School on Kinetics and Dynamics of Chemical Reactions

Automated Prediction of Reaction Mechanisms and Kinetics (Practical Session)

Emilio Martínez-Núñez (emilio.nunez@usc.es), University of Santiago de Compostela

The purpose of this session is to provide an introduction to the application of automated methods for the prediction of reaction mechanisms and kinetics. In particular, we will use AutoMeKin package[1] as implemented in the AutoMeKin Web Interface.[2] The AutoMeKin version installed on this server may help you predict reaction mechanisms for thermal and energy-selected unimolecular decompositions, as well as some bimolecular reactions associated with the investigated potential energy surface. For practical reasons, **the web-interface version of AutoMeKin has reduced capabilities. It is only available for small systems, and the electronic structure calculations are done at a semiempirical level (PM7 method).** Researchers interested in the full capabilities of AutoMeKin should download the program and use it on their own computational resources, following the instructions provided in the wiki.[3]

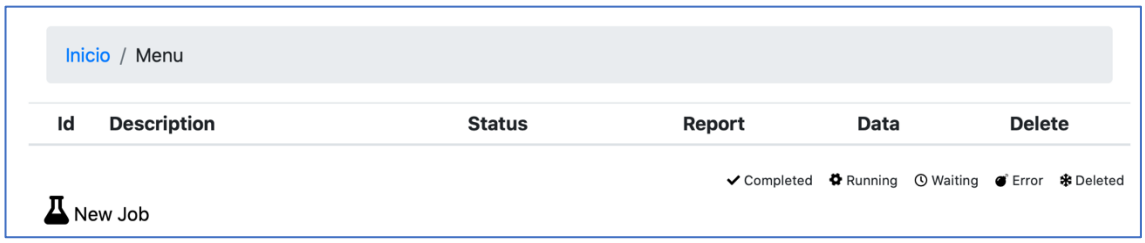
In this practical session, we will study the unimolecular decomposition of formic acid at 2000 K.

1. Create an account in the AutoMeKin Web Interface

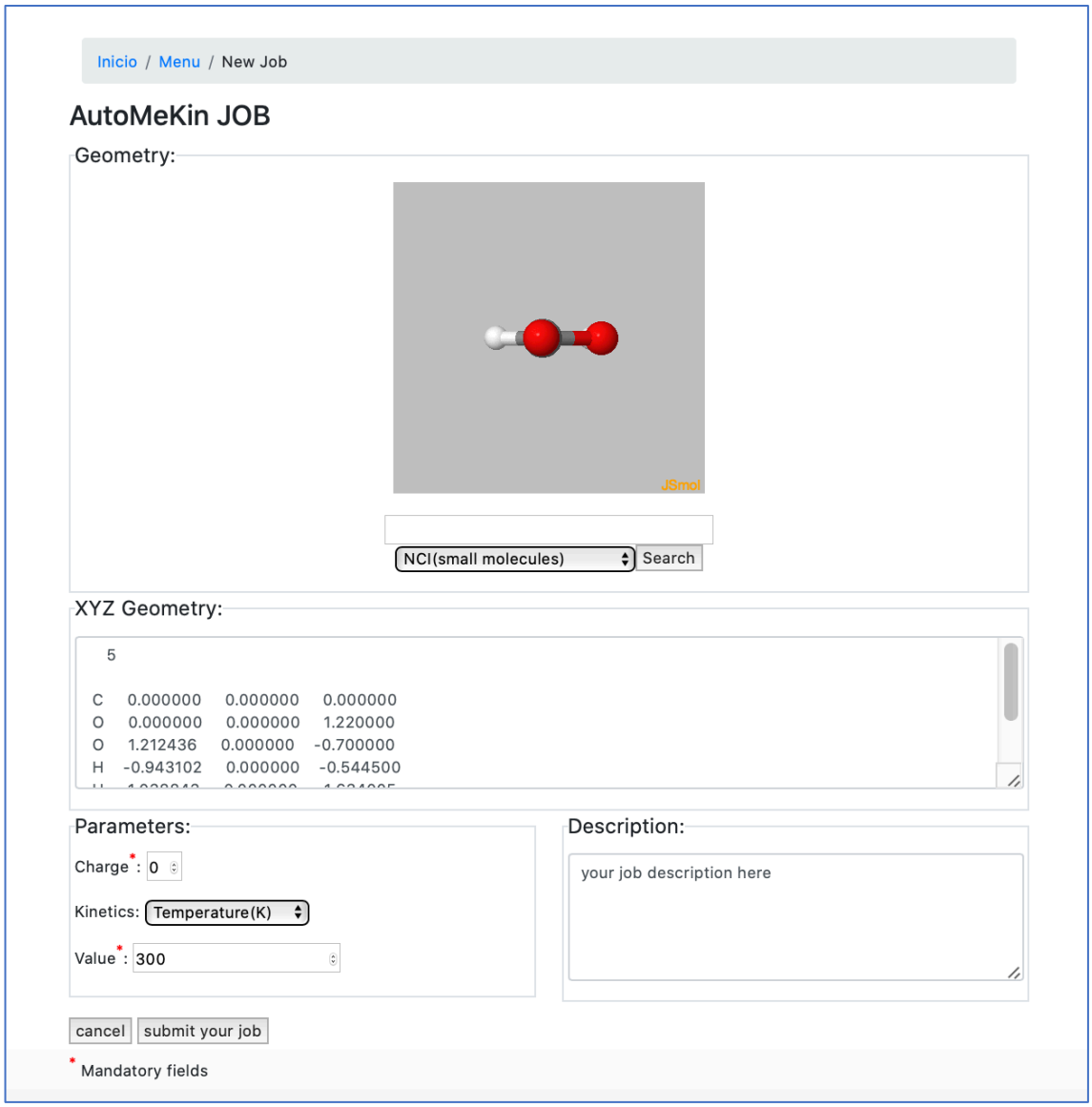
To create an account in this web interface, we need to specify an email address, the name of our institution (university, center or company) and provide a short description of the type of work you are interested in.

2. Submit a job

Once your account has been activated, you can submit jobs. When you log in the web interface for the first time, you will see the following:



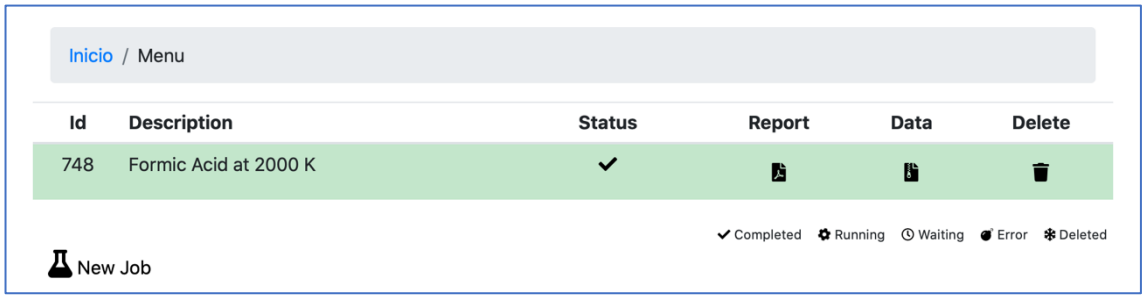
Clicking on “New Job”, the following window will be open:



As can be seen, the server includes the JSmol utility, which facilitates the introduction of a molecular geometry for the system. By default, the geometry of a conformation of formic acid is presented (it is not the most stable one). To consider a different system, you can write the name of a molecule and hit return, or you can write a new XYZ matrix in the “XYZ Geometry” section. Notice that the number of atoms in that section should

be the correct one. If the number is not correct, there will be an error in the execution. In addition to the molecular geometry, the user needs to specify, in the "Parameters" section, the charge of the system and the temperature (in K) or, alternatively, the energy (in kcal/mol). The "Energy" option in "Kinetics" involves the calculation of RRKM rate constants $k(E)$. The version of AutoMeKin used in the web interface was designed for unimolecular decompositions, although the program may find bimolecular reactions associated with the potential energy surface of the system. In the section "Description", you can write a title for your work.

Once you have selected your system and parameters, you can submit the job. For this tutorial, change the temperature to 2000 K (write only the numerical value as an integer), and write a title in the "Description" (I will write "Formic Acid at 2000 K"). Then you can log out. When the job has been completed, you will receive an email (from automekin.program@gmail.com) indicating that your job has finished. Then, when you log in again, you will see something similar to:



So, here we have the results for formic acid at 2000 K. This will be the example that we will analyze in this tutorial: the thermal decomposition of formic acid at 2000 K. Now, you can download the "Report" and the "Data" zip file.

3. Analyzing the results

3.1 The Report file. First, let's analyze the report. The first page of the report describes the files and figures included in it. Notice that the exploration of the PES is made by classical trajectories, which use random numbers for the initial conditions. Therefore, you may find some differences between the results obtained in two jobs that employ the same input data. The first file listed in the report is "convergence.txt", which collects the number of trajectories run by the program in a series of iterations, as well as the accumulated number of optimized transition states. In this example, the program

performed 10 iterations, with 500 trajectories per iteration, and found a total of 30 transition states.

The next file given in the report is MINinfo, which lists all the located minima, sorted by increasing ΔG **(ΔE in case of energy selected systems**). The values are given relative to the Gibbs energy of the (optimized) reference structure (the one specified in the "XYZ Geometry" section). This file also specifies the structures that are conformers. **IMPORTANT NOTE: In the present version of AutoMeKin, the program does not check whether all the conformers correspond, in fact, to minima on the PES. The user should check the results, e.g., visualizing the normal modes of vibration of the structures** (Molden files are include in the zip file called "Data"). A similar file, denoted TSinfo, is dedicated to transition states. As can be seen, the list of TSs shows that many of them have ΔG values smaller than that of the lowest conformation of the reactant. There may be two reasons for this type of result. (1) It may be the case of TSs corresponding to van der Waals structures formed by dissociation products. The default criteria to discriminate structures, and particularly TSs, are rather loose in order to avoid that possible relevant structures go unnoticed. This may lead to include in the TS list van der Waals structures, which do not play any relevant role in the reaction mechanism. (2) TSs with free energies smaller than that of the reference structure may also be found when the reference molecule has isomers that present much higher stability.

The following file is RXNet, which lists all the elementary reactions discovered by the program. The first column indicates the TS numbering, the second column ΔG (ΔE for energy selected systems), and the "Reaction path information" specifies the minima and/or products associated with the TSs (determined by the IRC calculations). We notice that in the KMC simulations, *elementary reactions leading to dissociation are considered as irreversible processes in the reaction mechanism*. Interestingly, AutoMeKin predicts the transition state of the following bimolecular reaction: $H_2 + CO_2 \rightarrow CO + H_2O$ (and the reverse one). We can visualize the structure of the associated TS and its vibrational normal modes from a Molden file included in the zip "Data" file (as described later on).

The following file, RXNet.cg, removes bimolecular processes from the RXNet file. In addition, it organizes elementary reactions into conformational reaction channels (CRCs) or "coarse-grained" channels, that is, elementary reactions that only differ in the conformation of the reactant are grouped in a single reaction. This is done to simplify the

reaction network. Finally, the word "DISCONN" indicates that the reaction is not accessible (i.e., it is disconnected from the accessible reaction network) at the investigated temperature (or energy).

The relevant reaction network is shown graphically in the "Complete Graph". In this figure, the nodes correspond to reactant, intermediates and products, and the widths of the edges are proportional to the number of paths connecting the corresponding nodes. The starting node, the reactant, is depicted in red.

The next figure of the report is the "Kinetics Graph", which displays only those nodes actively participating in the kinetics at the chosen temperature T (or energy E). Here, the widths of the edges are proportional to the total (forward + backward) reactive flux in the KMC simulations. The starting node, the reactant, is shown in red. The last figure depicts the populations of the relevant chemical species as a function of time, as determined by the KMC simulations. These two figures clearly point out that, according to the simulations, formic acid dissociates into carbon monoxide and water at 2000 K. Formation of molecular hydrogen and carbon dioxide is negligible.

3.2 The Data.zip file. If you unzip this file, a folder called "FINAL_LL_input" is generated, which contains a series of files as well as a folder called "normal_modes". The latter includes Molden files for visualization of all the structures. Some of the files within "FINAL_LL_input" are already included in the report file. There are two SQLite database files, min.db and ts.db, from which you can extract information, but they are not important for the present practical session.

To complete this practical session, try to visualize the minima and transition state structures gathered in the "normal_modes" folder. The files corresponding to the minima are named as MIN0001.molden, MIN0002.molden and so on, and as mentioned before, you can visualize these structures and their normal mode frequencies with Molden. The numbering corresponds to that specified in MININfo. Likewise, the files for the transition states are named as TS0001.molden, TS0002.molden and so on. It is important to analyze and check the results in detail. AutoMeKin helps you in predicting reaction mechanisms, but it is not infallible!

If you have any questions, do not hesitate to contact me.

References

[1] E. Martínez-Núñez, *Phys. Chem. Chem. Phys*. *17*, 14912 (2015); E. Martínez-Núñez, *J. Comput. Chem. 36*, 222 (2015); A. Rodríguez, R. Rodríguez-Fernández, S. A. Vázquez, G. L. Barnes, J. J. P. Stewart and E. Martínez-Núñez. *J. Comput. Chem. 39*, 1922 (2018).

[2] http://rxnkin.usc.es/amk

[3] https://rxnkin.usc.es/index.php/AutoMeKin