

## Pyrolysis of 2,5-Dimethylfuran – Shock Tube Study and Kinetic Modeling

Philipp Friese,<sup>1</sup> Tobias Bentz,<sup>1</sup> Lena Genthner,<sup>1</sup> Johannes Kiecherer,<sup>1</sup>  
 John Simmie,<sup>2</sup> and Matthias Olzmann<sup>1,\*</sup>

<sup>1</sup> Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

<sup>2</sup> Combustion Chemistry Centre, NUI Galway, Ireland

\* Corresponding author: matthias.olzmann@kit.edu

2,5-dimethylfuran (25DMF, structure see below) is a promising candidate for a so-called second-generation biofuel, which are biofuels that can be produced from residual or non-food biomass. To model the combustion of 25DMF, kinetic data for pyrolysis and oxidation reactions are needed. The pyrolysis of 25DMF is initiated by hydrogen split off from one of the methyl groups, because the corresponding bond dissociation energy is comparatively small due to resonance stabilization of the radical formed [1]. At low degrees of conversion, the subsequent bimolecular reactions  $H + 25DMF \rightarrow$  products are also important.

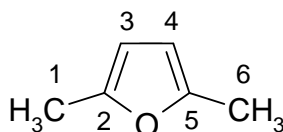
We studied the kinetics of these two reactions in a shock tube by monitoring hydrogen atoms with resonance absorption spectrometry. In the case of the unimolecular decomposition, the formation of H atoms as reaction product was observed, whereas for the bimolecular reaction, H atoms as a reactant were detected, which were produced from fast pyrolysis of ethyl iodide in an excess of 25DMF. The temperature range was 1280-1520 K and 970-1240 K, respectively, at pressures of 1.6 and 4.7 bar with argon as bath gas.

For the unimolecular decomposition, we found rate coefficients, which were pressure and temperature dependent. For the bimolecular reaction, no discernible pressure dependence could be detected, and the temperature dependence is weak [2]. The results for both reactions were analyzed in terms of statistical rate theory with molecular and transition state data from quantum chemical calculations. Master equations were used with specific rate coefficients from RRKM theory and a simplified statistical adiabatic channel model. The agreement between the measured and calculated rate coefficients is very good, which indicates the adequacy of the proposed mechanisms and the reliability of the quantum chemical results. For the  $H + 25DMF$  reaction, H atom addition to the carbon atom 2 or 5 with subsequent  $CH_3$  split off from the intermediate radical was identified as the dominating reaction pathway [2].

We additionally performed shock tube studies with time-of-flight mass spectrometry to examine the overall pyrolysis mechanism. We were able to monitor concentration-time profiles for 25DMF, furan, and  $C_2H_n$  ( $n = 2, 4, 6$ ). The results are discussed in terms of a mechanism proposed earlier by Lifshitz et al. [3] and more recent modifications.

### References

- (1) Simmie, J.M.; Curran, H.J. *J. Phys. Chem. A* **2009**, 113, 5128-5137.
- (2) Friese, P.; Simmie, J.M.; Olzmann, M. *Proc. Combust. Inst.* (submitted).
- (3) Lifshitz, A.; Tamburu, C.; Shashua, R. *J. Phys. Chem. A* **1998**, 102, 10655-10670.



Structure of 2,5-dimethylfuran.