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Ab initio group additivity model for the free radical reactions of nitrogen-containing compounds

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Highlights

- Kinetic models for gas-phase free radical chemistry
- Data generated only using first principle approaches
- Group additivity model for hydrogen abstractions and β-scissions of nitrogen-containing compounds

1. Introduction

Due to the gradually diminishing reserves of light crude oils, the use of alternative fossil resources, e.g. shale gas, shale oil and even heavy crude oil, is nowadays being considered in the energy and petrochemical sector. Simultaneously, government regulations and end-users are pushing the use of renewable feedstocks such as bio-derived or waste-derived naphthas. This shift in feedstock poses a challenge for the chemical industry as these feedstocks contain substantial amounts of hetero-atom containing species, which can also be present in case feed additives are used. The primary concerns caused by the presence of these hetero-atom containing species are related to safety, operability and quality of the product streams. In order to optimize a well-established chemical process such as pyrolysis or combustion for a new, alternative feedstock, knowledge about the underlying chemistry is essential. Over the last few years, automatic kinetic model generation codes have proven their use to build large gas-phase radical reaction mechanisms. The main hurdle for the current automatic network generators to cope with hetero-atom containing compounds is the scarcity of accurate thermodynamic and kinetic data. In this work, this lack of accurate data is addressed for nitrogen-containing compounds in particular by presenting new group additivity schemes for approximation of the Arrhenius parameters of the free radical reactions of these compounds.

2. Methods

A prerequisite for the generation of detailed kinetic models, is the availability of accurate kinetic data. For nitrogen-containing compounds, the use of experimental databases is not a plausible option as only for the most simple nitrogen-containing compounds experimental values are available. Another option is to calculate the kinetic parameters *ab initio* during the network generation, or so-called "on-the-fly". In spite of the ever-growing computational power, performing these "on-the-fly" *ab initio* calculations for each reaction is still computationally too expensive, especially for larger compounds. An alternative approach is to make use of approximation methods, of which Benson's group additivity method [1] is the most widely used. This method enables to approximate the Arrhenius parameters for a complete reaction family, such as e.g. hydrogen abstraction by a hydrogen atom, by adding contributions, which account for structural differences between the reaction of interest and the reference reaction, to the Arrhenius parameters of the reference reaction.

The derivation of a group additivity scheme requires an extensive database of accurate kinetic parameters, which originate either from experiments or *ab initio* calculations. Due to the lack of accurate experimental data for nitrogen-containing compounds, computational chemistry is the only viable alternative. In this work, Genesys [2], which is an automatic kinetic model builder developed at the Laboratory for Chemical

Technology, is used as a tool to generate this database of highly accurate *ab initio* parameters. Recently, several automation procedures have been incorporated in Genesys which enables the calculation of these parameters in an efficient manner.

3. Results and discussion

Group additivity values have been determined for intermolecular hydrogen abstractions from nitrogen-containing compounds by a hydrogen atom, a carbon-centered radical and a nitrogen-centered radical. For all reactions considered, an excellent agreement is obtained between the group additivity approximated and *ab initio* calculated rate coefficients. In Figure 1, the methodology is depicted for determining both the forward and reverse rate coefficient of the hydrogen abstraction from the N-H bond in diethylamine by a hydrogen atom making use of the calculated group additivity values.

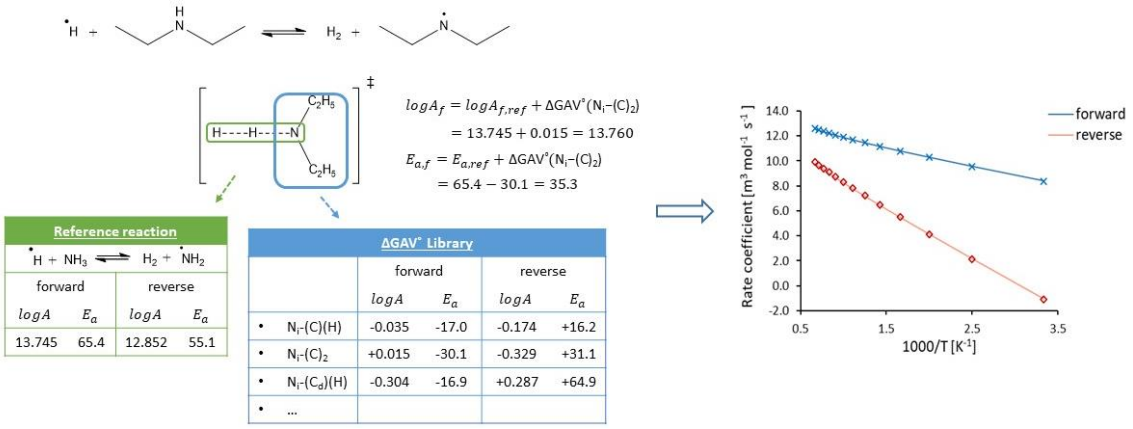

Figure 1. Methodology for determining the Arrhenius parameters of the hydrogen abstraction from the N-H bond in diethylamine making use of the calculated group additivity values. Arrhenius plot of both the forward (blue) and reverse (red) reaction rate coefficients: full lines indicate the *ab initio* calculated values, data points indicate the group additivity approximated values.

Using the same approach as for hydrogen abstractions, group additivity values are also determined for β-scission reactions. To validate the calculated group additivity values, pyrolysis experiments were performed of selected model nitrogen-containing compounds, i.e. diethylamine and dibutylamine, in a bench scale set-up. The decomposition of these aliphatic amine species is essential to gain insight into the decomposition of more complex species, such as morpholine, which can be considered as a biofuel model compound.[3] A kinetic model was constructed making use of the automatic kinetic model builder Genesys and subsequently used in a reactor model to simulate the experimental data. The initiation reactions are homolytic scissions of the C-C and C-N bond, forming an initial pool of radicals. Once radicals are created, chain reactions, mainly hydrogen abstractions and β-scissions occur one after another to form imines and nitriles respectively.

4. Conclusions

New group additivity schemes have been constructed to approximate the Arrhenius parameters for the free radical reactions of nitrogen-containing compounds, i.e. hydrogen abstractions and β-scissions. Incorporating these group additivity values in the automatic kinetic model builder Genesys enables the construction of kinetic models for these compounds.

References

[1] S.W. Benson, F.R. Cruickshank, D.M. Golden, et al., Am. Chem. Soc. 69 (1969) 279-324
[2] N.M. Vandewiele, K.M. Van Geem, M.F. Reyniers, G.B. Marin, Chem. Eng. J. 207 (2012) 526-538
[3] A. Lucassen, N. Labbe, P.R. Westmoreland, K. Kohse-Höninghaus, Combust Flame 158 (2011) 1647-1666

Keywords
Automatic kinetic model generation; group additivity; *ab initio* calculations; nitrogen