

A new generation of sulfiding agents – Towards a better understanding of the decomposition chemistry of polysulfides

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Highlights

- New thermodynamic and kinetic data for sulfides from quantum chemical calculations
- Detailed kinetic model for thermal decomposition of polysulfides
- Elucidation of the main decomposition pathways and their influence on the product distribution

1. Introduction

Sulfur-containing compounds, and in particular sulfides, play a key role in many industrial processes. Sulfiding agents are used for catalyst activation and as steam cracking additives they are linked to decreased CO formation and coke inhibition. Today, the industry standard is the use of dimethyl disulfide (DMDS) and dimethyl sulfide (DMS) as a source of sulfur. As a response to supply chain and sustainability challenges, polysulfides have been introduced in the chemical industry as a safer, more efficient, and more environmentally friendly alternative. Aside from limited experimental data about the conversion to H₂S and its performance compared to the traditional sulfiding agents, there is a lack of fundamental understanding of the governing decomposition mechanism and the sulfur-containing products distribution. Even though the main decomposition product remains H₂S, the presence of additional sulfur atoms in the sulfide components as well as the bulkier hydrocarbon side groups, significantly influence the main decomposition chemistry pathways and ultimately the formation of (unwanted) sulfur-containing side products.

2. Methods

Kinetic models are developed using the Reaction Mechanism Generation software (RMG) [1] for dimethyl disulfide (DMDS), di-tertiary butyl tetra sulfide (TBTS) and di-tertiary butyl pentasulfide (TBPS). Thermodynamic and kinetic parameters for the most important reactions to accurately describe the decomposition of these polysulfides are obtained from new quantum chemical calculations using the Gaussian16 software at the CBS-QB3 level of theory [2]. Reactor simulations are done in Cantera [3] for pyrolysis of the polysulfides in a one-dimensional tubular reactor with and without the presence of a hydrocarbon matrix, i.e. heptane.

3. Results and discussion

Similar to DMDS, the thermal decomposition of polysulfides is initiated via C-S and S-S bond scission. The presence of additional sulfur atoms in TBTS and TBPS significantly influences the bond strength of the S-S bonds and adjacent C-S bonds, c.f. Figure 1. Compared to DMDS, the bond dissociation energy (BDE) of the S-S and C-S bonds decrease with 32 and 10 kcal mol⁻¹ respectively which translates to a higher reactivity of TBTS and TBPS. The simulated profiles of the main sulfur-containing products formed during the thermal decomposition of TBTS in a heptane matrix are shown in Figure 1.

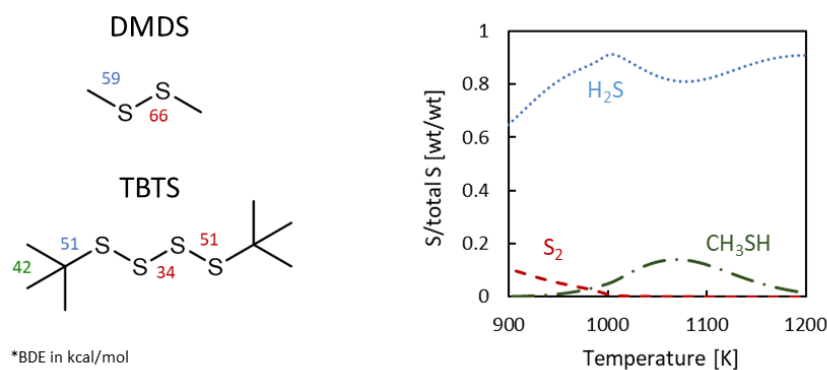


Figure 1. Left: Bond dissociation energies (BDE) in kcal/mol for DMDS and TBTS, right: simulated profiles [% S of total S] of the main sulfur-containing compounds as a function of temperature [K] for the pyrolysis of TBTS in a C_7H_{16} matrix.

At 1000 K, almost 90 % of the sulfur is converted to H_2S . The thiol CH_3SH is formed as a side product at intermediate temperatures, and after reaching a maximum at approximately 1100 K it is further converted to H_2S . Not carbon disulfide (CS_2) as is the case for DMDS, but elemental sulfur is another important side product, which can undergo precipitation leading to a drop in reactor pressure. When olefinic species are present in the system, which is the case when there is a hydrocarbon matrix, elemental sulfur can recombine with these olefins forming a solid polymeric compound. The side products formed during polysulfides decomposition can thus result in additional processing challenges from a safety point of view.

4. Conclusions

To address the lack of fundamental understanding of the thermal decomposition of alternative sulfiding agents, i.e. the polysulfides TBTS and TBPS, detailed kinetic models are developed based on new thermodynamic and kinetic data obtained from quantum chemical calculations at the CBS-QB3 level of theory. Compared to DMDS, both components are characterized by a higher reactivity. The main decomposition pathways lead to the formation of mainly H_2S and several sulfur-containing side products, including elemental sulfur which can introduce new processing challenges when using this alternative sulfur source.

References

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Keywords

Polysulfides; pyrolysis; computational; kinetic modeling