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

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Polysulfides play a critical role in the optimization of many chemical processes. Dimethyl disulfide, 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] Next to it, tetrasulfides are well known to be very efficient inhibitors or retarders of 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 those chemical processes, an accurate reaction network is required that succeeds in describing the specific 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 these reactions 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 rate coefficients for all reactions in the reaction 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 by summation of a limited amount of contributions that correspond with the molecule's or transition state's structure.[3, 4] 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. It was shown that composite methods, such as G3B3 and CBS-QB3, and the BMK and BH&HLYP functionals succeed to reproduce the experimental data quite well. From those methods, we selected CBS-QB3 as the most promising method to study the thermal decomposition of polysulfides.

In a first step, a reaction network was constructed that accounts for the thermal decomposition of dimethyl disulfide. However, making use of group additivity schemes, the reaction network can be easily extended to tri- or tetrasulfides. In this context, CBS-QB3 group additivity values were calculated for two reaction families, i.e. the hydrogen abstraction reactions and homolytic substitution reactions. Rate coefficients for the remaining addition/ß-scission reactions and intermolecular reactions were calculated from classical transition state theory, while variational transition state theory was used for the bond scission/recombination reactions.

The reaction network was used to simulate the thermal decomposition of dimethyl disulfide. Relatively good agreement with the experimental results presented by Coope and Bryce [5] is observed: the experimentally observed first order decomposition rate is predicted within a factor 3, while the ab initio based reaction network also succeeds to predict the temperature dependence of the selectivities.

Reference List

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