

# Environmental Chemistry of Cyclic Ethers and Esters: Reaction Kinetic and Photochemistry Studies

*Summary of PhD Thesis*

**Ádám Illés**

Thesis supervisor: Sándor Dóbé, DSc

**ELTE TTK Doctoral School of Environmental Sciences**

Head of Doctoral School: Imre Jánosi, DSc

**Environmental Chemistry Program**

Head of Doctoral Program: Tamás Turányi, DSc

**RCNS HAS**

**Institute of Materials and Environmental Chemistry**

**Green Chemistry Group**

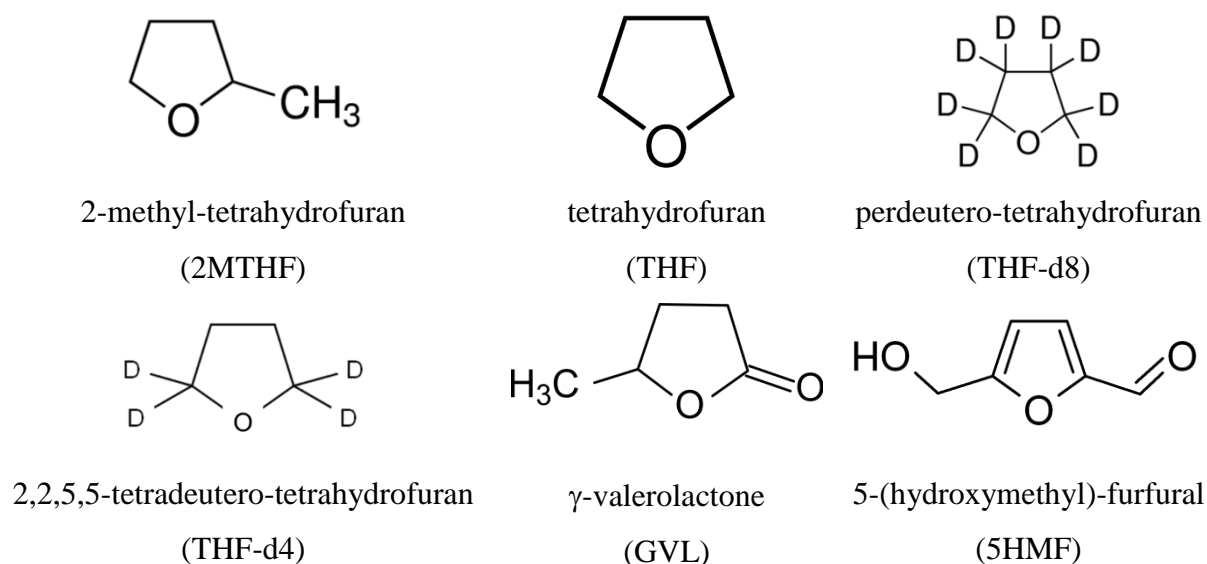


**Budapest, 2019**

## 1. INTRODUCTION

Fossil substances used for energy production, in the organic chemical industry and transportation, are increasingly important to be replaced by alternative, renewable raw materials due to their impact on climate change and engraved by their decreasing supply and increasing prices. The so-called second generation (2G) biofuels and chemicals are ones that can be produced from non-edible biomass and are gaining more and more importance. One of the most significant large-scale 2G biomaterials is levulinic acid (LA), which can be produced from biomass through 5-(hydroxymethyl)-furfural (5HMF), and can be further transformed into valuable molecules such as  $\gamma$ -valerolactone (GVL), ethyl levulinate (ELA), or 1,4-pentanediol. Dehydration of the latter produces 2-methyl-tetrahydrofuran (2MTHF).

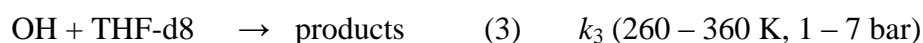
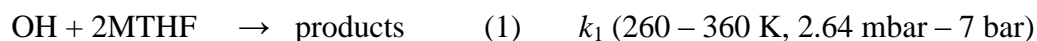
2MTHF is an excellent solvent and a potential biofuel which is liquid in a wide temperature range, and can therefore be used as a substitute for tetrahydrofuran (THF). THF is one of the most important organic solvents, its production from renewable materials is recently increasing.  $\gamma$ -valerolactone is a cyclic ester, which occurs in natural resources. Recently, Hungarian researchers have developed a very efficient catalytic method for its production from carbohydrates. 5-(hydroxymethyl)-furfural occurs also in nature, and it is a versatile platform molecule.



In the future, biomaterials produced on an industrial scale and widely used as solvents and fuels will inevitably get into the environment, where they influence the chemistry of the environment through their chemical and photochemical processes. Complex chemical

processes of the atmosphere and combustion are studied by computer models. Accuracy of the results largely depends on the reliability of the models and the accuracy of the input parameters, such as rate coefficients of elementary reactions, absorption coefficients, and photodissociation quantum yields. The subject of my thesis is the determination and discussion of such parameters.

Model molecules of my PhD research are cyclic ethers and cyclic esters, and the following elementary reactions and photochemical processes (1)–(6) have been investigated:



Rate coefficients ( $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ ) for elementary reactions have been determined, and their temperature and pressure dependences ( $T$ ,  $p$ ) have been studied. The kinetic results have been discussed in terms of structure-reactivity relationships. Tropospheric lifetimes of the studied molecules ( $\tau_{\text{OH}}(2\text{MTHF})$ ,  $\tau_{\text{OH}}(\text{THF})$ ,  $\tau_{\text{OH}}(\text{THF-d8})$  and  $\tau_{\text{OH}}(\text{THF-d4})$ ), as well as their Photochemical Ozone Creating Potentials ( $\varepsilon_{2\text{MTHF}}^{\text{POCP}}$ ,  $\varepsilon_{\text{THF}}^{\text{POCP}}$ ,  $\varepsilon_{\text{THF-d8}}^{\text{POCP}}$  és  $\varepsilon_{\text{THF-d4}}^{\text{POCP}}$ ) have been estimated. The absorption spectra of GVL and 5HMF have been determined in two solvents ( $\sigma_{\text{GVL}}(\lambda)$  and  $\sigma_{5\text{HMF}}(\lambda)$ ), and the photodissociation quantum yields of GVL,  $\Phi_5(248 \text{ nm})$ , and 5HMF,  $\Phi_6(308 \text{ nm})$  have been assessed at two exciplex-laser wavelengths.

In the kinetic literature, the elementary reactions of OH radicals have been studied most frequently, the results are discussed in several critical data evaluations because of their great importance in atmospheric chemistry and combustion. Although few works have been published on the OH + THF (2) reaction, but, to my knowledge, there is no data available on the OH-reactions of the deuterated THF derivatives, and only one publication has been reported on the kinetics of the OH + 2MTHF (1) reaction.

The photochemistry of GVL has been studied in our Research Group previously. The results obtained at the 248 nm photolysis wavelength are likely hampered by systematic

errors, therefore the absorption spectra have been remeasured, and the photodissociation quantum yields have been recalculated; the quantum yields have also been determined in distilled water.

In our Research Group the photophysics and photoreduction kinetics of 5HMF are being studied experimentally and by theoretical means. I have joined this study and determined the absorption spectra and photodissociation quantum yields of 5HMF as presented in my PhD Thesis.

## **2. EXPERIMENTAL**

I have used several experimental setups and methods in my reaction kinetic and photochemical experiments. Part of the experimental arrangements and methods were available for me, but I also participated in the development and optimization of the experimental techniques.

Kinetic experiments of the gas-phase elementary reactions were performed by using the so-called „direct” or „absolute” techniques, and beside them the relative-rate (RR) method. For the absolute methods the atoms and free radicals were detected directly by using optical methods. Application of the RR technique involved the comparison of the rate of the measured reaction with that of a reference reaction. In this way rate coefficient ratios were determined that were put to the absolute scale by means of literature data for the reference reaction.

The OH-reactions were studied at room temperature by the application of the Discharge Flow (DF) technique and, in the framework of a study tour in Germany, by employing the Pulsed Laser Photolysis (PLP) method. At applying the DF method, OH radicals were detected by resonance-fluorescence (RF), while in the PLP experiments the detection method was Laser Induced Fluorescence (LIF). The reactions were studied under pseudo-first-order conditions. Temperature dependence of the OH reactions was determined by using the RR method, where the depletion rates of the reactants were determined by gas chromatographic analysis (GC), using diethyl-ether and cyclohexane as reference reactants.

The DF experiments of the OH + 2MTHF (1) reaction were carried out in a tubular reactor in a fast flow of helium carrier gas. The reactor was equipped with a movable injector, positioned axially, in which the OH radicals were produced, by reacting NO<sub>2</sub> and H atoms generated by a microwave discharge. At the end of the injector the reactant immediately reacted with the OH radicals, the reaction time was determined by the distance between the

injector and the detector. OH radicals were detected by RF, and the reactions were carried out at low pressure ( $p = 2.64$  mbar).

In the PLP experiments, OH radicals were generated by exciplex-laser photolysis of nitric acid or tert-butyl hydroperoxide vapour. Following the laser flash, the OH radicals enter reaction with the reactant and their concentration decreases, which was determined by LIF method. The reactor and gas lines were made of stainless steel and reactions (1)–(3) could be tested at atmospheric and higher pressures ( $p = 1$ – $7$  bar).

The RR experiments were carried out at atmospheric pressure in a quartz cell filled with the OH radical source methyl nitrite, the reactant, reference reactant, and 2,2,2-trifluoroethanol GC internal standard in synthetic air buffer gas. The gas mixtures were irradiated using a modified movie projector, which resulted in the photooxidation of methyl nitrite and the formation of OH radicals. Gas chromatographic samples were taken at different time intervals, and the quantitative composition of the gas mixture was analyzed. Comparing the rate of loss of the reactant to that of the reference compound the rate coefficient ratio was obtained. Using the rate coefficients of the reference reaction the rate coefficient ratio is put to an absolute scale. Reactions (1)–(4) were studied in the temperature range of  $T = 260$  to  $360$  K at seven temperatures.

The photolysis experiments were carried out using exciplex lasers, and the depletion of the concentration of the studied molecules was determined by chromatographic analysis. At the photochemical study of GVL, a pulsed laser filled with KrF gas mixture ( $\lambda = 248$  nm) was used, and the decrease of the concentration due to laser photolysis was measured by a GC. The photodissociation of 5HMF was studied by a pulsed laser filled with XeCl gas mixture ( $\lambda = 308$  nm), and the depletion of concentration of 5HMF was followed by liquid chromatography (HPLC).

### **3. POSSIBLE PRACTICAL APPLICATIONS**

My PhD thesis presents essentially the results of a fundamental photochemical and reaction kinetic study which has, however, practical implications as well. I have determined reaction kinetics and photochemistry parameters of atmospheric chemistry importance that can be applied as input data into atmospheric chemistry model calculations. Such parameters are, for example, rate coefficients of OH reactions, absorption cross-sections and photodissociation quantum yields. The most important initial steps in the atmospheric

degradation of organic molecules are their reactions with OH radicals or photolysis. These are usually the rate-limiting steps in the atmospheric degradations of organic molecules.

The atmospheric lifetimes of the studied molecules with respect to their OH-reactions ( $\tau_{\text{OH}}$ ) are estimated by the measured rate coefficients providing  $\tau_{\text{OH}}(\text{2MTHF}) \sim \mathbf{11 \text{ hours}}$ ,  $\tau_{\text{OH}}(\text{THF}) \sim \mathbf{18 \text{ hours}}$ ,  $\tau_{\text{OH}}(\text{THF-d8}) \sim \mathbf{35 \text{ hours}}$  and  $\tau_{\text{OH}}(\text{THF-d4}) \sim \mathbf{35 \text{ hours}}$ . These are very short lifetimes that reflect the high reactivity of the cyclic molecules with OH radical, thus their accumulation not expected to be significant in the atmosphere.

The rate of ozone formation associated with the tropospheric degradation of organics may also be an important parameter concerning their environmental impact. Rapid OH reactions typically produce large amounts of harmful toxic ozone in the troposphere. I have estimated the Photochemical Ozone Creating Potential (POCP) of the studied cyclic molecules, which are the following:  $\epsilon^{\text{POCP}}_{\text{2MTHF}} \sim \mathbf{59}$ ,  $\epsilon^{\text{POCP}}_{\text{THF}} \sim \mathbf{55}$ ,  $\epsilon^{\text{POCP}}_{\text{THF-d8}} \sim \mathbf{42}$  and  $\epsilon^{\text{POCP}}_{\text{THF-d4}} \sim \mathbf{45}$ . These are approximately equal to the ozone creating potentials of alkanes and aliphatic ethers, but are significantly less than, for example, the POCP values of alkenes and dienes.

## 4. NEW SCIENTIFIC RESULTS

1. The rate coefficient of the gas-phase elementary reaction of OH with 2MTHF,  $k_1$ , has been determined by using two direct reaction kinetic methods (DF-RF and PLP-LIF) and the relative-rate method (RR-GC) at different pressures and temperatures. The rate coefficients determined with two independent methods at room temperature and atmospheric pressure show good agreement:  $k_1(298 \text{ K}, 1 \text{ bar}, \text{PLP-LIF}) = (2.15 \pm 0.11) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_1(298 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (2.57 \pm 0.61) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and agree reasonably well with literature. The rate coefficient is independent of pressure at atmospheric and higher pressures,  $k_1(298 \text{ K}, 1\text{--}7 \text{ bar}) = (2.41 \pm 0.54) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , however, it is significantly lower at around 2 mbar,  $k_1(298 \text{ K}, 2.64 \text{ mbar}, \text{DF-RF}) = (1.21 \pm 0.28) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The observed pressure dependence is in line with the suggestion that the reaction likely proceeds via the formation of hydrogen-bonded ‘pre-reaction’ complexes (PRCs).

2. The temperature dependence of the OH + 2MTHF (1) reaction was studied at atmospheric pressure in synthetic air. The rate coefficient decreases with increasing temperature which is in accordance with the results of the only experimental and combined theoretical studies in the literature. The Arrhenius expression, fitted to the experimental data, provides a small negative activation energy. The temperature dependence can be described well by the following expression:  $k_1(260\text{--}360 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (3.88 \pm 0.55) \times 10^{-12} \exp [(4.66 \pm 0.36 \text{ kJ mol}^{-1})/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

3. Kinetics of the elementary reaction of OH radical with tetrahydrofuran, OH + THF (2) have been studied by determination of the temperature and pressure dependences, and the primary deuterium isotope effect for the reaction. The rate coefficients determined by direct and relative methods at room temperature and atmospheric pressure show excellent agreement:  $k_2(298 \text{ K}, 1 \text{ bar}, \text{PLP-LIF}) = (1.48 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_2(298 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (1.58 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and agree reasonably well with the only, recently published kinetic data. The rate coefficient of the elementary reaction OH + THF (2) is independent of pressure at atmospheric and higher pressures:  $k_2(298 \text{ K}, 1\text{--}7 \text{ bar}) = (1.53 \pm 0.13) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

4. Similarly to the OH + 2MTHF (1) reaction, the rate coefficient of the OH + THF (2) reaction decreases slightly with increasing temperature. The observed negative temperature

dependence can be characterized by  $\sim -3 \text{ kJ mol}^{-1}$  Arrhenius activation energy, and applying the following expression:  $k_2(260\text{--}360 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (5.80 \pm 3.69) \times 10^{-12} \exp [(2.68 \pm 1.60 \text{ kJ mol}^{-1})/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

5. The kinetic isotope effect has been assessed by studying kinetics of the reactions of OH radicals with perdeutero-tetrahydrofuran (THF-d8) and 2,2,5,5-tetradeutero-tetrahydrofuran (THF-d4), OH + THF-d8 (3) and OH + THF-d4 (4). The following rate coefficient expressions have been determined:  $k_3(260\text{--}360 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (3.46 \pm 2.16) \times 10^{-12} \exp [(2.06 \pm 1.57 \text{ kJ mol}^{-1})/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  and  $k_4(260, 298 \text{ and } 360 \text{ K}, 1 \text{ bar}, \text{RR-GC}) = (3.88 \pm 3.56) \times 10^{-12} \exp [(2.68 \pm 2.29 \text{ kJ mol}^{-1})/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , from which the  $k_3 = (0.75 \pm 0.14) \times 10^{-11}$  and  $k_4 = (0.80 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  rate coefficients are calculated. Based on the ratio of the rate coefficients determined at room temperature,  $\sim 2$  primary kinetic isotope effect has been determined, which is a typical value for H-abstraction reactions:  $k_2(\text{OH}+\text{THF})/k_3(\text{OH}+\text{THF-d8}) = 2.11 \pm 0.52$  and  $k_2(\text{OH}+\text{THF})/k_4(\text{OH}+\text{THF-d4}) = 1.98 \pm 0.43$ .

6. The reaction of OH radicals with THF-d8 is independent of pressure at atmospheric and higher pressures:  $k_3(298 \text{ K}, 1\text{--}7 \text{ bar}) = (8.01 \pm 0.75) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

7. The absorption spectrum of GVL has been found to have a wide absorption band with maxima at 212 and 203 nm wavelengths in acetonitrile and water solutions, respectively. The absorption cross sections at the wavelength of the pulsed laser photolysis experiments are the following:  $\sigma_{\text{GVL}}(\text{CH}_3\text{CN}, 248 \text{ nm}, 298 \text{ K}) = (4.47 \pm 0.37) \times 10^{-21}$  and  $\sigma_{\text{GVL}}(\text{H}_2\text{O}, 248 \text{ nm}, 298 \text{ K}) = (2.50 \pm 0.13) \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ . Also, the absorption spectrum of 5HMF has a wide absorption band in the short-UV region with maxima at 281 and 285 nm wavelengths in 2-propanol and water solutions, respectively. The absorption cross sections at the wavelength of the PLP experiments are the following:  $\sigma_{5\text{HMF}}(2\text{-propanol}, 308 \text{ nm}, 298 \text{ K}) = (0.72 \pm 0.01) \times 10^{-17}$  and  $\sigma_{5\text{HMF}}(\text{H}_2\text{O}, 308 \text{ nm}, 298 \text{ K}) = (2.80 \pm 0.02) \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$ .

8. The photodissociation quantum yield of GVL (quantum yield of consumption) has been determined in water and acetonitrile solutions, and the following quantum yields have been proposed:  $\Phi_5(\text{H}_2\text{O}, 248 \text{ nm}, 298\text{K}) = 0.05 \pm 0.01$  and  $\Phi_5(\text{CH}_3\text{CN}, 248 \text{ nm}, 298\text{K}) = 0.10 \pm 0.03$ . According to the proposed photochemical mechanism, following light absorption, the GVL ring opens at different sites forming different biradicals that leads to the formation of the identified products. The biradicals can reform the initial GVL molecule, which explains the



less-than-unity quantum yield. The photodissociation quantum yield of 5HMF has been determined in water and 2-propanol solutions. The quantum yield decreases significantly with increasing light intensity, which can be understood by competitive photoreductive and triplet-triplet annihilation processes. The following quantum yields have been determined:  $\Phi_6(\text{H}_2\text{O}, 308 \text{ nm}, 298 \text{ K}) = 0.009\text{-}0.019$  and  $\Phi_6(\text{2-propanol}, 308 \text{ nm}, 298 \text{ K}) = 0.10\text{-}0.28$ .

**9.** Based on my kinetic results, the following conclusions can be formulated about **structure-reactivity relationships**: *i)* the cyclic ethers react by high rates with OH radicals, similarly to aliphatic ethers, which implies that the activating effect of the ether bond is manifested also in the ring structure; *ii)* the reactivity of 2MTHF with OH is the highest among the studied reactions which is due to the low C–H bond-dissociation energy at the  $\alpha$  carbon atom; *iii)* pressure dependence is observed at a few mbar of pressure only; *iv)* the studied reactions are likely to proceed via H-atom abstraction, occurring via formation of prereaction complexes (PRCs), and the reactions have no activation barriers.

**10. Atmospheric implications:** The following tropospheric lifetimes with respect to OH-reactions have been proposed: 2MTHF: 11 hours, THF: 18 hours, THF-d8: 35 hours and THF-d4: 35 hours, thus accumulation of these cyclic molecules is not expected in the atmosphere. The following Photochemical Ozone Creating Potentials (POCP) have been estimated:  $\epsilon^{\text{POCP}}_{2\text{MTHF}} \approx 59$ ,  $\epsilon^{\text{POCP}}_{\text{THF}} \approx 55$ ,  $\epsilon^{\text{POCP}}_{\text{THF-d8}} \approx 42$ , and  $\epsilon^{\text{POCP}}_{\text{THF-d4}} \approx 45$ , which are approximately equal to the ozone creating potentials of alkanes and aliphatic ethers, but are significantly less than, for example, the POCP values of alkenes and dienes. 2-methyl-tetrahydrofuran (2MTHF) has absorption in the VUV region, thus photolysis of the molecule is not expected to take place in the troposphere. The 5HMF molecule has significant absorption in the actinic region ( $\lambda > 290 \text{ nm}$ ), so its photodegradation can be of considerable significance in the troposphere.

## 5. LIST OF SCIENTIFIC PUBLICATIONS

### *Publications Directly Related to the PhD Thesis:*

1. Mária Farkas, Emese Szabó, Gábor László Zügner, Dóra Zsibrita, Ádám Illés, Balázs Petri, Sándor Dóbé: *Kinetic Studies of Second Generation Biofuels*, Proceedings of the European Combustion Meeting 2011, Paper No. 310.
2. Mária Farkas, Ádám Illés, Balázs Petri, Sándor Dóbé: *Direct rate constant for the reaction of OH radicals with the biofuel molecule ethyl levulinate*, Reaction Kinetics, Mechanisms and Catalysis, 104, 251-257 (2011). If.: 0.610. Cit.: 1.
3. Xinli Song, Gábor L. Zügner, Mária Farkas, Ádám Illés, Dariusz Sarzyński, Tamás Rozgonyi, Baoshan Wang, Sándor Dóbé: *Experimental and Theoretical Study on the OH-reaction Kinetics and Photochemistry of Acetyl-Fluoride (CH<sub>3</sub>(O)F) an Atmospheric Degradation Intermediate of HFC-161 (C<sub>2</sub>H<sub>5</sub>F)*, Journal of Physical Chemistry A, 119, 7753–7765 (2015). If.: 2.693. Cit.: 5.
4. Ádám Illés, Mária Farkas, Erzsébet Gombos, Gábor László Zügner, Gyula Novodárszki, Sándor Dóbé: *Kinetics of the Reaction of OH Radical with the biofuel molecule 2-Methyltetrahydrofuran*, Proceedings of the European Combustion Meeting 2015, Paper P1-10.
5. Farkas Mária, Illés Ádám, Gombos Erzsébet, Zügner Gábor László, Béres Marianna, Demeter Attila, Dóbé Sándor: *Második generációs bioüzemanyagok légkörkémiája: reakciókinetikai és fotokémiai kutatások*, Magyar Kémiai Folyóirat, 121:(2-3) pp. 102-109. (2015).
6. Farkas Mária, Illés Ádám, Zügner Gábor László, Szilágyi István, Décsiné Gombos Erzsébet, Dóbé Sándor: *Második generációs bioüzemanyagok reakciókinetikai és fotokémiai kutatása*, 1. MÉB Égéstudományi Konferencia, Budapest, ELTE, 2014. október 28., Konferencia Kiadvány, ISBN: 978-963-12-1258-7.
7. Ádám Illés, Mária Farkas, Gábor László Zügner, Gyula Novodárszki, Magdolna Mihályi, Sándor Dóbé: *Direct and relative rate coefficients for the gas-phase reaction of OH radicals with 2-methyltetrahydrofuran at room temperature*, Reaction Kinetics, Mechanisms and Catalysis, 119, 5–18 (2016). If.: 1.265. Cit.: 6.

8. Ádám Illés, Mária Nagy, Gyula Novodárszki, Magdolna R. Mihályi, Sándor Dóbé: *Temperature Dependent Rate Coefficient for the Reaction of OH Radicals with 2-Methyltetrahydrofuran in Gas Phase*, *Oxidation Communications*, 41, 189–194 (2018). If.: 0.489. Cit.: 1.
9. Ádám Illés, Erzsébet Gombos, Mária Nagy, Sándor Dóbé: *Relative-rate and photochemistry study of biomass-derived cyclic oxygenates*. 4. MÉB Égéstudományi Konferencia, Miskolc, ME, Magyar Égéstudományi Bizottság, 2018. November 10., ISBN 978-615-00-4216-9.

***Publications in Preparation Directly Related to the PhD Thesis:***

1. Ádám Illés, Zsófia Borbála Rózsa, Mária Nagy, Milán Szőri, Sándor Dóbé: *Experimental and theoretical study of the reactions of hydroxyl radicals with tetrahydrofuran and deuterio tetrahydrofurans*, *Chemical Physics Letters*, a benyújtás várható ideje: 2019. február. If.: 2.693
2. Attila Demeter, Ádám Illés, Marianna Béres, Szabolcs Góger, Sándor Dóbé, József Valyon, György Lendvai: *Photophysical Properties and Photoreduction Kinetics of 5-(Hydroxymethyl)-furfural*, *Journal of Physical Chemistry A.*, a benyújtás várható ideje: 2019 április. If.: 2.836.

***Other publications:***

1. Gyula Novodárszki, József Valyon, Ádám Illés, Sándor Dóbé, Magdolna R. Mihályi: *Synthesis and characterization of Al-magadiite and its catalytic behavior in 1,4-pentanediol dehydration*, *Reaction Kinetics, Mechanisms and Catalysis*, 121, 275-292 (2017). If.: 1.264. Cit.: 2.
2. Gyula Novodárszki, József Valyon, Ádám Illés, Sándor Dóbé, Dhanapati Deka, Jenő Hancsók, Magdolna R. Mihályi: *Heterogeneous hydroconversion of levulinic acid over silica-supported Ni catalyst*, *Reaction Kinetics, Mechanisms and Catalysis*, November 2018, DOI: 10.1007/s 11144-018-1507-9. If.: 1.515. Cit.: 1.

### ***Lectures in English:***

1. Ádám Illés: *Discharge flow study of the reaction of 2-methyltetrahydrofuran with OH radical*, Karlsruhe Institute of Technology, Group Seminar, Karlsruhe, Germany, March 4, 2016.
2. Ádám Illés, Mária Nagy, Gábor László Zügner, Matthias Olzmann, Sándor Dóbé: *Kinetic study of the biomass-derived renewable biomolecule 2-methyltetrahydrofuran*, Mini-conference on Biomass, Waste and Renewable Energy, Budapest, 2016. június 6.

### ***Lectures in Hungarian:***

1. Illés Ádám, Zügner Gábor László, Farkas Mária, Décsiné Gombos Erzsébet, Dóbé Sándor: *A hidroxilgyök és a 2-metil-tetrahidrofurán gázfázisú elemi reakciójának kinetikai vizsgálata*, MTA Reakciókinetikai és Fotokémiai Munkabizottság ülése, Debrecen, 2015. március 26.
2. Illés Ádám, Zügner Gábor László, Nagy Mária, Balla Áron, Dóbé Sándor, Matthias Olzmann: *Gyűrűs éterek léghőri élettartama: OH-reakciók kinetikai vizsgálata*, 5. Környezatkémiai Szimpózium, Tihany, 2016. október 6.
3. Illés Ádám, Zügner Gábor László, Nagy Mária, Dóbé Sándor, Matthias Olzmann: *Az OH-gyök gyűrűs éterekkel végbemenő reakciójának kinetikai vizsgálata abszolút és relatív kísérleti módszerrel*, MTA Reakciókinetikai és Fotokémiai Munkabizottság ülése, Mátraháza, 2016. november 3.
4. Illés Ádám: *Gyűrűs éterek és észterek környezeti kémiája: reakciókinetikai és fotokémiai kutatások - PhD értekezés alapjául szolgáló eredmények előzetes bemutatása*, MTA Reakciókinetikai és Fotokémiai Munkabizottság, a Koordinációs Kémiai Munkabizottság és a VEAB Kémiai Szakbizottság együttes ülése, MTA Székház, Veszprém, 2018. november 8.

### ***Posters***

1. Mária Farkas, Emese Szabó, Gábor László Zügner, Dóra Zsibrita, Ádám Illés, Balázs Petri, Sándor Dóbé: *Kinetic studies of second generation biofuels*, 5th European Combustion Meeting ECM 2011 Cardiff, United Kingdom, June 28 - July 1, 2011.

2. Mária Farkas, Ádám Illés, Balázs Petri, Dóra Zsibrita, Gábor László Zügner, Sándor Dóbé: *OH reaction kinetics of the biofuel molecules  $\gamma$ -valerolactone and ethyl levulinate*, 2nd Annual Meeting of CM0901, Zaragoza, Spain, September 7-9, 2011.
3. Mária Farkas, Emese Szabó, Ádám Illés, Balázs Petri, Dóra Zsibrita, Sándor Dóbé: *Reaction kinetics and photochemical study on the atmospheric fate of the biofuel molecules ethyl levulinate and  $\gamma$ -valerolactone*, 34th International Symposium on Combustion, Warsaw, Poland, July 29-August 3, 2012.
4. Ádám Illés, Mária Farkas, Gábor László Zügner, Erszébet Gombos, Sándor Dóbé: *Rate Coefficient for the reaction of OH radical with 2-Methyltetrahydrofuran*, 1<sup>st</sup> General Meeting of the SMARTCATs COST Action, Thessaloniki, Greece, August 26-28, 2015.
5. Gábor László Zügner, Ádám Illés, Jens Hetzler, Matthias Olzmann: *Kinetics of the Reaction of OH Radical with Cyclic Ethers*, 24th International Symposium on Gas Kinetics and Related Phenomena, York, United Kingdom, July 18-21, 2016.
6. Gábor László Zügner, Ádám Illés, Jens Hetzler, Sándor Dóbé, Matthias Olzmann: *Rate Coefficients for the Reactions of OH Radicals with Cyclic Ethers*, 2. MÉB Égéstudományi Konferencia, MTA TTK, Budapest, 2016, október 21.
7. Ádám Illés, Erszébet Gombos, Mária Nagy, Sándor Dóbé: *OH-reaction Kinetics and Photochemistry of Biomass-derived Cyclic Ethers*, Workshop on Gas-phase Reaction Kinetics of Biofuels Oxygenated Molecules, Milan, Italy, April 23–24, 2018.