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EXECUTIVE SUMMARY OF THE THESIS

Theoretical Investigation of the Reactivity of Methylcyclopentadiene

LAUREA MAGISTRALE IN CHEMICAL ENGINEERING - INGEGNERIA CHIMICA

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1. Introduction

Some of the main applications of theoretical chemical engineering are modelling and simulations. By using a computer, it is possible to model different applications such as the flow of a fluid inside a pipe, the transfer of heat or estimate reaction rate parameters. The latter application is part of the scientific field known as "quantum chemistry" or "computational chemistry". A computer is necessary to solve the required equations since the physical laws describing a system are not well known. An iterative procedure for numerical solutions is usually necessary.

Computations for chemical systems provide numerous advantages such as the ability to analyze transition states and short living molecules like the radicals, which is usually not possible to be analyzed by experiments. Besides the analysis of short living molecules, relatively higher accuracy for the analyzed systems can be achieved for a relatively cheap cost. Furthermore, in case of hazardous and dangerous materials, running simulations on a computer could allow the researcher to work safely.

Computational calculations are usually accomplished by a computer with many cores, or preferably by a High Performance Computer because of long computational times. It is reported in the literature that for some cases a regular computer would not be sufficient to find a solution because of its classical algorithms and the hardware.

Methylcyclopentadiene is a highly reactive molecule. It consists of six carbon and eight hydrogen atoms, with a five-carbon ring structure which has three single and two double bonds. The methyl molecule is attached to a carbon of the ring. Depending on which carbon it is attached to it can form three different isomers. Even though it is a reactive molecule, the chemistry behind its reactions is not so well known, which may become a cause of concern. Therefore experiments or molecular simulations, which aim to understand the reactivity of methylcyclopentadiene, are needed to design safer processes. In this framework, the aim of this thesis is to use molecular simulations to estimate the rate parameters of some reactions related to methylcyclopentadiene, and compare them with literature values by running kinetic simulations.

2. Methodology

The master equation can be utilized to find reaction rates between chemical species. It associates the microscopic processes to the

thermal reaction rates. In order to use the master equation, some properties such as the reaction pathways or energy transfer models must be known. The reaction pathways can be studied by ab initio electronic structure theory. The results of these calculations have to be integrated with transition state theory to obtain microcanonical rate constants. Once microcanonical rate constants are acquired, they can be merged with the energy transfer rates between molecules to find phenomenological rate constants.

For this thesis, four different computer programs are used. For the electronic structure calculations, Gaussian and Molpro are used. MESS is used for the master equation simulations. The last program, OpenSMOKE++ is used to run kinetic simulations after obtaining the rate constants for all the desired reactions.

Quantum mechanics proposes that properties such as the energy of a molecule can be achieved from the Schrödinger equation, which is known as:

$$\boldsymbol{H}\Psi = E\Psi \tag{1}$$

The exact solution of the Schrödinger equation is not so practical, which caused the development of computational calculations such as the ab initio methods. The ab initio methods require no experimental data and solves the problem solely based on the laws of quantum mechanics. There are different levels of calculations, the user has to determine the level by considering the computational costs and the desired level of accuracy into account.

Transition state is known as the intermediate states, which converts the reactants to the products, of a reaction. It is often associated with an energy barrier; the reaction proceeds once the top of the barrier is achieved. That place (highest energy point) is called as the transition structure. Transition state theory proposes that the energy of that point (height of the barrier) strongly influences the reaction rates.

Usually the electronic structure, and master equation calculations are carried out separately. However, a freely available code EStokTP [1] allows the users to do the electronic structure, transition state theory, and master

equation calculations together, and reports the temperature and pressure dependent rate constant parameters to the user. The code can be used to study abstraction, addition, beta-scission, isomerization, and barrierless reactions. In this thesis, only abstraction, beta-scission and isomerization models are used. Another useful code that was used in this thesis is MEL, which stands for Master Equation Lumping. It is used to assemble some of the chemical species, which have similar structures and reactivities, together. By doing so, the user can reduce the number of species and reactions, which will simplify the process.

Last part of the thesis corresponds to kinetic simulations, which are performed by using OpenSMOKE++. The software requires some input parameters such as reactor type, values of temperature and pressure, and inlet conditions as well as a kinetic mechanism. Kinetic mechanisms can be found in the literature. For this thesis the mechanism developed by the CRECK group of Politecnico di Milano is used. Every kinetic model includes elementary reactions, thermodynamic data of these reactions and the parameters for the rate constant. By using these models, the researchers can run simulations (computational experiments) for a system according to their interest.

3. Results

The reactions analyzed in this thesis can be classified into two groups. One of these groups investigate reactions starting from three different isomers of the methylcyclopentadiene molecules, each of these isomers are attacked by H, CH_3, OH and OOH molecules. The attacking molecules remove one hydrogen atom from methylcyclopentadiene by an abstraction reaction and cause them to turn into different radicals, which are called methylcyclopentadienyl radicals. The second group investigates decomposition of these radicals. While decomposing, the radicals can produce other different radicals by isomerization reactions or lose one more hydrogen atom and produce benzene or fulvene by beta-scission reactions.

The calculations begin with finding the energies of the species and constructing the potential

energy surfaces of the reactions. This part corresponds to the electronic structure calculations and is done by Gaussian and Molpro. Once the necessary results are obtained, master equations calculations are performed using the MESS software. The user specifies the range of temperatures and the pressures for which the rate constant calculations should proceed. For this thesis, the temperature range was between 300 K and 2500 K and the pressure range was 0.001 atm to high-pressure limits. Except for the abstraction reactions that have two van der Waals wells, all the plots for the rate constants that are reported in the result sections used the high-pressure limits, while for the cases with van der Waals wells the low-pressure limit (0.001 atm) rate constants are used.

As predicted by transition state theory, rate constants strongly depend on the height of the energy barrier. This could be clearly observed when the plots are examined. Some of the reactions, for example some isomerization reactions, have similar rate constants for the forward and the backward reactions, on the other hand some reactions such as beta-scission reactions that produce benzene or fulvene have major differences between forward and backward rate constants. For the cases with decomposition reactions, several radicals have similar energetic values. These radicals can be merged together with the intention to reduce the number of reactions. The code called MEL is used for lumping these radicals. The code uses the output files of MESS calculations as input, and generates rate parameters for the lumped system as well as plots that compare the mole fractions of species for a reference system by using the lumped model and the detailed (not lumped) model. The simulation results showed that the lumped model could be used for a wide range of temperatures, preferably at pressures above 1 atm.

Three different isomers of methylcyclopentadiene molecules are used as reactants for abstraction reactions. Four different radicals, namely H, CH_3, OH and OOH react with the three isomers to produce methylcyclopentadienyl radicals by removing a hydrogen atom. Abstraction from two of these three isomers can occur on two different sites. In the following, the comparison of different attacking sites of the same molecule, different attacking molecules and reactions of different isomers are analyzed. Even though the temperature and the pressure range are kept the same as for decomposition reactions, in order to obtain better fitting results the calculations at 300 K and 400 K are excluded from the collected data.

For almost all cases, the forward rate constants are found to be much higher than the reverse rate constants. The results are summarized according to the abstracting radical to be able to see the effects of both the reaction site and isomers on the rate constants. This is accomplished by plotting the forward rate constants (for the same attacking molecule) on the same graph. Just like the decomposition reactions, the results appeared to have good agreement with the potential energy surfaces.

Once the rate parameters are obtained, they can be implemented in literature kinetic mechanisms. For this thesis, the kinetic mechanism developed by the CRECK group of Politecnico di Milano is used, which contains thousands of reactions.

According to a literature article, which describes the experimental setup conducted in their experiments as well as the inlet conditions, kinetic simulations are carried out for the described system using OpenSMOKE++. The article also reports the mole fractions of some of the species that appear in the outlet of the reactor, which could be used for comparing the results of the simulations performed in this thesis.

The abstraction rate constants were already present in the mechanism, as they were obtained from previous works. To be able to see how accurate the abstraction rate constants found from this thesis are, two separate simulations are conducted for the system that is described in the reference article. One of the simulations included the rates of the original CRECK mechanism and the other one was with the parameters obtained from this thesis. It is worth to mention that only the abstraction rates are replaced in the mechanism, the decomposition rates are not added at this stage. Additionally, the rate constants for each abstraction reaction, at different temperatures, are computed both

for the modified and the original mechanism, and they are compared with each other. The comparison showed similar, though not equal values between the rate constants computed in this thesis and those present in the original CRECK mechanism. This is clearly observable when the rate constants from the CRECK mechanism (two separate rates were present) and this thesis are compared for the hydrogen attack, which is reported in Figure 1:
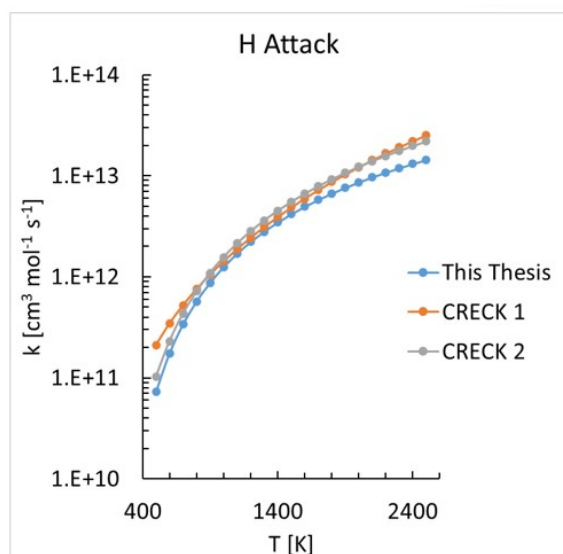

Figure 1: Comparison of the abstraction rate constants by H attack computed in this thesis and the one present in the original CRECK mechanism.

It should be noted that CRECK mechanism does not include three different methylcyclopentadiene isomers, but just a single molecule. Because in this thesis were performed calculations with three different isomers, in order to make a comparison the values of the computed rate constants have to be reduced to a single value. To achieve that, thermodynamic parameters such as partition functions (translational, rotational, vibrational, etc.) are used to achieve a weighted average of the referred isomers. Hence, the comparison shown in Figure 1 is obtained for the following reaction:

$$C_5H_5CH_3 + H \Rightarrow C_5H_4CH_3 + H_2 \qquad (2)$$

Where $C_5H_5CH_3$ represents methylcyclopentadiene isomers and $C_5H_4CH_3$ stands for methylcyclopentadienyl radicals.

After the rate constants are compared, a third simulation is run with the kinetic mechanism that is completely modified with the rate constants obtained from this thesis. In other words, both the abstraction rates and the decomposition rates are added to the mechanism. The chemical composition computed at the outlet of the reactor is then compared with the literature data. For most of the analyzed species, the trend of the curves showed similar behavior. For a number of species not only the shape of the curve but the values were very similar when they are compared with each other.

Finally, to recognize which reactions are dominating for the major species that are analyzed in this thesis, rate of production and sensitivity analysis are carried out. These analyses are performed for the species: methylcyclopentadiene, methylcyclopentadienyl, benzene, and fulvene.

4. Conclusions

The main purpose of the thesis was to determine accurate rate constants through the solution of the master equation, using parameters determined through ab initio methods. The rate constants are investigated for different reactions, all involving methylcyclopentadiene or its radicals. Determining the reactivity of this molecule plays a crucial role, since it is a highly reactive substance, and its chemistry is not very well known due to lack of experiments. The simulations are done with the computer programs Gaussian, Molpro, MESS and OpenSMOKE++. Besides these, two separate freely available codes, namely EStokTP and MEL are used.

The main conclusions of this thesis involve the changes in the energies of the molecules as they react, such as migration of the electron density or an atom from one carbon atom to another one as well as bond breaking and forming. The changes in the energies are reported on a potential energy surface. The rate constants are then determined. It is found that they show a huge dependence on the energy barrier, as predicted by transition state theory. Some of the chemical species that show similar behaviors are lumped together in order to simplify the reaction scheme. The results of the master

equation lumping calculations showed that these species could actually be lumped together for a huge range of temperatures and pressures (better results are achieved for pressures above 1 atm).

Finally, to be able to compare how accurate the determined values are, kinetic simulations are performed. It is found that the obtained rate constants show values similar to those of the literature. This is an important conclusion because the literature values are obtained from experiments, and achieving similar values mean the rate constants calculated by ab initio methods are very similar to real-life experiments. Also, the values of the mole fractions of some species for an experiment reported in the literature are compared with the mechanism modified according to this thesis. Once again, very similar trends and values are achieved for most of the analyzed species. This shows the accuracy of the used model for a real-life experiment.

One important remark is that some of the reactions, i.e. decomposition reactions, analyzed in this thesis were not present in the kinetic mechanism obtained from the literature, since these reactions showed good agreement for an experimental case, they can be implemented in the used kinetic mechanism in the future. They could be beneficial for some reactions that include species related to methylcyclopentadiene.

5. Bibliography

The theory behind the calculations are mostly obtained from the book of Jensen [5], which provides detailed descriptions of the theories to understand the concepts related to ab initio calculations. These calculations such as the electronic structure calculations, and master equation solutions are performed with the software called Gaussian [4], which is a quantum chemistry software specifically used for computational calculations related to chemical systems. The steps of calculations are followed a freely available code called EStokTP [1], which allows the users to start the calculations from finding properties of the chemical species and complete the calculations by finding rate parameters for different reactions with minimal human interventions.

The calculations are carried out for the chemical species called methylcyclopentadiene and its radical versions (methylcyclopentadienyl radicals). A work found on the literature [3] is used as a basis for the possible reactions and possible species that could be included in the reaction scheme. Once the calculations are obtained from EStokTP, it is possible to compare the results with some values found in the literature, the software called OpenSMOKE++ [2], which allows the user to perform some kinetic simulations is used for that purpose.

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