

# Kinetics of the Reaction of OH Radical with Cyclic Ethers

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Simple cyclic ethers such as 2-methyltetrahydrofuran (MTHF), tetrahydrofuran (THF), and 2,5-dimethyltetrahydrofuran (DMTHF) have become a focus of interest as green solvents, renewable platform molecules, and promising ‘second generation’ biofuels. Among them MTHF is one of the most promising biomolecules that can be produced from biomass with high yields through levulinic acid by using patented procedures.<sup>1</sup> The reactions of cyclic ethers with OH radicals are of importance concerning both their atmospheric fate and their combustion chemistry.

Kinetics of the OH reactions with the above mentioned furanics were studied in a slow-flow reactor by applying pulsed laser photolysis/laser-induced fluorescence technique. HNO<sub>3</sub> or tert-butyl hydroperoxide were photolyzed with a KrF excimer laser at 248 nm to produce OH radicals. The probe-laser system consisted of a dye laser operated with Rhodamine 6G and pumped by a Nd:YAG laser at 532 nm. The experiments were carried out in a temperature range of 208–298 K at pressures between 30 and 7000 mbar He under pseudo-first order conditions. Experiments at higher temperatures are being in progress.

The rate coefficients of all three reactions studied show a negative temperature dependence (Fig. 1), but no pressure dependence was observed. The determined rate coefficient for the reaction

OH + MTHF → products agrees well with the literature data<sup>2</sup> at room temperature, but we have found a weaker temperature dependence. The H-abstraction by OH radical is preceded by the formation of pre-reaction H-bonded complexes (PRC) having the substantial stabilization energy of about −26 kJ mol<sup>−1</sup>.<sup>3</sup> The methyl substitutions enhance the reactivity 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 the bath gas molecules and that it is the thermalized complex that undergoes water elimination to complete H-abstraction.

**Figure 1.** Temperature dependence of the rate coefficients

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(1) Hayes, D. J. *Catal.Today* **2009**, 145, 138-151.

(2) Wallington, T. J.; Siegl, W. O.; Liu, R.; Zhang, Z.; Huie, R. E.; Kurylo, M. J.; *Environ. Sci. Technol.* **1990**, 24, 1596-1599.

(3) Simmie, J. J. *Phys. Chem. A* **2012**, 116, 4528-4538.