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Rule-based ab initio kinetic model for alkyl sulfide pyrolysis

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HIGHLIGHTS

- Rule based generation of an alkyl sulfide pyrolysis kinetic model.
- Chemical data derived from high level ab initio calculations.
- Data estimation by group additive methods.
- Model validation against existing experimental data.

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ABSTRACT

The use of a rule-based automated kinetic model builder Genesys is illustrated for the thermal decomposition of diethyl sulfide and ethyl methyl sulfide. Rule-based automatic kinetic model generation builds-upon the users' expert knowledge to define constraints per reaction family to limit the model size and exclude species and reactions that are considered irrelevant. In the case of alkyl sulfide pyrolysis intermolecular hydrogen abstractions, intermolecular additions/β-scissions and intermolecular homolytic substitutions are used to iteratively expand the model not considering species with more than 5 heavy atoms. Furthermore, the formation of biradical species and cyclic structures was avoided. Rate coefficients of elementary reactions and thermochemical properties of molecules were estimated through group additive methods, with parameters solely derived from high level ab initio calculations. 39 reactions were added to the model after the automatic generation out of which 37 got rate constants assigned from ab initio calculations. The generated model, consisting of 444 reactions between 28 molecules and 38 radical species, was validated using experimental data for the thermal decomposition of diethyl sulfide and ethyl methyl sulfide and showed that measured and predicted species mole fractions are in good agreement. However, there is a clear need for more accurate and more detailed experimental data for the pyrolysis of sulfur containing compounds.

1. Introduction

Kinetic models of complex chemical processes can easily contain thousands of reactions between hundreds of species [1]. To cope with the level of complexity, the automated construction of such models represents an interesting alternative to manual derivation. Many groups have looked into the possibility of automated construction of kinetic models [2–6]. For historical reasons, these programs are often constrained to species involving only a limited number of elements, such as carbon and hydrogen, making them less suitable for applications in which hetero-elements such as sulfur are involved. The extension of existing programs to new chemical elements, or new types of atoms is not straightforward. For example, differences in electron valency or the number of lone electron pairs in hetero-elements may induce the creation of structures that are not prevalent for hydrocarbons. Obviously, the presence of hetero-elements may lead to new types of reactions that do not occur for hydrocarbons. Often, the incorporated algorithms in the program are tailored for a specific subspace of molecules, and not based on first principles that would make them more generally applicable. Finally, the associated chemical data of the program to determine model parameters is not sufficient to adequately predict thermochemistry and kinetics that involve other hetero-elements than the software was developed for.

Sulfur compounds are important substances in many industrial processes [7–9]. Steam cracking feedstocks can contain up to 1000 ppm of sulfur compounds such as thiols, sulfides and

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thiophenes [10]. They can influence the product distribution and are thought to play a role in the inhibition of CO formation and in coke formation [11–16]. In order to improve understanding of the role of sulfur compounds in steam cracking, the decomposition of several sulfur compounds and the pyrolysis of several mixtures containing hydrocarbons and sulfur compounds have been studied experimentally [15,17–21]. An alternative to conducting experiments is the construction of a kinetic model to gain a better understanding of the reactive behavior of alkyl sulfides. A detailed kinetic model provides a starting point to further elucidate the underlying chemistry by comparing model predictions with experimental data. Recently, it was shown that the use of ab initio methods such as CBS-QB3 can be used for the accurate calculation of thermochemistry and rate coefficients for sulfur compounds [22]. Therefore, the incorporation of model parameters derived from ab initio calculations rather than from fitting to experiments, becomes a viable option for kinetic model construction.

Recently, a new automated kinetic model construction program, i.e. Genesys, was introduced [23]. Through the use of chemoinformatics libraries, graph theoretic algorithms were applied allowing the construction of kinetic models regardless of the type of chemical elements involved. The same graph algorithms allowed the use of predictive group contribution methods for the estimation of thermochemical properties and rate coefficients. To illustrate the functionality of Genesys, a kinetic model was automatically constructed for the thermal decomposition of two alkyl sulfides: diethyl sulfide (DES) and ethyl methyl sulfide (EMS) with reaction rate coefficients and thermodynamic values based on a group additivity model. This process is chosen to demonstrate the kinetic model generation procedure for a process containing the hetero-element sulfur. Also, sufficient knowledge of the relevant chemistry and thermochemical and kinetic data is available to construct of a quantitative model that can be used in numerical simulations. Simulations were carried out of the experiments of Zheng et al. [24,25] and the resulting model predictions were compared to the measured product mole fractions to validate the generated kinetic model.

2. Kinetic model construction

The aim of a kinetic model generation program is to generate an accurate and detailed kinetic model, while minimizing the number of unimportant species and reactions. Genesys starts from two fundamental principles to construct kinetic models, i.e. a thorough understanding of the relevant chemistry of the process, and the availability of thermochemical data for the calculation of the species properties and the reaction rate coefficients. Guided by those principles, a number of reaction family templates were created that are necessary to automatically construct a kinetic model by an iterative procedure. First, a starting pool of molecules that are known as important intermediates species in the thermal decomposition of DES and EMS based on literature data was provided. Next, the available reaction family templates are repeatedly applied, and the eligibility of the pool of initial species to react according to one of the reaction families, is verified, cf. Fig. 1. New product molecules arise from the application of the matched reaction family and serve as reactants for the next iteration in the model building process. Finally, the expansion of the kinetic model terminates when the molecules in the model no longer give rise to new products.

Three reaction families were considered during the automated enlargement of the kinetic model: intermolecular hydrogen abstraction reactions, intermolecular addition/β scission reactions and intermolecular homolytic substitutions. In principle, other reaction families, such as homolytic bond-scission reactions, could also be included to enlarge the reaction network. However, the inclusion of an additional reaction family in the network generation scheme also requires the systematic assignment of rate coefficients to all of the generated reactions resulting from that reaction family. Arrhenius parameters of reactions originating from the reaction families, are obtained using group contribution methods [26], as will be explained in detail in Section 2.2. Unfortunately, these types of group contribution methods are not available for every type of reaction family relevant for alkyl sulfide decomposition. For reactions such as homolytic bond-scission reactions, intermolecular radical recombination reactions and intramolecular H-abstraction reactions, Arrhenius parameters cannot be determined using the group contribution methodology because there are no group additive values available for these reaction families.

Important reactions that do not belong to one of the three considered reaction families used by Genesys (cf. Fig. 1) are added after the network generation procedure. For example, disulfanylmethane (H_3CSSH) can be formed through a recombination reaction of methylthio radicals ($H_3CS^{\cdot}$) and thiyl radicals ($HS^{\cdot}$), cf. R1.

(R1)

Because radical recombination reactions are not included as a reaction family, this reaction is manually added, once the network generation procedure is finished. However, since H_3CSSH can only be formed through this reaction during the thermal decomposition of DES and EMS, further decomposition reactions of H_3CSSH are not included, unless H_3CSSH is added to the initial pool of molecules, next to the reactants.

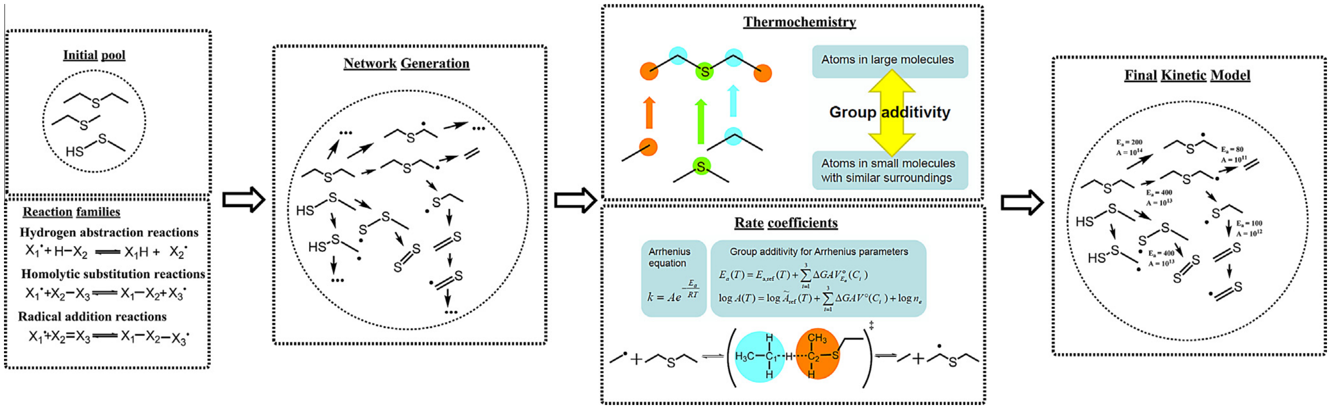

Fig. 1. The methodology used by Genesys to create kinetic models.