

EFFICIENT NUMERICAL METHOD TO INTEGRATE MULTI-WELL MASTER EQUATION FOR CHEMICAL REACTION RATES ESTIMATION*

VIATCHESLAV BYKOV¹ AND ANDREY KOKSHAROV²

¹Karlsruhe Institute of Technology, Institute of Technical Thermodynamics,
 Engelbert-Arnold-Strasse 4, Geb.10.91, 76131 Karlsruhe, Germany

²German Aerospace Center (DLR), Stuttgart, Germany

Chemical Master Equation (CME) approach can be efficiently used to evaluate rate coefficients of elementary chemical reactions on the level of molecular dynamics [1]. However, conventional methods to handle this problem especially for multi-well systems remain rather empirical and are computationally demanding [2]. The conventional method leads to a coupled linear but highly dimensional systems of equations, which are employed to delineate estimations for elementary reactions rates [2,3].

In this study a quasi-spectral method to integrate single-, multi-well CMEs systems will be presented [3]. For given reactions system CMEs are integrated such that the evolution over the whole energy range of entire populations of the species involved can be determined. The latter can be used to define the rates of elementary reactions in a systematic manner. We present a method to estimate reaction rate constants by solving inverse problem for rates of a phenomenological model. The suggested approach is illustrated by the problem of the allene isomerization into propyne through cyclopropene. The comparison of the conventional method and the proposed method will be presented demonstrating performance and to validate the suggested approach to compute the chemical reaction rates.

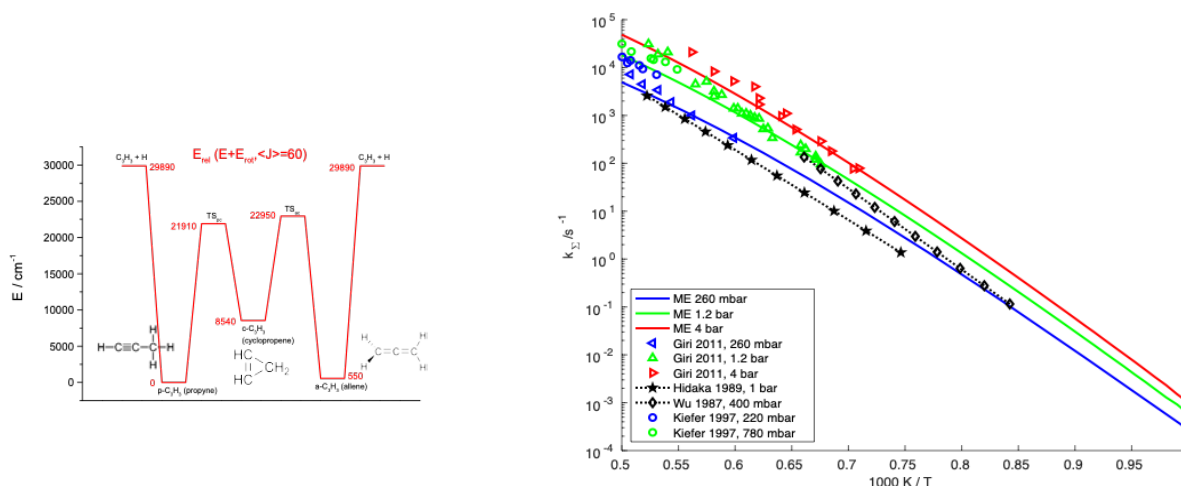


Fig.1. Left: Schematic potential energy diagram of the allene-propyne isomerization; Right: Comparison of the allene decomposition rate for different pressures as function of the initial temperatures.

Figure 1 on the left shows schematically the energy wells for allene, propyne and cyclopropene correspondingly. The reaction rates are computed by using the detailed solution of the CME [3,4]. The detailed solution of the species population over energies evolving in time [4] is then used to estimate the kinetic parameters of the phenomenological model. The latter is applied to describe the concentration (mass of the population) evolving in time. This way the results of the detailed evolution are fitted to the model which is based on the mass action and Arrhenius laws. The rates of these elementary reactions are compared to experiments and shown on the right of Fig. 1.

REFERENCES

- [1] Gilbert, R. G.; Smith, S. C. Theory of Unimolecular and Recombination Reactions; Blackwell: Oxford, UK, 1990.
- [2] Miller, J. A.; Klippenstein, S. J. J Phys Chem A, 110 (2006) 10528–10544.
- [3] Kiefer, J. H., S. S. Kumaran und P. S. Mudipalli, Chemical physics letters, 224(1-2) (1994) 51–55.
- [4] Koksharov et al, Quasi-Spectral Method for the Solution of the Master Equation for Unimolecular Reaction Systems, International Journal of Chemical Kinetics 50(5) (2018) 357-369.

* The work was supported by the DFG-TRR 150 project, project number: 237267381.