

Kinetic Investigation of the Reactions of Cyclic Ethers with Hydroxyl Radicals

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Diminishing fossil-fuel reserves and growing concerns about global warming indicate that sustainable energy sources are increasingly needed. A promising biofuel candidate is 2,5-dimethylfuran (DMF), which is relatively easily accessible from cellulose and has advantageous physical properties [1]. Moreover, DMF and 2-methylfuran (MF) are directly emitted into the atmosphere from incomplete combustion of fossil fuels, waste, and, in particular, from biomass burning [2]. Here, chemical degradation is mainly initiated by reaction with OH. Furthermore, in low-temperature combustion, fuel + OH reactions are of particular importance.

In our contribution, we report on experimental investigations of the DMF + OH and MF + OH reactions. The experiments were carried out at 295–560 K for DMF and 295–410 K for MF in a slow-flow reactor in a pressure range of 7–21 bar with helium as bath gas. The OH radicals were produced by laser flash-photolysis of nitric acid and detected time-resolved by laser-induced fluorescence under pseudo-first order conditions.

For neither of the two reactions, a pressure dependence of the rate coefficient was observed in the pressure range of our experiments. The temperature dependence of the rate coefficients is shown in Fig. 1, and a comparison with literature data is given. Bierbach *et al.* [3] and Aschmann *et al.* [4] determined rate coefficients at room temperature and atmospheric pressure.

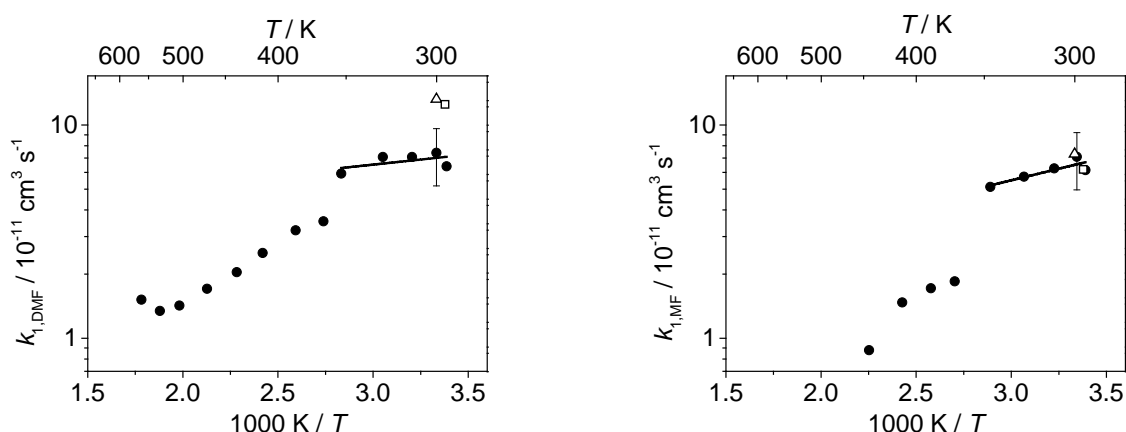


Figure 1: Arrhenius plots of the experimentally determined rate coefficients $k_{1,\text{DMF}}$ (black circles, left panel) and $k_{1,\text{MF}}$ (black circles, right panel) in comparison with the results from Bierbach *et al.* [3] (triangles) and Aschmann *et al.* [4] (squares); (solid lines) least-squares fits for $295 < T/\text{K} < 350$, see Eq. (1) and (2), estimated error of $\pm 30\%$.

If we compare the values of the rate coefficients $k_{1,\text{DMF}}$ and $k_{1,\text{MF}}$ at 298 K with the previously published results, there is a disagreement of ~50 % for the reaction of DMF + OH, whereas the values for 2MF + OH agree very well.

In the entire temperature range studied, both reactions show non-Arrhenius temperature dependence with obviously two kinetically different regimes. At $T < 350$ K the measured values of k_1 were nearly independent of temperature, whereas for $T > 350$ K a pronounced decrease was observed for increasing temperature. Accordingly, a simple Arrhenius fit is only useful in a limited range. Linear least-squares fits to the relevant points (cf. Fig. 1) result in the following expressions:

$$k_{1,\text{DMF}} = (3.38 \pm 1.00) \times 10^{-11} \exp\left(\frac{219 \text{ K}}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad T = 295\text{--}350 \text{ K}, P = 7\text{--}21 \text{ bar} \quad (1)$$

$$k_{1,\text{MF}} = (1.23 \pm 0.37) \times 10^{-11} \exp\left(\frac{500 \text{ K}}{T}\right) \text{ cm}^3 \text{ s}^{-1} \quad T = 295\text{--}350 \text{ K}, P = 13\text{--}21 \text{ bar} \quad (2)$$

The overall temperature dependence of the rate coefficients is in line with those observed in reactions of OH with other unsaturated hydrocarbons, especially with aromatic compounds. It may be explained by a non-reversible addition of the OH radical to the aromatic ring in the first regime, and increasingly important thermal back-dissociation of the OH-adduct in the second regime. A corresponding modeling is underway in our laboratory.

References

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