Summary of the work of Maarten Sabbe

Ab initio based kinetic modeling
for the simulation of industrial chemical processes

Summary

Many industrial processes are based on radical gas phase chemistry. Detailed kinetic models are the most versatile way to model the chemistry for this processes, which is necessary for an optimal chemical reactor optimization and design. Due to the highly reactive nature of radicals however, the reaction networks easily contain up to hundreds of species and thousands of reactions. Providing these networks with the required thermodynamic and kinetic data is one of the largest challenges in chemical reaction engineering. Since experimental data are only available for a limited number of reactions, typically a mixture of experimental and predicted data is used, optimizing the kinetics of key reactions to fit the observed conversions and selectivities. The parameter fitting can obscure possible deficiencies in the reaction network and/or description of the transport phenomena, which hampers a general application of the developed kinetic model.

Therefore a consistent set of ab initio based kinetic and thermodynamic data has been developed for hydrocarbon gas phase radical chemistry. The thermodynamic and kinetic data are calculated using detailed group additive models based on state-of-the-art high accuracy quantum chemical calculations including corrections for hindered internal rotation and tunneling when necessary.

In order to validate the developed models, simulations of pilot and industrial steam cracking reactors over a wide range of process conditions are performed, using only these thermodynamic and kinetic data without any experimental input. The detailed reaction network, containing 1514 reactions, is automatically generated using recently developed rate-based algorithms. It is shown that, without adjusting any parameter, the main product yields can be predicted within 15% rel. of the experimentally observed cracking yields. This indicates the tremendous potential of integrating ab initio methods with engineering models for accurate reactor simulations.

Introduction

One of the main objectives of chemical engineering is the design and optimization of chemical plants to maximize product yields as well as energy efficiency, next to an evaluation of the industrial feasibility of new processes. Kinetic modeling plays a pivotal role in reaching this objective as the design and optimization of chemical reactors requires a thorough and quantitative knowledge of the kinetics of the occurring chemistry. The capability to predict reliably the behavior of chemical reactions over a broad range of temperatures and pressures would, in principle, enable the a priori design of new chemical reactors and chemical processes. In recent years, it has become possible to predict accurately the behavior of some rather complex gas phase chemical reaction mechanisms such as, for instance, the atmospheric

chemistry involved in ozone depletion or the chemistry occurring in steam cracking and pyrolysis of hydrocarbons. The development of these models requires a tremendous experimental effort over several decades involving a huge amount of work by a large number of researchers. Much faster and more efficient methods are required for the development of kinetic models that reliably predict the chemistry involved in chemical processes and that can be used as a tool for design and optimization. However, for an a priori prediction of the behavior of even well-established gas phase industrial processes, several technical hurdles need to be overcome. This work aims to provide proof-of-principle that the complex kinetic behavior in gas phase reaction mechanisms can be reliably predicted over a broad range of conditions by integrating state-of-the-art quantum chemistry techniques with engineering models at larger length and time scales. This would show that ab initio modeling of gas phase reactions from molecular to industrial scale has now come within reach.

Many of the largest scale industrial chemical processes are based on free-radical chemistry, such as polymerization processes, combustion, pyrolysis and steam cracking. Accurate kinetic modeling of free radical chemistry requires a detailed reaction network that can contain hundreds of species and several thousands of elementary reactions. For every elementary reaction, thermodynamic and kinetic parameters are required. The determination of all these parameters is one of the largest challenges in kinetic modeling. Due to the complexity of the radical chemistry, experimental determination of kinetic parameters is complicated and, hence, only a limited number of experimentally determined thermodynamic and kinetic parameters are available in literature. Therefore, simulations of reaction networks typically involve the use of an inconsistent mixture of experimentally determined, predicted and fitted thermodynamic and kinetic data. In the last decennia, the increased accuracy of computational chemistry methods and the increase in computer performance have made it possible to calculate the required data using quantum chemical methods. However, despite their improved computational efficiency, ab initio methods are still too demanding to determine accurate data for all of the hundreds of species and thousands of reactions in radical reaction networks, particularly when larger species are involved. Therefore, often structure-property engineering methods, such as group additivity based methods, are applied to predict the thermochemistry and kinetics required in large reaction networks. Group additive methods partition a molecule in subunits called groups, and group additivity assumes the contributions of these groups to molecular properties, the so called group additive values *GAV*, to be additive. In this work the group additive models are based on the Benson method,[4] which defines a group as 'a polyvalent atom together with all of its ligands' and is denoted as $X-(A)_i(B)_j(C)_k(D)_l$ with X the central atom surrounded by i ligands A, j ligands B etc. The local definition of the groups requires the use of so-called non-nearest-neighbor effects to account for non-localized interactions on a larger scale than that of a group.

Objective

The aim of this research is to develop a consistent set of thermodynamic and kinetic data for the gas phase radical chemistry of hydrocarbons based on ab initio quantum chemical

Table 1: Mean Absolute Deviations (MAD) on differences between calculated and experimental values.

	$\Delta_f H°$(298 K) kJ mol^{-1}	$S°$(298 K) J/mol·K	$Cp°$(298 K) J/mol·K
Number of species	51	39	46
MAD	1.3	1.2	1.8

calculations. The obtained ab initio data will be applied to construct group additive models for a fast prediction of the thermodynamic and kinetic parameters required in reaction networks for radical-based gas phase chemistry. The studied reaction families involve (i) carbon-centered radical addition and β scission, (ii) hydrogen-radical addition and β scission and (iii) hydrogen abstraction reactions. To show the applicability of the thermodynamic and kinetic group additive models obtained in this work, a pilot and industrial reactor simulations for the steam cracking of light hydrocarbons are performed.

Thermochemistry

Thermodynamic values are of prime importance in reaction networks for the calculation of the heat of reaction and of reaction equilibria. Reaction equilibria are commonly calculated based on the standard enthalpy of formation $\Delta_f H°$, the standard entropy $S°$ and the heat capacity $C_p°$. These properties have been calculated using ideal gas statistical thermodynamics based on the CBS-QB3 high accuracy compound method. Standard enthalpies of formation are obtained using the atomization enthalpy method, applying bond additive corrections to account for incomplete description of the electron correlation energy.[5] For standard entropies and heat capacities, which are very sensitive to the treatment of the internal rotations, all rotations were treated as one-dimensional hindered internal rotations (1D-HR).[6] These computational approaches yield a good agreement with experimental values, with a mean absolute deviation of 1.3 kJ mol^{-1} for $\Delta_f H°$(298 K), 1.2 J mol^{-1} K^{-1} for $S°$(298 K) and 1.8 J mol^{-1} K^{-1} for $C_p°$(298 K), see Table 1.

From the calculated thermochemistry for 265 hydrocarbons and hydrocarbon radicals, 95 group additive values are determined, from which 41 have never been determined before. The most valuable new group additive values are the 25 newly determined *GAV*s for radicals as these are indispensable to predict equilibria for radical reactions. Next to the determination of *GAV*s, the ab initio calculated data allowed an extensive evaluation of corrections for non-nearest-neighbor effects. A consistent counting scheme for these interactions is provided, and it is shown that radical-specific non-nearest-neighbor corrections are significantly different from those in stable molecules.

Kinetics

For the modeling of kinetics, the group additive model for calculation of activation energies introduced by Saeys et al.[7] is applied and extended for pre-exponential factors including

Table 2: Mean factors of deviation <ρ> between calculated and experimental rate coefficients (CBS-QB3 calculated rate coefficients with correction for internal rotation about the forming/breaking bond, and inclusion of tunneling correction for hydrogen addition and abstraction).

T (K)	Carbon radical[1]		Hydrogen radical[2]		Hydrogen[3]	Mean
	addition	β scission	addition	β scission	abstraction	
300	2.1	3.3	1.7	2.3	10.0	3.9
600	3.2	2.5	1.5	2.2	3.9	2.7
1000	3.9	2.6	2.0	1.8	3.6	2.8
Nr. of reactions in test set	8	6	7	6	21	48

corrections for hindered rotation and tunneling. Starting from the group additivity assumption for the enthalpy and entropy of activation, a group additive model is constructed that calculates the activation energy and pre-exponential factor of a given reaction as perturbations, $\Delta GAV°$, to the Arrhenius parameters of a reference reaction. The main advantage of this approach over other methods is the very broad application range and the temperature independence of the group additive values $\Delta GAV°$, since the reference reaction accounts for most of the temperature dependence of the Arrhenius parameters.

The rate coefficients from which the group additive values are derived are calculated using conventional transition state theory. Several ab initio methods were evaluated by comparing calculated with experimentally determined rate coefficients. Over the different reaction families, best agreement was obtained using the multi-compound CBS-QB3 method, including 1D-hindered rotor corrections for internal rotation about the forming/breaking bond in the transition state and accounting for tunneling using the Eckart method (see Table 2).

C-radical addition For carbon-centered radical additions, the calculated rate coefficients agree well with experimentally observed rate coefficients with a mean factor of deviation of 3, as benchmarked on a set of 9 reactions.[1] The consistent set of 46 group additive values $\Delta GAV°$ for activation energies and pre-exponential factors is validated on a test set of 13 reactions. In the absence of severe steric hindrance and resonance effects in the transition state, the rate coefficients predicted by group additivity are within a factor of 3 of the CBS-QB3 ab initio rate coefficients for more than 90% of the reactions in the test set, which is better than many DFT-based methods for this reaction family.[8]

H-radical addition For hydrogen radical additions, the same computational approach yields a mean factor of deviation with experimental rate coefficients of only 2 in the range 300-1000 K, on a set of 7 reactions.[9] Application of the obtained group additive values for 33 groups to predict the kinetics for 11 addition/β scissions yields rate coefficients within a factor 3.5 from the CBS-QB3 results except for 2 β scissions suffering from severe steric effects. The group additive method is also applied to predict rate coefficients for a set of 7 reactions with experimentally known rate coefficients (300-1000 K). The mean factor of deviation is 2, showing that the group additive method can accurately predict H-addition kinetics.

Hydrogen abstractions The computational approach yields a mean factor of deviation of 6 on the rate coefficients for a set of 21 reactions (298-1000 K).[3] The group additive values for 52 groups are not sufficient to describe all details of the kinetics, since resonance and hyperconjugative cross-stabilization of the transition state occurs. The introduction of 4 cross-stabilization corrections based on the transition state topology account for all stabilization effects.[10] Evaluation of the method for 23 reactions yields a mean factor of deviation between group additive prediction and CBS-QB3 calculation of 3 at 300 K and 1.6 at 1000 K. In a comparison with 6 experimental rate coefficients (600-719 K), the mean factor of deviation is less than 3.

Pilot and industrial reactor simulation The consistently obtained thermodynamic data, rate coefficients and group additive models are finally applied a validating reactor simulation, in casu simulations of steam cracking reactors.[11,12] Steam cracking of hydrocarbons is one of the basic processes in the petrochemical industry. Based on saturated hydrocarbons that range from ethane and light naphtha to heavier crude oil distillates, the building blocks of petrochemistry are produced: unsaturated hydrocarbons such as ethene, propene, butadiene and aromatics. These compounds are precursors to a wealth of end-user and consumer products, with polymer materials in first place.

Steam cracking is performed in tubular reactors at typical operating conditions of 900-1200 K and 0.1-0.4 MPa. Steam dilution suppresses side reactions and coke formation by a reduction of the partial pressures of the hydrocarbons. The reactor coils are suspended in large gas-fired furnaces, the so-called hot section. The reactor effluent is separated in the cold section, consisting of consecutive distillation columns and extractors. Both the hot and the cold section are very energy intensive, and as such steam cracking is the most energy consuming process in the chemical industry, with a global share of 8% of the total energy use of the chemical industry and a emission of 180-300 10^6 ton CO_2 per year. This leads to a strong economical incentive to optimize steam cracking reactors.

The advantage of simulating steam cracking is the abundant experimental data available for the pilot plant of the Laboratory for Chemical Technology of the UGent, which allows validation of the kinetic models over a broad range of conditions. The feedstock comprises of various mixtures of methane, ethane, propane and butane, and the simulations cover a wide range of reactor conditions, varying coil outlet pressure, temperature, steam dilutions and geometries.

The reaction network is automatically generated using rate-based algorithms, using the developed group additive models for the prediction of the kinetics. These algorithms generate a reaction network starting from the feedstock molecules and a given set of reaction rules, yielding all possible intermediates and reactions. The network generation stops if all rates of formation of species that are not included in the network are below a given threshold.[13]
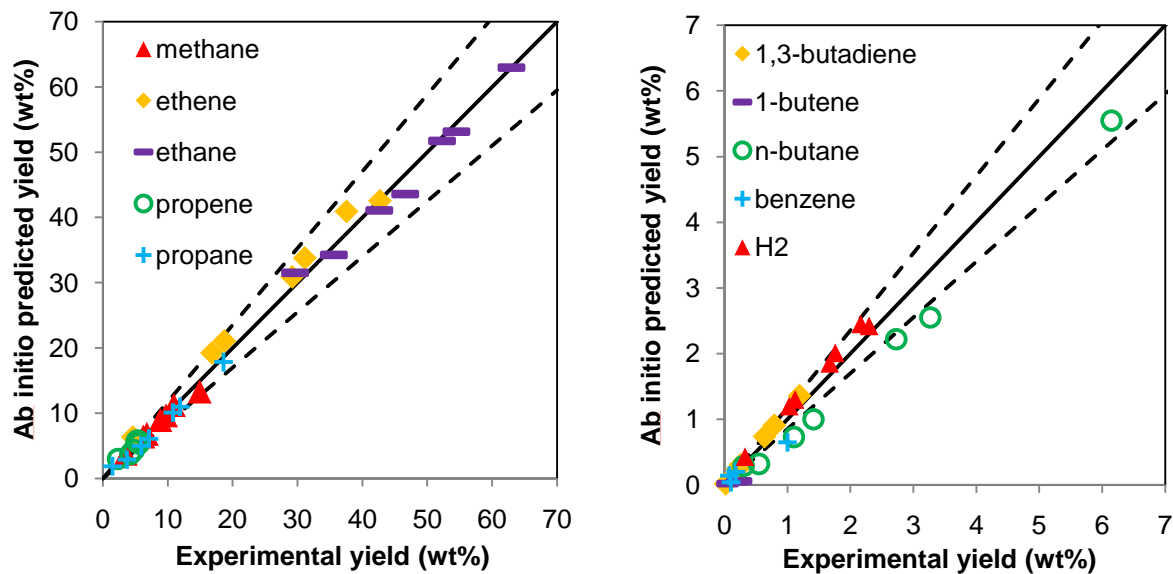
Figure 1: Ab initio predicted versus experimental product yields for the cracking of a $C_1/C_2/C_3/C_4$ mixture in 7 pilot plant experiments. Major yields are shown in the left panel, minor yields in the right one. Conditions: Coil outlet Temperature = 1005 – 1119 K, Coil Outlet Pressure = 1.52 – 1.57 10^5 Pa; mixture composition: 3 wt% C_1 - 67 wt% C_2 - 22 wt%C_3 -

With this approach, for the first time an industrial steam cracker furnace is simulated on an entirely ab initio basis, which avoids the traditional use of experimental, predicted and fitted data in order to overcome the lack of availability of kinetic and thermochemical data.[11,12] The pilot plant is simulated using a 1D-reactor model and the industrial plant using 2D reactor modeling, to account for strong radial gradients in industrial reactors.[14] The first principles based simulation results are compared to experimental cracking yields from 19 experiments on a pilot plant set-up and 2 industrial steam crackers. A good agreement is obtained with pilot and industrial data, with all main yields reproduced within 15% up tot benzene, over a range of reactor conditions. Figure 1 illustrates the good agreement for a set of 7 pilot cracking experiments of a $C_1/C_2/C_3/C_4$ mixture. Only for the methane and propene formation during ethane cracking, the simulations yields larger differences. As no parameter has been adjusted and no experimental values have been used, the agreement can be considered remarkable. The observed differences in product yields can be largely attributed to a few hydrogen addition reactions that seem to be too fast. Pressure dependence, which is currently neglected, probably needs to be taken into account for these reactions.

The full ab initio simulation has also shown that the vast majority of the benzene is formed via a pathway initiated by vinyl radical addition to 1,3-butadiene, and subsequent cyclization and dehydrogenation. Propargyl radical recombination, which is sometimes advocated to be the main pathway towards benzene under pyrolysis conditions, plays only a marginal role under steam cracking conditions.

Conclusions and key innovations

Group additive models are constructed in this work based on high-accuracy quantum chemical calculations. They allow to accurately predict the thermochemistry of hydrocarbons and hydrocarbon radicals, and the kinetics of a broad range of hydrocarbon radical additions and hydrogen abstractions relevant in gas phase chemistry. The main key innovation is the construction of a consistent approach for the calculation of thermodynamics and kinetics based on CBS-QB3 based group additivity, thus avoiding the combination of inconsistent data. The innovations on the thermodynamic field pertain in the first place to the modeling of hydrocarbon radicals, for which very few information was available until this work was published, and in the second place the thorough evaluation of the non-local effects, identifying particularly the effect of sterical interactions on the entropy, which are regularly counter-intuitive. For kinetics, the developed methods assure an accurate prediction of the intrinsic kinetics for a very broad range of hydrocarbon reactants.

From the successful simulation of an industrial cracker several conclusions can be drawn. First, the success of the simulation delivers a proof-of-principle that the integration of computational chemistry methods with engineering tools at larger time and length scales provides a predictive tool that can be used for the design and optimization of industrial chemical processes. The methodology developed in this work is able to provide radical reaction networks with reliable kinetic and thermodynamic data and requires no adjustable parameters nor direct experimental data. Second, because of the absence of fitted data that could compensate for possible deficiencies in the reaction network, it has been shown that the reaction network is complete, in the sense that it describes all the relevant chemistry occurring under steam cracking conditions.

Although the data obtained in this work cover only hydrocarbon radical gas phase reactions, the rate coefficients obtained using the developed ab initio based group additivity methods represent the intrinsic chemical kinetics of the reactions and, hence, are independent of the studied process. Therefore, the developed group additive models can be applied in other reaction networks as well, including the description of hydrocarbon reactions in reaction networks including hetero atoms. The application range of the group additive models developed in this work covers processes based on gas phase radical chemistry, such as radical polymerization processes, partial oxidation and pyrolysis processes. Currently the developed group additive models for hydrocarbon chemistry are already applied in the description of organosulphur and oxygenate chemistry.

The final conclusion is that ab initio methods can be considered a feasible tool for the modeling of chemical processes based on gas phase radical chemistry. The simulation of a chemical reactor built on ab initio calculations and kinetic models only, without a single adjusted parameter or experimental value, is within the reach of the current methods. The challenge is now to extend this work to more complex processes, and to apply the methodology to unexplored reaction conditions and feeds, as well as novel processes.

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