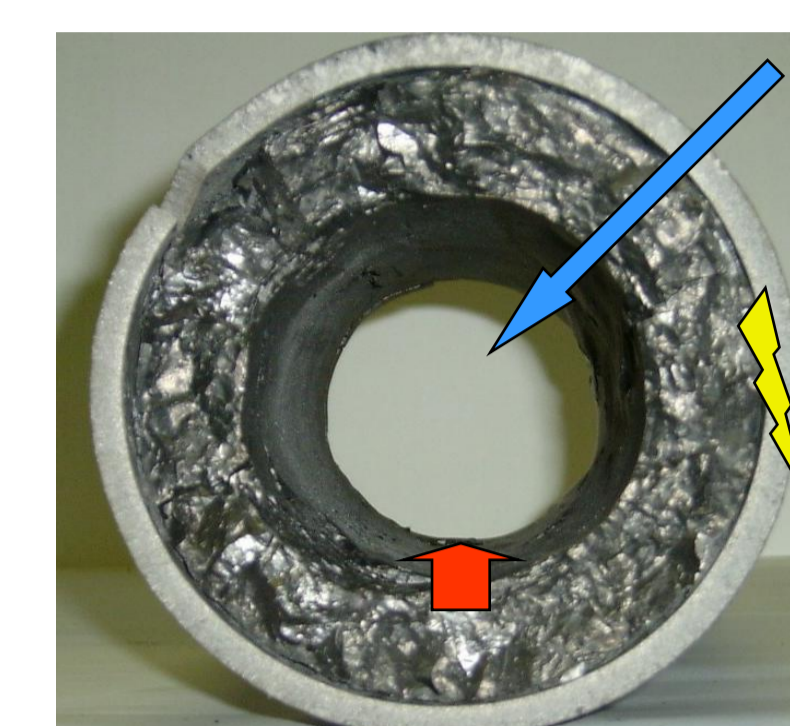
Introduction

Polysulfides have many industrial applications: CO and coke inhibition during thermal cracking of hydrocarbons, hydrotreatment catalysts activation and chain length control of polymerization reactions.

In order to optimize the deployment of sulfur compounds, accurate reaction networks are required that describe the reaction behaviour of these compounds under process conditions.

This work focusses on the thermal decomposition of dimethyldisulfide (DMDS).

Coke formation on reactor tubes



heat transfer hampered

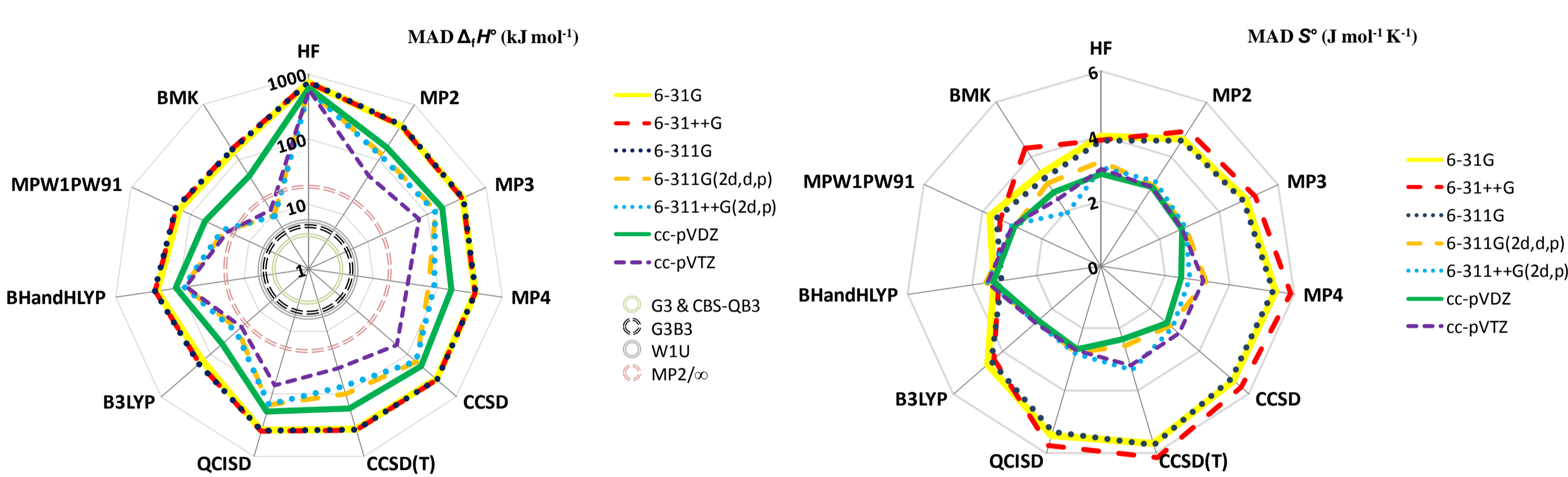
metal embrittlement

increased pressure drop

Level of theory study

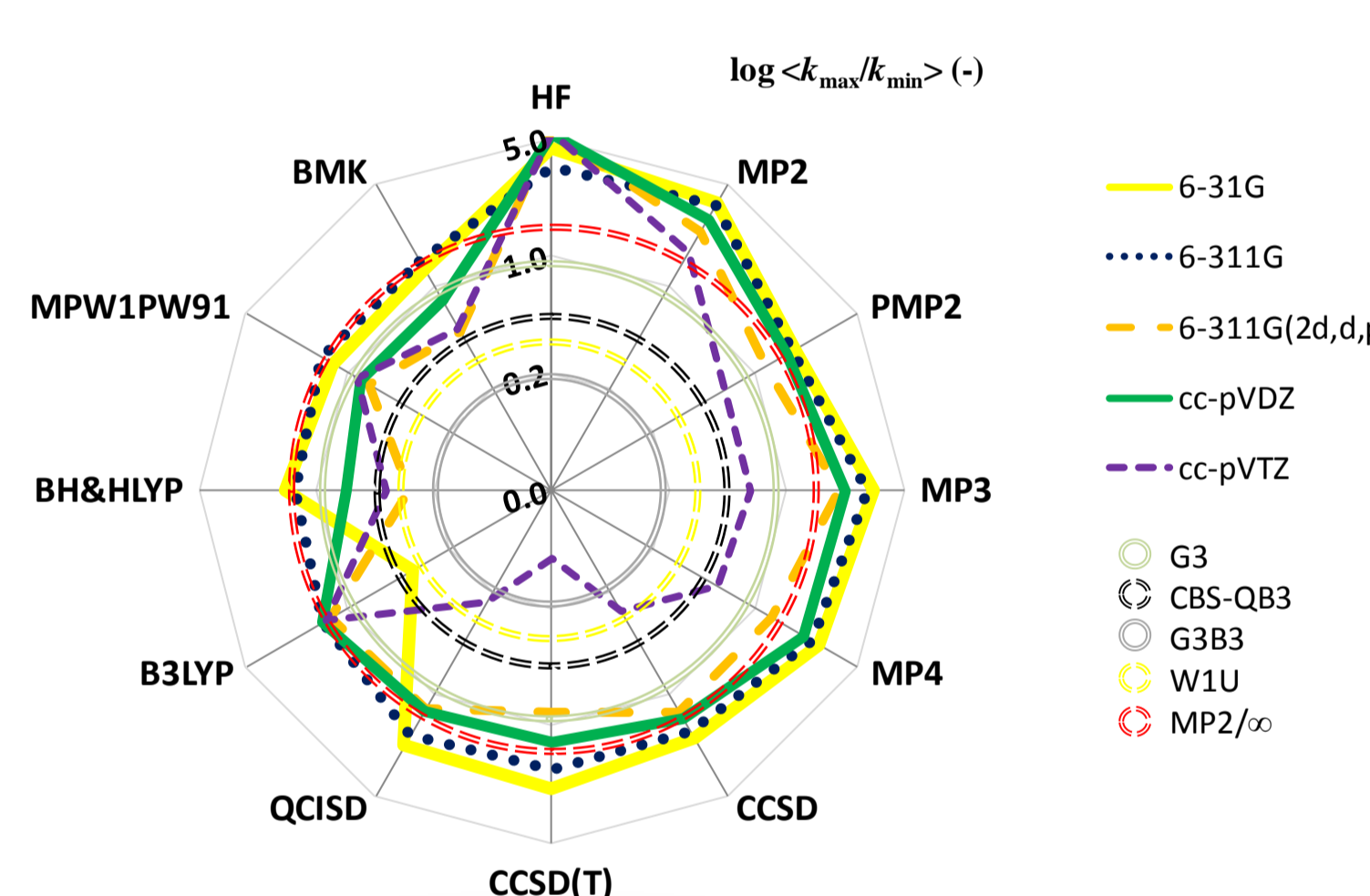
Thermochemistry

5 compounds: H_2S , $H_2C=S$, CH_3SCH_3 , $HSSH$, CH_3SSCH_3



Rate coefficients

- $H_2S + H^\bullet \rightarrow H_2 + HS^\bullet$
- $H_2S + CH_3^\bullet \rightarrow CH_4 + HS^\bullet$
- $CH_3SCH_3 + H^\bullet \rightarrow CH_3SH + CH_3^\bullet$
- $CH_3SSCH_3 + H^\bullet \rightarrow CH_3SH + SCH_3^\bullet$
- $H_2C=S + CH_3^\bullet \rightarrow C_2H_5S^\bullet$



Computational methodology

Classical transition state theory: $k_{CTST}(T) = \kappa_{Eckart} \frac{k_B T}{h} \frac{q^\ddagger}{q_{react}} e^{-\frac{\Delta^\ddagger E(0K)}{RT}}$

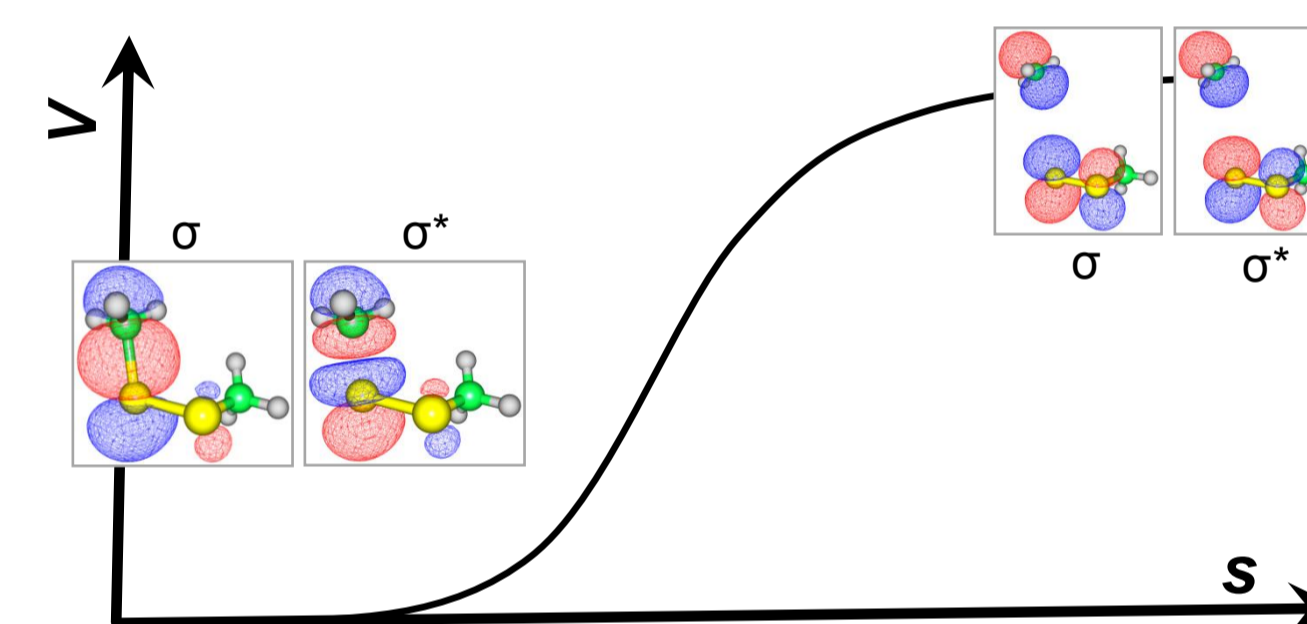
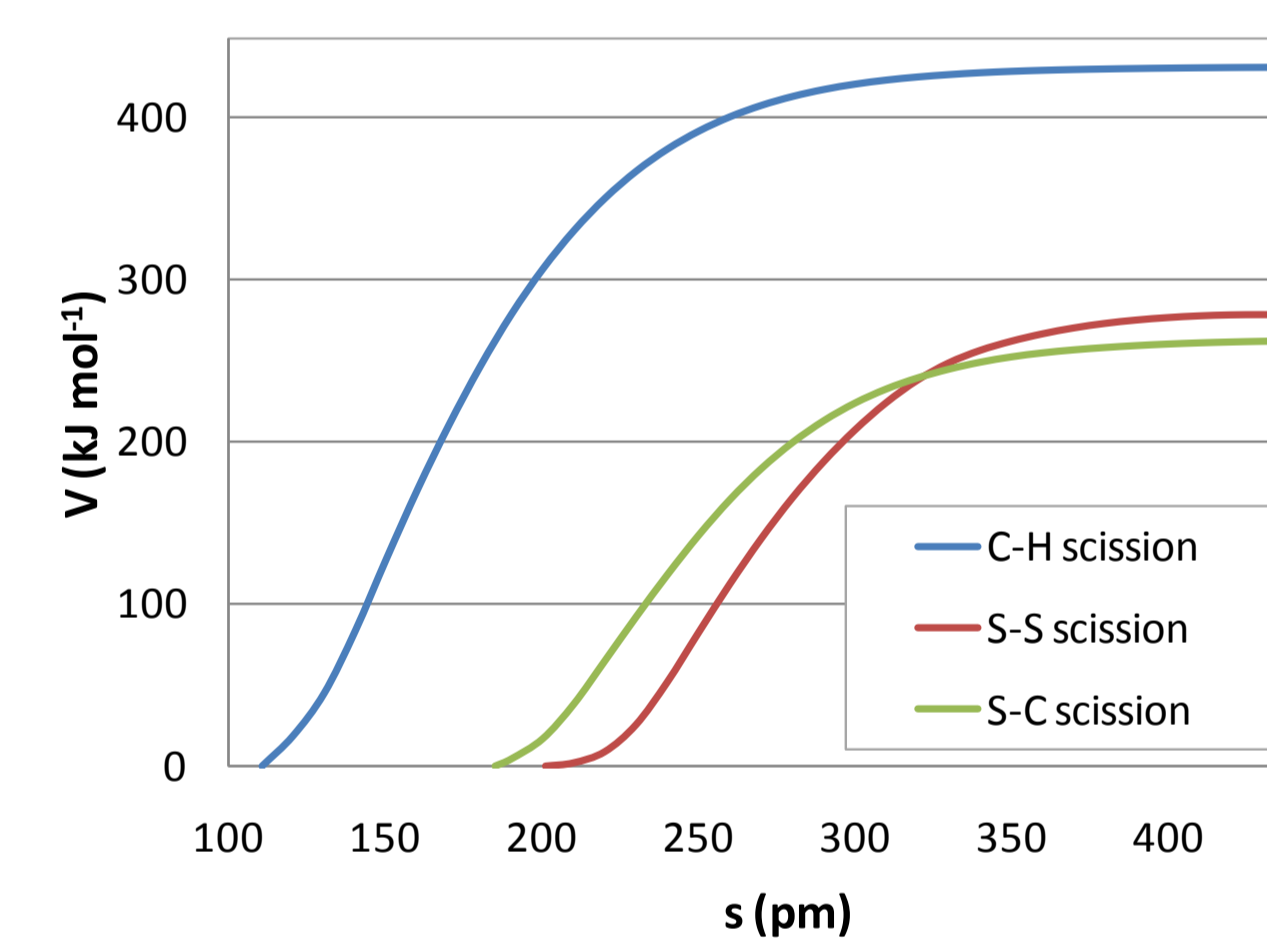
General applicable for reactions that have a maximum potential energy along the reaction coordinate, e.g. substitution reactions and addition/ β -scission reactions

Variational transition state theory: $k_{VTST}(T) = \min_s \frac{k_B T}{h} \frac{q^\ddagger(T,s)}{q_{react}} e^{-\frac{\Delta^\ddagger E(0K)(s)}{RT}}$

For radical recombination and bond scission reactions, no transition state can be found and a more generalized theory has to be applied

The reaction coordinate s is scanned for the minimum reaction flux

CASSCF/6-311G(2d,d,p) for bond scission in CH_3SSCH_3



CAS calculations along s :

- energy and spin multiplicity
- geometry (moments of inertia)
- transitional modes

$$q^\ddagger(T,s) \cong q_{elec}(s) q_{trans}(T) q_{ext.rot}(T,s) q_{vib.cons}(T) q_{vib.ts}(T,s)$$

Thermal decomposition of DMDS

Kinetic model \rightarrow elementary reactions \rightarrow **kinetic parameters**

experiment: time consuming, expensive but robust
simulation: cheap, general applicable

Radical reaction network

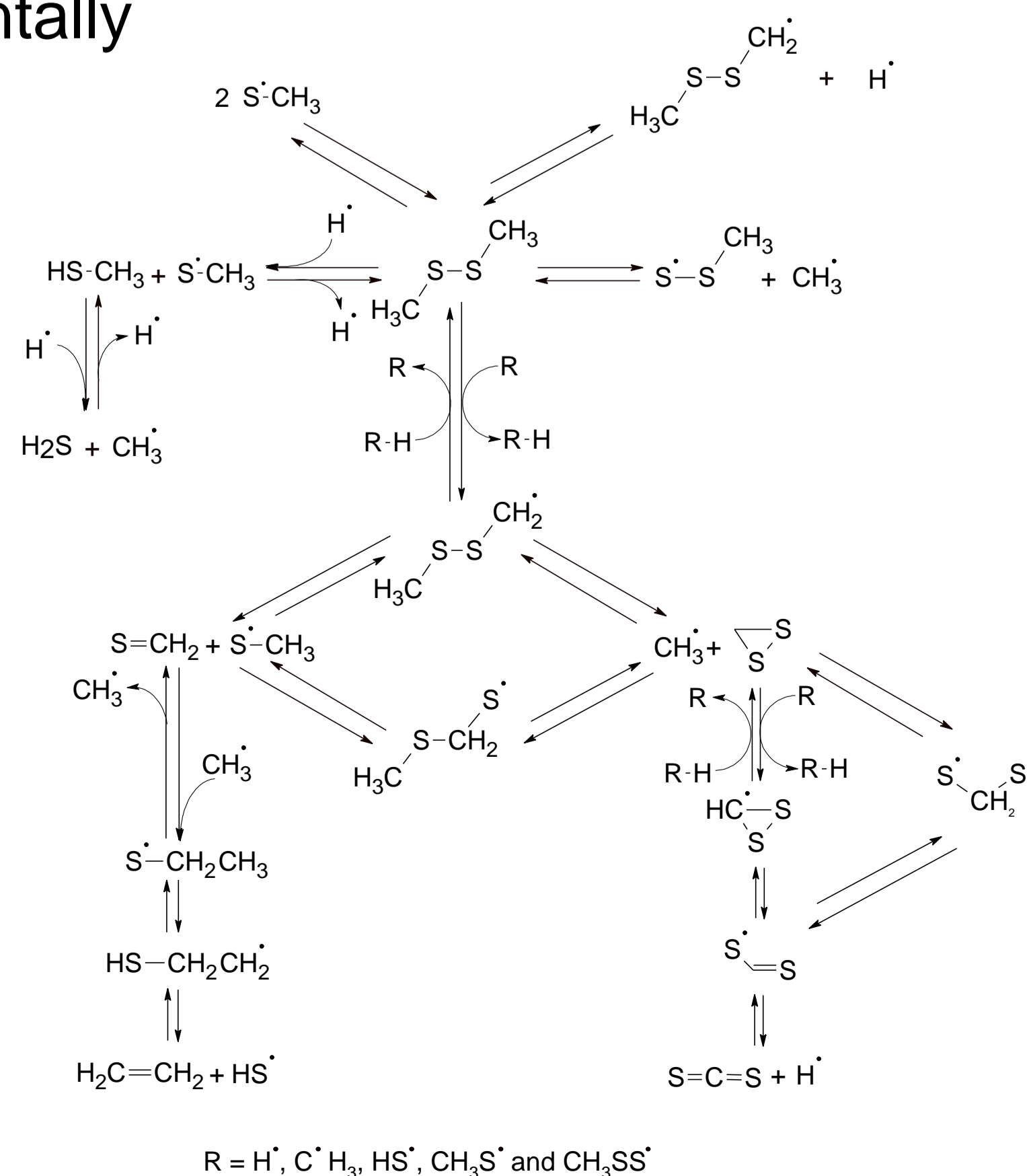
- 4 bond scissions / recombinations: $X-Y \leftrightarrow X^\bullet + Y^\bullet$
- 16 homolytic substitution reactions: $X^\bullet + Y-Z \leftrightarrow X-Y + Z^\bullet$
- 7 additions / β -scissions: $X^\bullet-Y-Z \leftrightarrow X=Y + Z^\bullet$

Accurate prediction of experimentally observed yields (± 600 K, 0.1 bar)

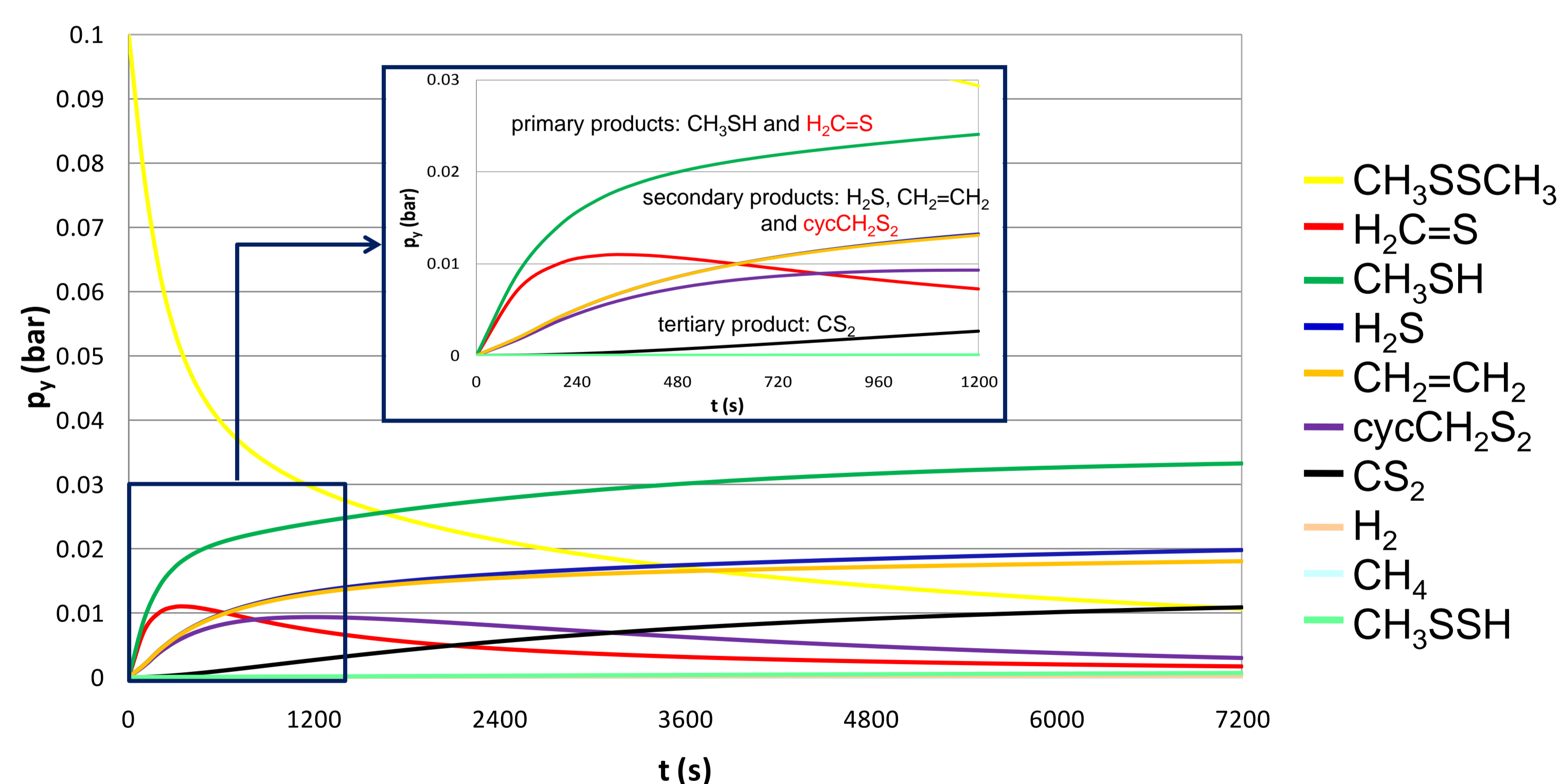
| [mol%] | EXP* | SIM |
|-------------|------|-----|
| H_2S | 31 | 20 |
| $CH_2=CH_2$ | 16 | 18 |
| CH_3SH | 38 | 34 |
| CS_2 | 10 | 11 |

Decomposition rate k_{max} [s^{-1}]

| T [K] | EXP* | SIM | EXP/SIM |
|-------|----------------------|----------------------|---------|
| 600 | 8.1×10^{-4} | 5.3×10^{-4} | 1.5 |
| 650 | 1.5×10^{-2} | 8.7×10^{-3} | 1.7 |
| 700 | 1.8×10^{-1} | 9.9×10^{-2} | 1.8 |



Simulated thermal decomposition of DMDS (homogenous batch reactor, 615 K, 0.1 bar)



Conclusions

A level of theory study was conducted on the accuracy of different ab initio methods to describe the thermochemistry and thermodynamics of organosulfur compounds. The CBS-QB3 composite method yields an ideal trade-off between accuracy and computational requirements.

A radical reaction network was constructed describing the thermal decomposition of DMDS.

Simulations show excellent agreement with the experimental data. First order decomposition rates of DMDS are reproduced within a factor 2, while the product yields are described accurately.

* Coope J.A.R. and Bryce W.A., Can. J. Chem., 32, 768 (1954)