

# Chemical Kinetics – Fundamentals and Applications in Atmospheric and Combustion Chemistry

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*The research of our group is aimed at understanding the kinetics and mechanisms of chemical reactions in the gas phase at a molecular level and to provide reliable and physically reasonable thermodynamic and kinetic parameters. We experimentally determine rate coefficients, their temperature and pressure dependence, product branching-fractions etc. and analyze these observable quantities, using statistical rate theory. We use shock tubes with different detection techniques and slow-flow reactors with laser photolysis/laser-induced fluorescence setups. The rate theory calculations are based on molecular and transition state data from quantum chemical calculations. The thermodynamic and kinetic parameters obtained are then used to model complex chemical systems mainly from combustion and atmospheric chemistry. Most recently, we also started studying ultrafast photolytic processes with relevance in atmospheric chemistry (see the contribution from PD Dr. A.-N. Unterreiner).*

## Shock tube studies

Shock tubes are quite universal tools to study high-temperature reactions in the gas phase ( $800 \text{ K} < T < 3000 \text{ K}$ ). A gas mixture is rapidly ( $t < 1 \mu\text{s}$ ) heated by a travelling shock wave, and species formed behind the shock front are time-resolved detected, where we use absorption spectroscopy<sup>[1]</sup> and mass spectrometry.<sup>[2]</sup> Kinetic data are inferred from the concentration-time profiles. A recent example from our research is the reaction between H atoms and 2,5-dimethylfuran (25DMF), a potential biofuel<sup>[1]</sup>. The H + fuel reaction is important for the ignition behavior of any fuel, because it competes with the chain-branching step  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ . We studied  $\text{H} + 25\text{DMF}$ , using the reaction sequence  $\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_5 + \text{I} \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{I}$  to produce H atoms. Concentration-time profiles of H atoms were determined by recording the absorption of the Lyman  $\alpha$  line. The experimental setup with a microwave discharge lamp as a light source is shown in Fig. 1, and a typical concentration-time profile is displayed in Fig. 2. The rate coefficient is obtained from a fit to the curve. Quantum chemistry and statistical rate theory is then used to characterize the different product channels<sup>[1, 2]</sup>. In a similar manner we study high-temperature reactions of other oxygenated species<sup>[3]</sup> and the kinetics of early chemical steps in soot formation<sup>[2]</sup>.

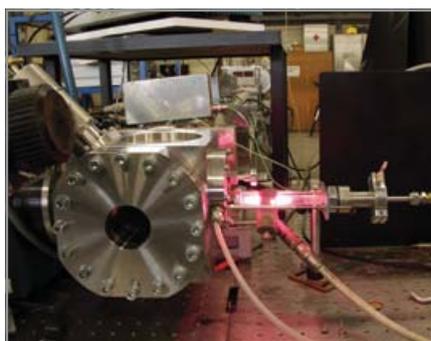


Fig. 1 Shock tube with microwave discharge lamp.

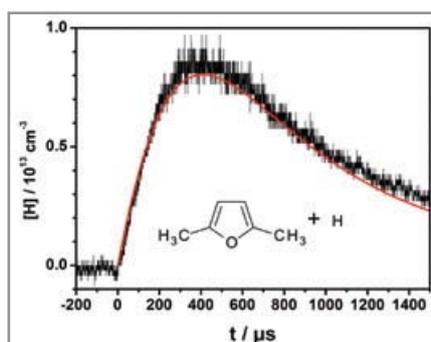


Fig. 2 Measured and modeled concentration-time profile from a shock tube experiment.

## Laser photolysis/laser-induced fluorescence (LIF) studies

With our laser photolysis setups, see Fig. 3, we are able to study radical reactions in a temperature range from 200 to 600 K at pressures between 0.1 and 100 bar. Recent examples are the reversible

ring-opening reaction of the cyclohexoxy radical (production by laser-flash photolysis of  $c\text{-C}_6\text{H}_{11}\text{ONO}$ , time-resolved detection by laser-induced fluorescence)<sup>[4]</sup> and the  $\text{NCN} + \text{NO}$  reaction ( $\text{NCN}$  production by photolysis of  $\text{NCN}_3$ , detection by LIF)<sup>[5]</sup>. The former reaction occurs in the atmospheric degradation of cyclic hydrocarbons and is an interesting example for the role of entropy in chemical kinetics. The rate coefficient of the ring closure reaction has a very low entropy of activation and can only be described by transition state theory reasonably well, if the 5 torsional degrees of freedom in the open-chain radical are treated as hindered internal rotors with exactly counted partition functions<sup>[4]</sup>. The  $\text{NCN} + \text{NO}$  reaction is of interest for the NO formation in combustion under fuel-rich conditions. The complicated temperature and pressure dependence of its rate coefficient (see Fig. 4) can be explained in terms of the potential energy surface of the reaction<sup>[5]</sup>.

## Statistical rate theory calculations

To further extend the range of application of statistical rate theory, we also collaborate with other experimentally working groups<sup>[3, 6]</sup>. Moreover, we perform theoretical and modeling studies in combination with methodic developments<sup>[7]</sup>. Examples cover such different areas as the degradation of aluminum clusters by  $\text{Cl}_2$  in a FT-ICR mass spectrometer<sup>[6]</sup> or the atmospheric oxidation of sulfur compounds<sup>[7]</sup>.

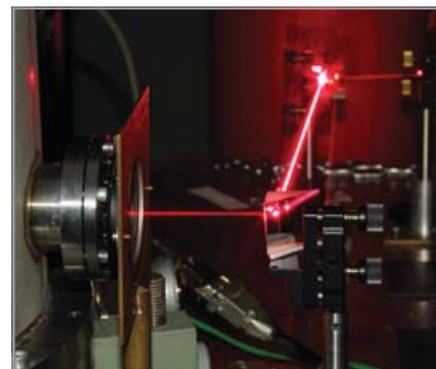


Fig. 3 Photolysis reactor, excitation laser for LIF.

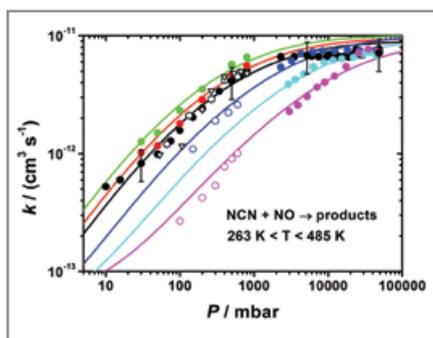


Fig. 4 Experimental and calculated falloff curves (Reprinted with permission from Ref. 5. Copyright (2012) American Chemical Society).

By this combination of experimental and theoretical methods, the molecular mechanism and the kinetics of many elementary chemical steps in the gas phase can be quantitatively understood.

### Selected Publications

- [1] The reaction of 2,5-dimethylfuran with hydrogen atoms – an experimental and theoretical study, P. Friese, J. M. Simmie, M. Olzmann, *Proc. Combust. Inst.* 34, 233 (2013).
- [2] The phenyl + phenyl reaction as a pathway to benzynes: an experimental and theoretical study, S. H. Dürstein, M. Olzmann, J. Aguilera-Iparraguirre, R. Barthel, W. Klopper, *Chem. Phys. Lett.* 513, 20 (2011).
- [3] HCO formation in the thermal unimolecular decomposition of glyoxal: rotational and weak collision effects, G. Friedrichs, M. Colberg, J. Dammeier, T. Bentz, M. Olzmann, *Phys. Chem. Chem. Phys.* 10, 6520 (2008).
- [4] On the thermal unimolecular decomposition of the cyclohexoxy radical – an experimental and theoretical study, O. Welz, F. Striebel, M. Olzmann, *Phys. Chem. Chem. Phys.* 10, 320 (2008).
- [5] Kinetics of the NCN + NO reaction over a broad temperature and pressure range, O. Welz, M. Olzmann, *J. Phys. Chem. A* 116, 7293 (2012).
- [6] On the kinetics of the  $Al_{13}^- + Cl_2$  reaction: Cluster degradation in consecutive steps, M. Olzmann, R. Burgert, H. Schnöckel, *J. Chem. Phys.* 131, 174304 (2009).
- [7] Kinetics of the chemically activated  $HSO_5$  radical under atmospheric conditions – a master equation study, N. González-García, M. Olzmann, *Phys. Chem. Chem. Phys.* 12, 12290 (2010).



**Matthias Olzmann** studied chemistry at the Technical University of Leuna-Merseburg and received his doctoral degree in 1985 (with K. Scherzer).



Afterwards he worked as a lecturer at Leuna-Merseburg, later at the Martin-

Luther-University of Halle-Wittenberg, where he finished his habilitation in 1999. During this time, in 1990/91, he spent one year as a visiting fellow at the University of Göttingen (with J. Troe). After a stay as visiting assistant professor at Massachusetts Institute of Technology (with M. J. Molina) in 2000, he became a senior lecturer at the Uni-

versity of Karlsruhe (TH). In 2003 he was appointed as a professor of physical and environmental chemistry at the University of Wuppertal but returned to the University of Karlsruhe (TH) in 2004 to take his current position as head of the Molecular Physical Chemistry Group at the Institute of Physical Chemistry.