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Full Professor. Molecular Physical Chemistry. Born 1946; study of physics 1966-70 (Göttingen); 1971-75; assistant at the Institute of Physical Chemistry Ecole Polytechnique Fédérale de Lausanne (Switzerland); 1974 Dr. sc. tech. (Ecole Polytechnique Fédérale de Lausanne (Switzerland)); 1975-76 Postdoctoral Fellow, IBM Research Laboratory in San Jose (California, USA); 1977-92 research associate Institute for Physical Chemistry (University Göttingen); 1985 invited researcher at RISO (Roskilde, Denmark); 1988 Habilitation and *venia legendi* for Physical Chemistry (University Göttingen); 1993 apl. Professor (University Göttingen); since 1993 Full Professor for Physical Chemistry (University Karlsruhe); 1998 invited Professor at the University of Lille 1 (France). 2000-02: Vice rector of the University of Karlsruhe (TH); since 2002: Rector of the University of Karlsruhe (TH).

Principal Research Interests

Pressure and Temperature Dependence of Unimolecular and of Bimolecular Complex-Forming Reactions. Unimolecular and bimolecular complex-forming reactions play an important role in atmospheric chemistry as well as in combustion processes. In general, the rate constants of these reactions show a pronounced temperature and pressure dependence. We are investigating these reactions using laser-flash-photolysis combined with time resolved UV/Vis-absorption-spectroscopy or with laser-induced-fluorescence. The experimental conditions can be varied between 1 and 1000 bar total pressures within a temperature range from 80 to 800 K. The main objective of these investigations is to experimentally approach the high-pressure limiting rate constant, which is closely related to the properties of transition states. Our experimental results provide a database which we use to test ab-initio potential energy surfaces as well as statistical theories.

We also use the shock tube technique combined with different absorption techniques (conventional UV/Vis-, laser- and atomic resonance absorption spectroscopy) as well as mass spectrometry to investigate these reactions at high temperatures (T: 500 – 3000 K, p: 0.05 – 5 bar). The focus of the studies has been the determination of incubation

times which provides information on energy transfer processes. Furthermore, we have determined branching ratios of multi channel reactions as a function of pressure and temperature. To analyze our experimental results we use unimolecular rate theory. We have developed methods for the solution of two dimensional master-equations to describe the complex pressure and temperature dependence of the rate constants of these reactions. The same formalism is used to analyze induction times and branching ratios of multi-channel decomposition reactions.

Femtosecond Spectroscopy. Solvated electrons in polar liquids and molten alkali halides have been studied by pump probe and transient anisotropy spectroscopy. Due to the broad absorption spectra with half-widths of 0.5 to 1 eV, a spectral tunability of the laser system from the UV- to the NIR region with pulse durations below 100 fs is required. According to our analysis, the lifetime of the excited state of solvated electrons in polar liquids is shorter than 100 fs and the subsequent ultrafast evolution of the transient absorption can be interpreted in terms of the ground state dynamics of solvated electrons. In this project we focus both on the generation process of solvated electrons as well as the dynamics of equilibrated species. The behaviour of excess electrons in molten salts is primarily governed by hopping processes of F-centre-type electrons. These jumps occur with a time constant of 200 fs.

One of the fastest of all chemical reactions involves intramolecular shifts of hydrogen atoms. Such reactions occur within 100 fs. Studies on our model system cycloheptatriene have required the development of ultrashort laser pulses in the spectral UV-region with less than 50 fs pulse duration. Polarization-dependent investigations have demonstrated that the change of the transition dipole moment is directly related to the sigmatropic [1,7] hydrogen atom shift. Theoretical investigations have shown that this fast process is possible due to conical intersections of the potential energy surfaces.

Selected Publications

1. "A detailed experimental and theoretical study on the decomposition of methoxy radicals", H. Hippler, F. Striebel, B. Viskolcz, PCCP **2001**, *3*, 2450 - 2458.
2. "Branching ratios and incubation times in the thermal decomposition of methyl radicals: Experiments and theory". R.A. Eng, A. Gebert, E. Goos, H. Hippler, C. Kachiani, PCCP, **2001**, *3*, 2258 - 2267.
3. "Temperature-dependent studies of solvated electrons in liquid water with two and three femtosecond pulse sequences", A. Hertwig, H. Hippler, A.-N. Unterreiner, PCCP, **2002**, *4* (18), 4412 - 4419.
4. "Observation of the Hydrogen Migration and the Isotope Effect in 1,3,5-Cycloheptatriene by Femtosecond Spectroscopy", A. Hertwig, H. Hippler, A.-N. Unterreiner, and J.-P. Yang, PCCP, **2003**, zur Veröffentlichung eingereicht.