

Shock-Tube/TOF-MS Studies and Kinetic Modeling of the Pyrolysis of Furan Derivatives

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Due to decreasing fossil-fuel reserves, sustainable energy resources will have to replace fossil fuels in the near future. Particularly in the transport sector, liquid fuels have many advantages. Besides their high energy density, they can be easily stored and efficiently distributed. Possible candidates to replace common liquid fossil fuels are furan derivatives, in particular 2,5-dimethylfuran (25DMF). Prior to widespread use, however, a detailed understanding of the combustion chemistry of furans is necessary. Pyrolysis and oxidation experiments help to setup adequate combustion mechanisms, and comparative studies of different furans can give further mechanistic insights to verify reaction pathways and to allow the establishment of structure-reactivity relationships.

We studied the pyrolysis of three different furanic compounds, namely furan itself (F), 2-methylfuran (2MF), and 2,5-dimethylfuran (25DMF) in separate shock-tube experiments, using electron impact time-of-flight mass spectrometry (TOF-MS) for detection. We performed experiments in a temperature range of $T = 1000\text{--}2000\text{ K}$ and at pressures of $P \sim 1\text{ bar}$. In Figure 1 exemplary mass spectra are shown.

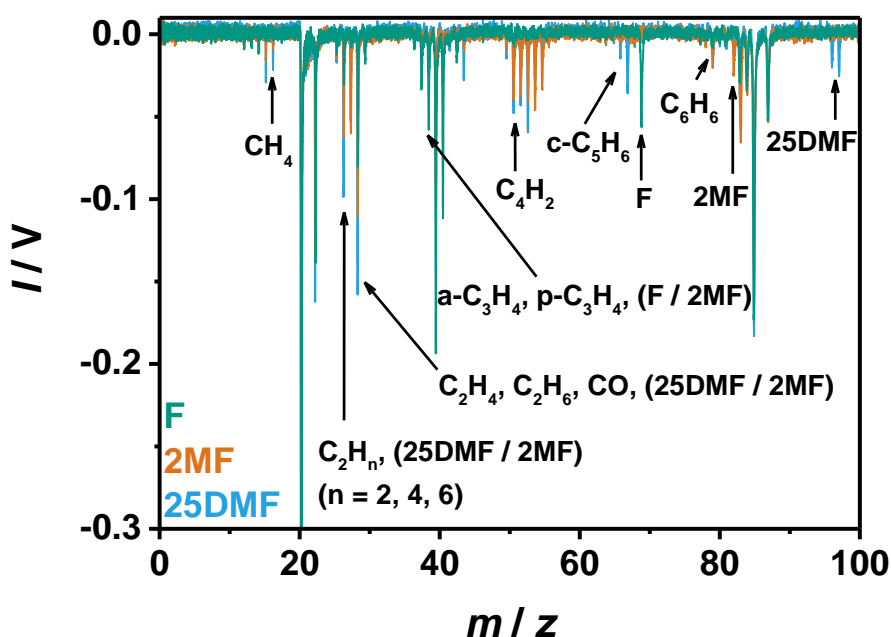


Figure 1: Mass spectra obtained at $T \sim 1440\text{ K}$ and $P \sim 1\text{ bar}$ for a reaction time of $t = 1.67\text{ ms}$ with an electron energy of $E = 50\text{ eV}$. Species names in parentheses denote fragment peaks. The signals at m/z 20 and 22 are due to the bath gas neon and the signals at m/z 41–43, 80, 82–84, and 86 are due to the internal standard krypton.

Besides the corresponding reactant (F, 2MF, or 25DMF), we were able to simultaneously detect several products like CO, methane, propyne, and benzene. Table 1 gives an overview of all assigned peaks in the different pyrolysis experiments. Note that some of the species are not present in the entire temperature range and/or show intermediate-like behavior.

Table 1: Detected species in our TOF-MS experiments: minor products are indicated by +, major products ($[\text{product}]/[\text{reactant}]_0 > 0.2$) are indicated by ++.

	CH ₄	CO	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆	a-C ₃ H ₄	p-C ₃ H ₄	C ₄ H ₂	c-C ₅ H ₆	C ₆ H ₆
F		++	++	+	+	+	++	+		+
2MF	+	++	++	+	+	+	+			+
25DMF	++	++	++	+	+				+	+

We used the detailed reaction mechanism set up for all three furans published in 2014 by Liu *et al.* [1] to model, compare, and discuss our experimental results. The simulations were performed with the program package openSMOKE [2,3]. Both the experiments and the simulations were performed for reaction times near $t = 2$ ms. Figure 2 shows exemplary concentration-time profiles of products built up during the pyrolysis of furan. The comparison between experimental and modeling results shows a reasonable agreement for all three compounds in the entire temperature range.

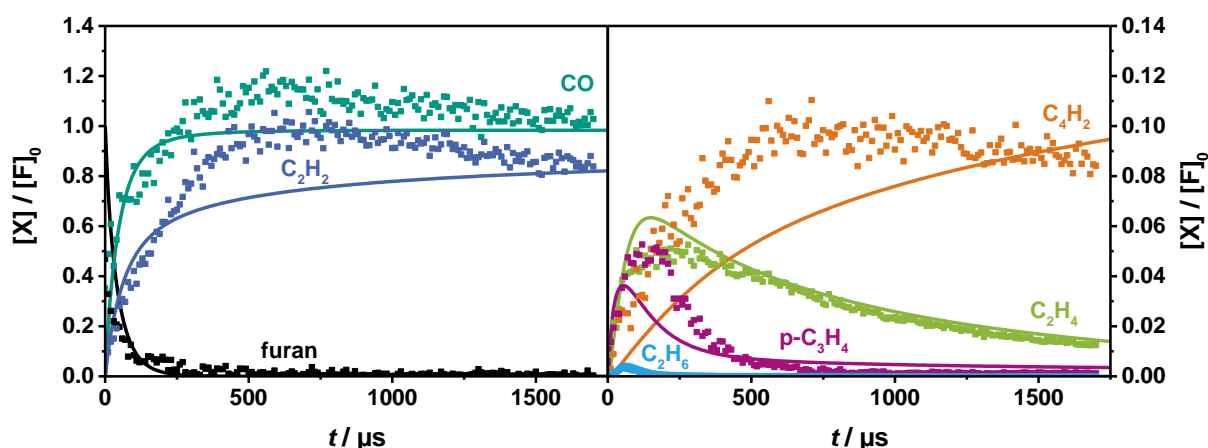


Figure 2: Concentration-time profiles obtained at $T \sim 1920$ K and $P \sim 1$ bar for the reactant furan and several pyrolysis products. Symbols: TOF-MS results, lines: kinetic modeling with the mechanism from Liu *et al.* [1]. Note the factor of 10 difference in the ordinates.

References

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- [2] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, *Combust. Flame* **2013**, *160* (5), 870-886.
- [3] A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, *Combust. Flame* **2009**, *156* (10), 2010-2022.