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Automatization of theoretical kinetic data generation for tabulated TS models building

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Abstract

Estimation of kinetic parameters is a key aspect of chemical combustion modeling and several approaches were developed to approximate unknown data. We present here a code in python, capable to build TS model tables automatically for intramolecular H-shift reactions. The code generates the kinetic rate rules for all the possible combinations of alkyl-substituted reactions. The results obtained by the code were compared with the ones obtained manually and most of them had very similar values. These tables can be directly used to improve kinetic data of reaction mechanisms used for combustion modeling.

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1. Introduction

Reaction mechanisms describing the chemical conversion of alternative fuels in a wide range of temperatures and pressures are essential to design new less carbon-intensive combustion systems. They account for hundreds of species and thousands of reactions and the compilation of a large amount of reliable thermochemical and kinetic data necessary to accurately predict important observables in combustion (flame velocities, ignition delay times, heat releases and pollutant formations) is a great challenge. Thus, the use of methods that allow the fast and high-throughput calculations of the lacking data is unavoidable [1]. Usually, thermodynamic data are directly obtained by the group-additivity method proposed by Benson [2], while the current estimation methods for reaction rates are based on reaction similarities [3], i.e. using accurate rate coefficients obtained from high-level theories or measured by experiments to estimate the reaction rate constant for a family of similar reactions. Historically, one of the first approaches proposed by Bell, Evans and Polanyi [4] to retrieve the rate constants was based on a linear relationship between the activation energy and the enthalpy of reaction considering the pre-exponential factor as constant for a family of reactions. Several other approaches have been developed to estimate rate coefficients. For instance, correlations can be derived from group contribution methods analogous to the ones applied in the thermodynamic data calculations [4]. Kinetic constants can also be quickly obtained via the tree-averaging approach, used in the RMG automated reaction mechanism generator [5], in which the unknown kinetic constant is calculated as the averaging of the constants of closest reactions in the reaction family tree. Quantitative Structure-Reactivity Relationships (QSRR) is also a broad applied approach that associates kinetics constants parameters with the structural characteristics of the reactions by creating a table of rate rules containing parameters for each reaction type inside a reaction class [6,7]. It is worth noting that a key aspect of the rate rules definition is the delimitation of the reaction moiety attributes that will be used to define the reaction types [6]. Simultaneously, computational power and optimizations algorithm advances allow the possibility of applying highly accurate electronic calculations for a larger number of species, which encouraged the application of on-the-fly methods to calculate lacking thermodynamic properties of molecules and radicals as well as unknown kinetic constants for reactions, directly on the reaction mechanisms. The implementation of an algorithm of 3D structures generation including a random search for conformers was added and tested in the reaction mechanism generator (RMG) showing improvements in cyclic structures treatments, for which the group contribution methods are not sufficiently accurate [8]. More recently, the thermodynamic properties of the

structures involved in the oxidation of *n*-butane were automatically calculated using high-level electronic calculations [9] by a predictive automated computational thermochemistry (PACT) software, which included Monte-Carlo search of conformers, multiple steps geometry optimization, high-level energy calculations, and anharmonic hindered-rotor treatments.

The determination of rate constants is a more complex task, divided into two main steps: first, the *ab initio* calculation of the stationary points on the potential energy surface (PES) or the whole minimum energy pathway (MEP) is performed. Then, an appropriate kinetic theory, such as the transition state theory or the variational transition state theory is applied, depending on the characteristics of the reaction. One of the key aspects of kinetics automatization is the definition of the transition state structures from the 2D or even 1D mechanism reactions representation. One alternative to retrieve intermediate structures is the exploration of the PES to identify reaction pathways [10]. Among all these studies, we can cite the work of Bhoorasingh and West in 2015 [11] who used molecular groups to estimate the distances separating reactive atoms in the TS structure and allowed the modifications of the reactant structures to build first guesses for the TS used for electronic structure optimizations and IRC searching. Their code was later integrated with a canonical transition state calculator into the AutoTST code [12] used to calculate high-pressure limit rates for H-shift reactions, additions, and abstractions. Another code from Van de Vijver et al [13] allowed the on-the-fly calculations of high-pressure limit kinetic rates for 8 types of reactions, by applying reaction templates to retrieve the TS structures. Regarding the investigation of PES, the KinBot code [14] can automatically characterize unimolecular reaction stationary points from species containing C, H, O, and S atoms. The first guesses for the intermediate structures are built based on unique moieties applied on the reactant, that are used to retrieve geometry templates, available for a set of 18 reaction families. These structures are then submitted to different levels of electronic structure calculations performed in external quantum chemistry packages and the results are organized by the code creating input files for master equations applications. In 2019, the EStokPT code was conceived by Cavallotti et al. [15], which generates the necessary intermediates structures using reaction class interatomic distance and includes a variety of advanced options for electronic structure calculation levels, kinetic solver options and corrections. Four reaction types were included in the first version of the code: abstractions, additions, isomerizations and beta-scissions. More recently, AutoMech [16] code was developed to integrate the options of EStokTP code and reaction mechanisms, allowing the on-the-fly calculations of kinetic data. Another approach for automatic TS

structure identification was proposed by Li et al. [17] for the cyclization reactions of QOOH radicals and the elimination reactions of RO₂, in their method the TS geometries are divided into two parts: the reaction center and the substituents. The reaction center includes the reactive atoms and the atoms between them and its geometry is conserved for a reaction type independently of the substituents.

The advances of the so-called “on-the-fly” kinetic and thermochemistry calculations are essential to improve the accuracy of reaction mechanisms. However, these approaches are computationally expensive and are not yet feasible for molecule sizes representative of usual fuels. In a recent work, we showed that the rate rule approach (based on correlations) for the isomerization reaction classes is no longer feasible for any degree of branching in alkyl groups and we proposed a new approach based on tabulated model transition states (TMTS)[18] as an alternative for costly on-the-fly calculations, with more accurate coefficients than the previously rate rules. In this approach, methyl groups represent alkyl groups and all combinations of substitutions in the model TSs are included in a table with associated *ab initio* rate coefficients. We proposed tables for 1-3, and 1-4-H-atom shifts and showed that the

Fig. 1. Building of all substituted structures based on a non-substituted structure for a 4-membered ring TS.

construction of a table for 1-5 or 1-6-H-atom shifts would require thousands of *ab initio* calculations[18]. Here, we present a python code for the automatic creation of TS model tables focusing on the isomerization of alkyl radicals and comparing with the results of the kinetics calculated by hand. The code allows the construction of branched structures reactions based on initial minimal structures of reactant, transition state, and product. The code then runs electronic structure calculations automatically, and the results are retrieved by the code to be used as input for kinetic calculations based on transition state theory. Finally, the code sorts and organizes the produced kinetic coefficients in a TS model table that can be used in the development of reaction mechanisms.

2. Code description

High pressure-limit rate constants are automatically calculated for H-shifts with a given TS cycle size. The code generates all the possible combinations of alkyl-substituted reaction structures, based only on the minimal (non-substituted) reactant, transition state, and product structures. Each structure is automatically submitted to geometry optimization and frequency calculations, high-level energy single point calculations, as well as the relaxed scans of the

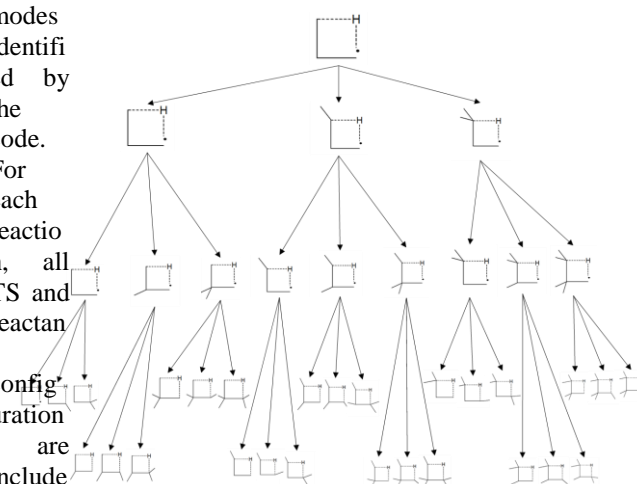
torsional modes identified by the code.

For each reaction, all TS and reactant configurations are included and sorted according to their reaction pathway.

The results of electronic calculations are retrieved by the code and used to apply the transition state theory, including 1D-HRU treatments for torsional modes[19] and Eckart potential-based tunneling coefficients [20]. Eventually, the code arranges the kinetic rate and coefficients in TS model tables that can be read for kinetic data estimations or coupled to automatic generator of kinetic models.

2.1. Structures representation and generation

All molecules, radicals and transition states are represented by two attributes: their cartesian coordinates and a list of bonds for carbon atoms. In a first step, the initial xyz coordinates of non-substituted reactant, product and transition state (multiple transition state configurations, such as chair and boat for 6-membered ring, can be included) are recovered from an input files (.xyz or Gaussian formats) containing the coordinates. This set of files is used as a basis for the reaction moiety investigation, with the hydrogen atoms being replaced by methyl groups to generate the branched structures, considering that the reaction moiety remains similar for the different levels of branching. Different positions (equatorial and axial) of the substituents can be identified on a cyclic TS and their combination generates several different configurations and multiple elementary reaction pathways that must be included for the kinetic rates calculations. A three-like structure is applied to create all the combinations of methyl-substituted structures based on the initial structures. The three allows the creation of all possibilities of structures (xyz coordinates) with substituents being H or CH₃ for reactants, products and transition states, as illustrated in Figure 1.

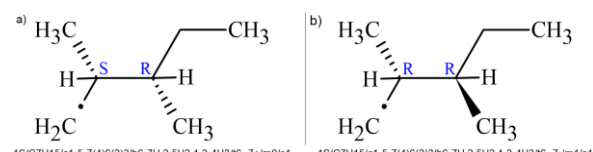


In some cases, the same structure can be generated twice. For this reason, a filter is used in the code to avoid performing expensive electronic calculations in double. To filter products and reactants, the International Chemical Identifier (InChI) [21] is used to compare the structures. The InChI codes were chosen in particular for their ability to identify multiple chiral centers, which indicates that diastereomers should be considered in the kinetic calculations. Figure 2 illustrates a reactant with two chiral centers, which results in two diastereomer configurations (RR and RS) that are neither superimposable nor mirror image of each other. In this case, they can be differentiated by their InChI \t stereochemical layer.

Fig. 2. Two diastereomers of a reactant with their InChI. a) SR diastereomer, b) RR diastereomer. The InChI code does not identify the classification of chiral center as R or S, it only differentiates the centers on the same structure.

Because of the cyclic structure of the transition states, a specific filtering process was developed, based on the calculated distance between the substituents of the carbon atoms and the transferred hydrogen atom. This approach differentiates between axial/equatorial positions of the substituents and allows the identification of identical TS structures. Importantly, the code selected the radicals based on the sum of distances between carbon atoms in order to identify the most extended, since this is generally the most stable configuration for hydrocarbon chains [17].

The identification of the dihedrals corresponding to torsional modes is assembled from the list of carbon bonds. The current version of the code allows the

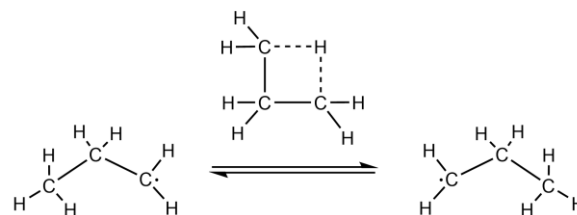


identification of all dihedrals for C, H and O containing species.

2.2. Electronic structures calculations

The 3D structures generated with the code are submitted to electronic structures calculations performed using Gaussian 16 software [22]. A pre-optimization step was adopted for reactants, products (at the PM6 level) and transition state (at PM3 level). The pre-optimized structures are then submitted to optimization and frequencies calculations at the B3LYP/6-311(d,p) level. The electronic energies were calculated using the CBS-QB3 composite method. Relaxed scans of torsions were performed at the B3LYP/6-311(d,p) level with steps of 10° . These methods were selected based on our previous studies [18] that indicated low uncertainties levels (a maximum factor of 2.2) compared to advanced level

of theories for hydrogen transfers in alkyl radicals. It can be noted that the code is flexible and can use other levels of theory such as those commonly found in



Gaussian software. The code prepares and run the Gaussian inputs on the computing resources of the EXPLOR computer center of the Université de Lorraine.

2.3. Electronic calculation results treatment

Once the Gaussian calculations are completed, the code scans the output files to retrieve the optimized geometries, frequencies, electronic energies, and the torsional potentials. During this screening, the code verifies if the convergence was achieved. If it is not the case, a new input is created including force constants calculations. The code also verifies if the dihedral scans resulted in lower energy conformers, in which case another input is created for the calculations with the lower energy geometry.

The identification of external symmetry is performed by the code that calls an external software: Platon [23]. This software was originally created for crystallography applications, but it contains options for non-crystallographic structures. This software identifies the external symmetry using the SYMMOL algorithm from T. Pilati & A. Forni [24]. Platon also identifies and classifies chiral centers (R or S) in the geometry, which is used for the identification of the number of optical isomers and stored for reaction pathways sorting. Each reactant represented in Figure 1 passes through different transition states and the code is able to reconstruct the elementary pathways between reactants and TS from the chiral center identifications.

The potential curves of relaxed scans are read by the code and identified either as free or hindered rotor, according to the maximal energy difference. For the cases studied here, a threshold value of $0.8 \text{ kcal mol}^{-1}$ was chosen to consider a torsion as hindered rotor. The potential curve is fitted as a Fourier expression with 20 parameters that will be used to solve the 1D Schrodinger equation and correct the vibrational partition function with the 1D-HRU method[19]. Our code checks the quality of the fits and warns the user if the Fourier expression points present an average absolute deviation (AAD) compared to the original potential curve higher than certain threshold ($0.01 \text{ kcal mol}^{-1}$) or if a given point presents an absolute deviation higher than a certain limit ($0.05 \text{ kcal mol}^{-1}$).

The symmetry of the torsional mode is identified using two approaches: either by the analysis of the potential curves or by the analysis of the structure

itself. The first approach is applied mainly to hindered rotors that generally have an evident symmetry that can be identified by maximal and minimum. For free rotors, however, the identification of symmetry by the potential curves is not straightforward, thus the code analyses the bonds of each pivot atom to recognize similar substituents and calculate the torsional symmetry. In the case of free rotors, the associated vibrational frequency is identified in the normal modes of the Gaussian output file and removed from the partition function.

2.4. Kinetic parameter calculations and post-treatment

Once the geometries, energies and torsional potentials are retrieved and analyzed, input files for the ThermRot code [19] are automatically prepared by the code for each reaction pathway. ThermRot calculates high-pressure rate constants using canonical transition state theory:

$$k(T) = \kappa(T)n_e \left(\frac{k_b T}{h}\right) \frac{Q_{TS}(T)}{Q_R(T)} \exp\left[\frac{-\Delta E^\ddagger}{RT}\right]$$

where $\kappa(T)$ is the factor for tunnelling effect corrections, calculated by ThermRot using an Eckart potential, n_e is the statistical factor, Q_{TS} and Q_R the partition functions of the transition state and the reactant, ΔE^\ddagger the electronic energy difference between reactant and transition state. The resultant output files containing the high-pressure limit rates at different temperatures and the kinetic coefficients are recovered by the code and organized in an Excel file in the format of TS model tables.

3. Results and discussion

The code was tested for the 1,3-H-shift reactions with the starting point geometry of TS and radicals represented in Figure 3. The hydrogen in the structures were replaced by methyl according to the combinations obtained by the tree structure described in section 2.1. All possible combinations of branched reactants were produced, which lead to 27 reactions and a total of 89 structures: reactants, products and transition states, some reactions having multiple TS conformers. The structures generated agreed with the ones produced manually in our previous work [18]. For each structure, the dihedrals that must be treated as hindered rotors were identified, yielding more than 400 relaxed scans among the 89 structures.

One challenge faced by the Gaussian calculations was the convergence of the dihedral potential scans: a total of 25 cases underwent this issue. These potential energy scans were reinitiated manually with another optimization algorithm. From the resultant electronic calculations, the first launch of the code identified ten structures for which a more stable geometry was

found by scans of dihedrals. The code generated new input files that were launched and used to replace the former structures. Finally, once all the structures were converged, the code was able to retrieve the data necessary to TST application and run ThermRot code automatically for all reactions, with the results being organized in an excel file.

Most part of the rate constants obtained automatically were similar to the ones calculated manually, with differences of less than 20% mostly due to distinction in the optimized geometry and fitting deviations. The high-pressure limit kinetic rate constants of 1,3 H-shift reaction of primary alkyl radicals are presented in Figure 4, for reactions forming primary (pp), secondary (ps) and tertiary (pt) radicals as products. These reactions were previously studied by our group [18] and by Wang et al [6], both of them agreeing with the results from the code.

The activation energy decreases in the sense $pp > ps > pt$, correlating with the reaction enthalpy that decreases with the substitution. Similarly, the barrier also decreases for thermoneutral reactions with increasing branching level (eg. $pp > ss > tt$). The kinetic rate constants obtained with the code also indicated the high impact of the branching on the TS cycle, following the results already discussed by our group [18]. An interesting example of the code potential is the reaction of a branched secondary radical (3-methyl-2-pentanyl) forming another secondary radical, containing three TS conformers presented in Figure 5. This reaction passes through three different TS as the relative positions of the methyl substituents (trans- and cis-) may vary. The code was able to generate and include all the TS configurations and obtain a single high-pressure limit rate constant, which is an important feature, especially for branched structures. We showed that, for H-shift, not accounting for all TS for such reactions can lead to

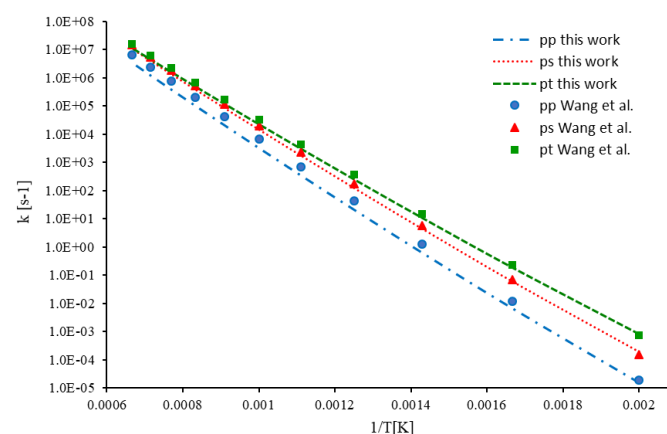


Fig. 4. Reaction rates for pp, ps and pt 1,3 H-shift reactions from this work and from Wang et al.[6]

errors of factors higher than 3 on the rate constants.

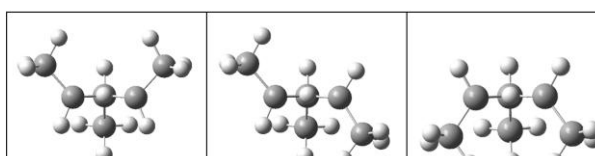


Fig. 5. Three TS conformers identified by the code for 1,3-H-shift reaction of the 3-methyl-2-pentanyl, view perpendicular to the cycle from the transferring H side.

In some cases, a high deviation was observed when rate constants computed automatically and manually were compared. We found that this was caused by different numbers of optical isomers or external symmetry identified for the structures. Revisiting the manually-built structures, it was observed that the code was able to correctly identify symmetries and isomers accurately. These results indicate the importance of the automatization to decrease the number of manual errors on the process of building new rate rules for reaction mechanisms.

4. Conclusion

A code in python for the automatic generation of tables of TS models for kinetic rate rules of isomerization reactions is presented here. The code was able to generate all the necessary structures, launch and treat electronic calculations, as well as apply transition state theory to obtain the high-pressure limit rate constants for 1,3-H-shift reactions, with all the possible methyl-substituted structures. The rate constants from the code were compared with literature data and showed good agreement, indicating the capacity of the code to correctly derive the rates for alkyl isomerizations. In particular, the code was able to automatically calculate the kinetics of a reaction with multiples transition state conformers, which is an essential feature for the acquisition of accurate rate coefficients. The results also corroborate the importance of automatization to avoid human-induced errors on the identification of isomers and symmetry. The code will be applied to create TS model tables for the most important alkyl H-shifts (1,5 and 1,6 -H-shift reactions) and also adapted to replicate the methodology for other reaction classes.

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