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

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Introduction

Polysulfides play a critical role in the optimization of many chemical processes. Dimethyl disulfide (DMDS), for example, is used as coke inhibiting additive in steam cracking furnaces and can also be used as photolytic initiator during free radical polymerization.[1, 2] Also tetrasulfides are frequently used in chemistry, mostly as inhibitors during polymerization reactions. Despite the industrial significance of polysulfides, experimental and theoretical studies concerning their reaction behavior are scarce.

In order to optimize the deployment of sulfur compounds during chemical processes, accurate reaction networks are required that describe the reaction behaviour of these compounds under process conditions. In the case of radical chemistry, reaction networks can easily contain up to thousands of elementary reactions and for each of them accurate thermochemical and kinetic parameters need to be at hand. As experimental work is often very expensive and time consuming, ab initio tools are attractive alternatives to obtain the required kinetic and thermochemical data. Due to the limited amount of resources and the complexity of many reaction networks, it is quasi-impossible to calculate ab initio rate coefficients for all of the reactions occurring in the network. To circumvent this problem, use can be made of group additivity schemes. These schemes permit to calculate thermochemical and kinetic data for all reactions within a reaction family from a limited amount of contributions, relating to the molecule's or the transition state's structure.[3, 4]

Methodology

An extended level of theory study has been conducted to evaluate the accuracy of different ab initio methods in predicting thermochemical and kinetic data for organosulfur compounds.[5] It was shown that composite methods, such as G3B3 and CBS-QB3, reproduce the experimental data quite well. Also with the BMK and BH&HLYP functionals accurate rate coefficients could be obtained. From those methods, CBS-QB3 was selected as the most promising method to study the thermal decomposition of polysulfides.

Rate coefficients for homolytic substitution reactions and addition/ß-scission reactions were calculated using conventional transition state theory within the high pressure limit:

$$k_{\infty}(T) = \frac{k_B T}{h} \frac{q_{\ddagger}}{q_{\mathrm{reactant(s)}}} e^{-\frac{\Delta^{\ddagger} E}{RT}}$$

with $\Delta^{\ddagger}E$ the zero point energy corrected energy barrier calculated at the CBS-QB3 level of theory and $q_{\ddagger}$ / $q_{\mathrm{reactant(s)}}$ the molar partition functions of respectively the transition state and reactant(s). For homolytic scission reactions flexible transition state theory (FTST) was applied, using the VARIFLEX program.[6] In order to simplify the FTST calculations all five transitional modes were treated as free rotors.

When possible, use has been made of additivity schemes to estimate rate coefficients for the reactions occurring in the reaction network. Group additivity schemes developed by Sabbe et al.[4] for ß-scission reactions and by Saeys et al.[7] for hydrogen abstraction reactions have shown to be powerful tools to obtain reliable kinetic data. These group additivity schemes were initially developed for hydrocarbons but prove throughout this work to extrapolate successfully to organosulfur compounds.

Results

A reaction network was constructed containing almost 500 reactions. The main decomposition reactions are shown in Figure 1. DMDS mainly decomposes to H_2S, $CH_2{=}CH_2$, CS_2 and CH_3SH. Other products that are formed are H_2, CH_4 and some polysulfides. A simplified reaction network, such as presented in Figure 1, is able to yield accurate selectivities but overestimates the rate of the DMDS decomposition significantly. It was found that in order to accurately describe the thermal decomposition of DMDS, the formation of other polysulfides has to be accounted for, such as for example dimethyltri- and dimethyltetrasulfides. A reaction network able to accurately describe the thermal decomposition of DMDS hence also has to account for the decomposition of other polysulfides.

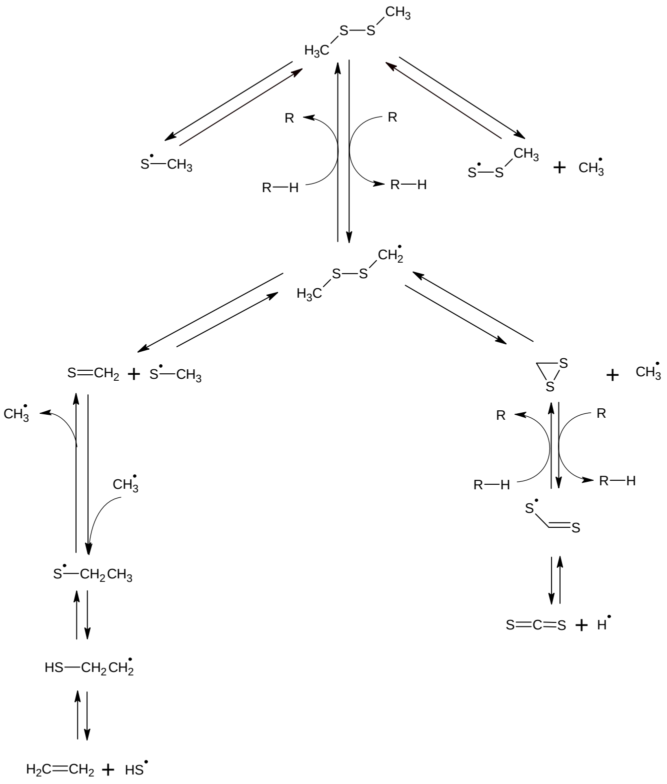

Figure 1 Main reaction paths during the thermal decomposition of DMDS

The extended reaction network was used to simulate the thermal decomposition of dimethyl disulfide. A limited number of experimental data on the decomposition of DMDS has been presented by Coope and Bryce at 318°C [8] and by Braye and Sehon.[9]. A simplified reactor model, i.e. the homogenous batch reactor, was used to simulate the experimental data. Despite the simplified reactor model, the experimental trends reported by Coope and Bryce at 318°C [8] could be captured. The experimentally observed first order decomposition rate is underestimated by a factor 3 and the ab initio based reaction network succeeds to predict the temperature dependence of the selectivities. The relative good agreement between experiment and simulations can also be seen from Table 1. In this table a comparison is given between the simulated and experimentally observed gas phase composition after 2h of reaction. To compensate for the slower first order ab initio decomposition rate, the simulation was conducted at a slightly higher temperature (615 K). Both experiment and simulation indicate that the main decomposition products are H_2S, CH_3SH and CS_2. The simulation also shows that small amounts of CH_4 and H_2 are formed, which is also supported by the work of Braye and Sehon.[9]

Table 1: Experimental and simulated gas phase composition after 2h of DMDS decomposition at ±600 K (mol%).

Component	Coope and Bryce [8]	Simulated (615 K)
$CH_3S_xCH_3$	6	10
$CH_4 + H_2$	0	6
C_2	18	20
H_2S	35	23
CH_3SH	42	24
CS_2	11	17

Reference List

1. Wang J, Reyniers MF, Marin GB. Influence of dimethyl disulfide on coke formation during steam cracking of hydrocarbons. *Ind Eng Chem Res* 2007; **46(12)**:4134-4148.
2. Kern RJ. Some Sulfur Compounds As Polymerization Sensitizers. *Journal of the American Chemical Society* 1955; **77(5)**:1382-1383.
3. Saeys M, Reyniers MF, Marin GB, Van Speybroeck V, Waroquier M. Ab initio group contribution method for activation energies for radical additions. *AIChE J* 2004; **50(2)**:426-444.
4. Sabbe MK, Reyniers MF, Van Speybroeck V, Waroquier M, Marin GB. Carbon-centered radical addition and beta-scission reactions: Modeling of activation energies and pre-exponential factors. *ChemPhysChem* 2008; **9(1)**:124-140.
5. Vandeputte AG, Reyniers MF, Marin GB. A theoretical study of the thermodynamics and kinetics of small organosulfur compounds. *Theor Chem Acc* 2009; In press.
6. Robertson S, Wagner AF, Wardlaw DM. Flexible transition state theory for a variable reaction coordinate: Analytical expressions and an application. *J Phys Chem A* 2002; **106(11)**:2598-2613.
7. Saeys M, Reyniers MF, Van Speybroeck V, Waroquier M, Marin GB. Ab initio group contribution method for activation energies of hydrogen abstraction reactions. *ChemPhysChem* 2006; **7(1)**:188-199.
8. Coope JAR, Bryce WA. The thermal decomposition of dimethyl disulphide. *Can J Chem* 1954; **32(8)**:768-779.
9. Braye EH, Sehon AH, Darwent Nd. Thermal decomposition of sulfides. *J Am Chem Soc* 1955; **77**:5283.