

## Scientific Report

*COST Action:* “**Chemistry of smart energy carriers and technologies – SMARTCATs CM1404**”

*Title of STSM project:* „**Pulsed-laser kinetic study of the reactions of OH radicals with cyclic ethers**”, proposed by Á. Illés

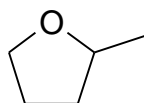
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*Host institution:* Institute of Physical Chemistry – Molecular Physical Chemistry Group, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

*Head of host research group:* **Prof. Dr. Matthias Olzmann**

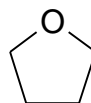
*Date of visit:* January 18 – March 18, 2016

Simple cyclic ethers, such as **(1)**–**(2)**, have entered the focus of interest as green solvents, renewable platform molecules and promising ‘second-generation’ biofuels that can be produced from biomass [1] providing the potential to mitigate global warming.



MTHF **(1)**

2-methyltetrahydrofuran



THF **(2)**

tetrahydrofuran

The reactions of cyclic ethers with OH radicals are of importance concerning both their atmospheric fate and their combustion chemistry. Besides the practical need to provide rate parameters for computer models, kinetic studies of OH + cyclic-ether reactions are of great interest from a basic reaction kinetic point of view as well, in particular because they are likely to proceed through the formation of pre-reaction complexes (PRCs) [2].

Recently, as part of my PhD research program at Budapest, I have started a detailed investigation of the kinetics of the reaction of OH with MTHF:



In a series of investigations performed at room temperature, I have applied at Budapest the direct kinetic technique of low-pressure fast discharge-flow (DF) coupled with resonance fluorescence detection of OH radicals (RF) ( $T = 298 \text{ K}$ ,  $p = 2.8 \text{ mbar He}$ ). The rate

coefficient determined has been found to be more than 50% lower than that reported at higher pressures, above ~50 mbar [3], which may indicate a possible pressure dependence.

My visit to Karlsruhe provided the possibility to study the reactions of cyclic ethers with OH radicals at still higher pressure, and over a wide pressure range. I have got acquainted with new experimental techniques at KIT and got new results with methods that are not available for us in Budapest. I have learned and applied the pulsed laser photolysis (PLP) – pulsed laser-induced fluorescence (PLIF) experimental technique (see e. g., [4] and references therein). I studied the kinetics of reaction (1) at pressures of 3, 5, and 7 bar at room temperature. Additionally, I have performed survey experiments of the reactions OH + THF (2) and OH + THF-d8 (3) at these pressures.

The experiments were carried in a slow-flow reactor with helium as the bath gas by using pulsed laser photolysis/laser-induced fluorescence for production/detection of OH radicals in an excess of the reactant to ensure pseudo first-order conditions. The reactor was a cylindrical stainless steel cell equipped with three quartz windows. The temperature was measured at the entrance and exit of the cell with thermocouples, and the difference between the two values never exceeded 2 K, the average was taken as reaction temperature. The gas flow was controlled by three mass flow controllers, and accumulation of reaction products was avoided by choosing appropriate flow velocities.

Two radical sources, nitric acid and tert-butyl hydroperoxide, were used as precursors for OH, which allowed to assess potential systematic errors. The precursors were photolyzed with a KrF-excimer laser at a wavelength of 248 nm. The probe laser system consisted of a dye laser operated with Coumarin 153 and pumped by a XeCl-excimer laser at 308 nm. The frequency of the dye laser output was doubled with a BBO crystal to obtain the OH excitation wavelength of 281.9 nm. The nonresonant fluorescence of OH at  $308 \pm 1$  nm was detected perpendicular to the antiparallel photolysis and probe laser beam. The influence of scattered light was minimized by filtering out other wavelengths with a monochromator. The temporal resolution of the experiment was achieved by varying the time delay between the photolysis and probe laser pulses in steps of 0.2  $\mu$ s with a delay generator. The repetition rate was 10 Hz. The gas mixtures were prepared manometrically in gas cylinders and allowed to homogenize for at least 24 hours before use.

The reactions showed no pressure dependence (Fig. 1), and the determined rate coefficient for the reaction of OH + MTHF  $\rightarrow$  products (1) agrees well with the literature value at room temperature [3]. The following average rate coefficients have been obtained in the pressure range of 3-7 bar (the errors represent  $2\sigma$  statistical uncertainty):

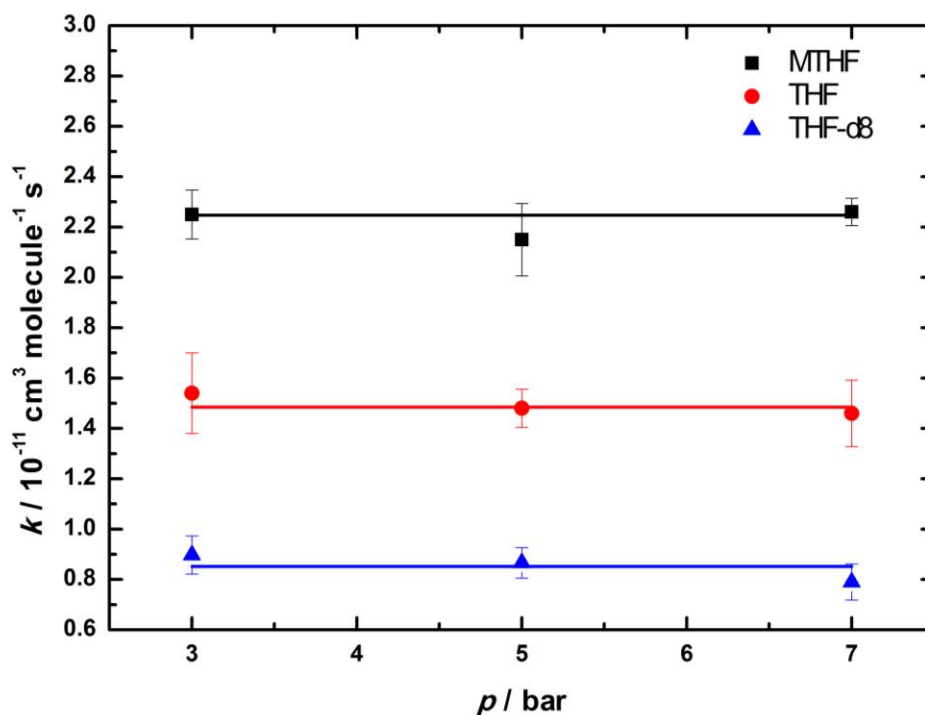
$$k_1 = (2.25 \pm 0.09) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (1.48 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_3 = (8.51 \pm 0.82) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

As is obvious from these results, methyl substitution enhances the reactivity of the cyclic ether THF, which is due to the increased number of abstractable H atoms and the formation of more stable PRCs. The pressure independence of the reactions indicates that the PRC has lost its excess energy by multiple collisions with bath gas molecules and that it is the thermalized complex that undergoes water elimination to complete the H-abstraction process. The primary kinetic deuterium isotope effect observed for the reactions OH + THF (2) and OH + THF-d8 (3) is  $k_2/k_3 = 1.74 \pm 0.44$ . This is a relatively small value, implying that additional experiments at other temperatures and pressures should be performed to obtain further information.

Our results will be presented at the forthcoming Gas Kinetics Symposium in York [5].



**Figure 1.** Pressure dependence of the rate coefficients of OH reactions with cyclic ethers MTHF, THF, and THF-d8 ( $T = 298 \text{ K}$ ).

- [1] Hayes, D. (2009). An examination of biorefining processes, catalysts and challenges. *Catal. Today* 145:138-151.
- [2] Simmie, J. (2012). Kinetics and Thermochemistry of 2,5-Dimethyltetrahydrofuran and Related Oxolanes: Next Next-Generation Biofuels. *J. Phys. Chem. A* 116:4528-4538.
- [3] Wallington, T., Siegl, W., Liu, R., Zhang, Z., Huie, R. and Kurylo, M. (1990). The Atmospheric Reactivity of Alpha-Methyltetrahydrofuran. *Environ. Sci. Technol.* 24:1596-1599.
- [4] Bänisch, C., Kiecherer, J., Szőri, M. and Olzmann, M. (2013). Reaction of Dimethyl Ether with Hydroxyl Radicals: Kinetic Isotope Effect and Prereactive complex formation. *J. Phys. Chem. A* 117:8343-8351.
- [5] Zügner, C. L., Illés, Á., Hetzler, J. and Olzmann, M. (2016). Kinetics of the Reaction of OH Radical with Cyclic Ethers. *24<sup>th</sup> International Symposium on Gas Kinetics and Related Phenomena*, University of York, 17-21 July 2016 (submitted for poster).

Budapest, 14 April 2016

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