J1. The Thermal Unimolecular Decomposition of HCO: Falloff in Different Bath Gases and Isotope Effect

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Formyl radicals (HCO) are formed in combustion processes in the course of the oxidation of hydrocarbons. Under combustion conditions their fate is determined by the competition between unimolecular decomposition, which yields H-atoms and is thus a chain carrier, and reactions with H, OH or O_2, which yield H_2, H_2O and HO_2, respectively, and are thus chain terminating processes. For a reliable modeling of combustion processes an accurate knowledge of the rate constants for all reactions mentioned above is needed. Recently, we studied the decomposition at temperatures between 590 and 800 K and pressures ranging from 1 to 150 bar helium in order to characterize the pressure and temperature dependence of the thermal rate constant [1]. We have been able to show that the experimentally observed pressure dependence of the rate constant is not in agreement with the results of a combined RRKM/ME calculation. While the experimentally observed rate constant scales roughly with $[M]^{0.87}$ the calculations predict that it is in the low pressure range even at pressures as high as 150 bar. However, a Lindemann-Hinshelwood-type calculation based on the resonance lifetimes calculated by Schinke and co-workers allows for a description of the experimentally observed pressure dependence (see Ref. [1]). In our presentation we will present new data for nitrogen (T = 590 – 700 K, p = 1 – 80 bar) and argon (T = 643 K, p = 5 – 55 bar) as bath gases in order to characterize the pressure dependence in different environments. Additionally, we will present experimental results on the decomposition of DCO (T = 643 – 800 K, p = 1 – 170 bar He) in order to test, if the theoretical model presented in Ref. [1] is able to predict the isotope effect correctly.

[1] H. Hippler, N. Krasteva, F. Striebel, *Phys. Chem. Chem. Phys*., 2004, **6**, 3383.

J2. Kinetics and Thermochemistry of the Addition of Atomic Chlorine to Acetylene

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The reaction

$$Cl + C_2H_2\ (+\ Ar) \rightarrow \bullet CH{=}CHCl\ (+\ Ar) \qquad (1)$$

has been studied over the temperature range 288 – 440 K. Atomic Cl was generated by 193 nm excimer laser photolysis of CCl_4 and was monitored by time-resolved resonance fluorescence at $\lambda \approx 130$ nm. The pressure-dependent second-order rate constant k_1 was obtained over 30 - 500 mbar of Ar bath gas, and RRKM modeling yields the third-order low-pressure limiting value for recombination of $1.5 \times 10^{-31} \exp(944/T)$ cm^6 $molecule^{-2}$ s^{-1}. Error limits are about ±15%.

At the high end of the temperature range equilibration was observed, and bi-exponential decays of atomic Cl were fit to a scheme based on reaction 1 and the processes

$$\bullet CH{=}CHCl\ (+\ Ar) \rightarrow Cl + C_2H_2\ (+\ Ar) \qquad (-1)$$

$$\bullet CH{=}CHCl \rightarrow \text{loss without regeneration of Cl} \qquad (2)$$

$$Cl \rightarrow \text{diffusive loss} \qquad (3)$$

The ratio k_1/k_{-1} yields the equilibrium constant for reaction 1, and a preliminary Third Law analysis yields ΔH_{298} for reaction 1 of -73 kJ mol^{-1}. The corresponding $\Delta_f H_{298}$(CH=CHCl) is 275 kJ mol^{-1}. This is the first direct measurement of the thermochemistry of any chlorovinyl radical, and provides an anchor for relative enthalpies determined via ab initio computational methods.

The rate of process 2 is found to be pressure independent and proportional to $[C_2H_2]$, and is tentatively assigned to β-chlorovinyl + acetylene addition at the high pressure limit.

C-Cl bond strengths in α and β-chlorovinyl radicals are discussed, and experimental and computational results compared. The wide-amplitude anharmonic C-C-Cl bending mode, with minima in the *cis* and *trans* conformations, is characterized and implications for *cis*/*trans* product branching discussed.

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J3. Experimental and Theoretical Study on the H + CH_3CCH Reaction

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In the reaction of H-atoms with propyne (CH_3CCH) the direct abstraction step,

$$CH_3CCH + H \rightarrow CH_2CCH + H_2 \qquad (1)$$

competes with two complex-forming bimolecular reactions:

$$CH_3CCH + H \rightarrow CH_3CHCH \rightarrow CH_3 + C_2H_2 \qquad (2)$$
$$CH_3CCH + H \rightarrow CH_3CCH_2 \rightarrow H + CH_2CCH_2 \qquad (3)$$

Both propargyl (CH_2CCH) and acetylene (C_2H_2) are known to be precursor molecules for the formation of aromatic and poly-aromatic hydrocarbons in pyrolysis and combustion processes and, thus, the branching ratio between (1) and (2) is of particular interest.

In our contribution we will present a combined experimental and theoretical study on the H + CH_3CCH reaction. Experiments were performed behind shock waves in the temperature range from 1200 to 1400 K and at pressures between 1.3 and 4 bar of Ar. H atoms were generated by thermal decomposition of ethyl iodide (C_2H_5I), and the reaction progress was monitored using H atom resonance absorption spectroscopy (H-ARAS). All experiments were performed under pseudo-first order conditions with the propyne concentration being a factor of 10 to 20 higher than the H-atom concentration. From the experiments we were able to deduce the sum of the rate coefficients k_1+k_2. Information on the branching ratio between reactions (1) and (2) was obtained from the theoretical study, in which we used *ab initio* methods to characterize stationary points of the potential energy surface and statistical rate theories to calculate rate coefficients for the competing reactions.

The H + propyne reaction is also an important chain-branching step in the pyrolysis of propyne. Therefore, we will also present first results of propyne pyrolysis experiments, in which a time-of-flight mass spectrometer was coupled to a shock tube to monitor product formation online. The monitoring of reaction products will allow for a critical test of the rate coefficients deduced from the experiments with H-atom detection.

J4. High-temperature Reactions of OH with Benzene and Toluene: Kinetic Studies by Shock Tube / Pulsed Laser-induced Fluorescence Imaging Method

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The elucidation of oxidation, pyrolysis and formation mechanisms of aromatic hydrocarbons in various combustion systems is one of the most important tasks in combustion chemistry. However, the kinetic information is limited because of the lack of sensitive detection method for the key species at elevated temperature.

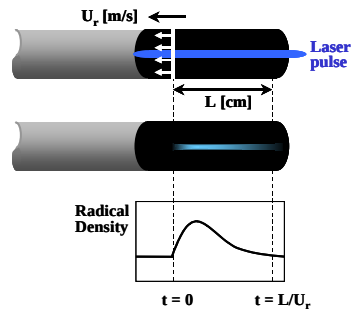

Fig.1. Basic principle of shock tube / pulsed laser-induced fluorescence imaging method.

The reactions of the hydroxyl radical with benzene and toluene have important roles in various systems (reaction 1 and 2):

$$OH + C_6H_6 \rightarrow \text{products} \qquad (1)$$
$$OH + C_6H_5CH_3 \rightarrow \text{products} \qquad (2)$$

In the present work, the high-temperature reactions of OH with benzene and toluene have been investigated by shock tube / pulsed laser-induced fluorescence imaging method (ST-PLIFI), developed recently in our laboratory.

The basic principle of this apparatus is shown in Fig. 1. Since the gas behind the reflected shock wave is stationary, the gas at the shock front corresponds to heating time = 0 and gas at length L behind the shock front corresponds to heating time = L / U_r, where U_r is the reflected shock velocity. The spatial distribution of chemical species exactly corresponds to the time profile. By introducing a pulsed probe laser light in the axial direction of shock tube at the moment of the passage of wavefront through the observation section, the recorded one-dimensional fluorescence image corresponds to the time profile of the target chemical species.

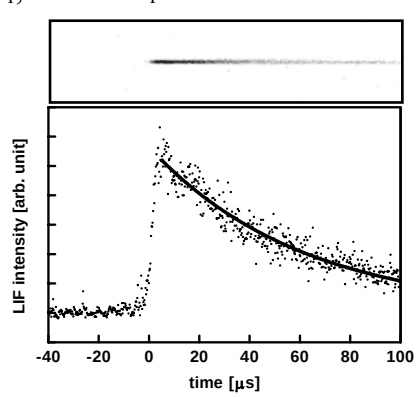

Fig.2. A PLIF image and [OH] time profile: T = 1451 K, P = 1.80 atm, $[HNO_3]_0 = 1.38\times10^{13}$ molecules cm^{-3}, $[C_6H_6]_0 = 1.87\times10^{15}$ molecules cm^{-3}.

OH radicals were generated by thermal decomposition of nitric acid and tertiary butyl hydroperoxide (TBHP). OH was measured by LIF exciting around 282 nm. Fig. 2 shows

a typical LIF image and its conversion to [OH] time profile in HNO_3 with benzene. The overall rate constants were derived by the single exponential analysis. Because of the high detection sensitivity, the initial OH-radical concentration could be kept low enough, ~1 × 10^{13} molecules cm^{-1}, to prevent the influence of side reactions. There was no contradiction in the rate constants between two precursors, nitric acid and TBHP. Arrhenius expressions for reaction (1) and (2) were obtained (units: cm^3 $molecule^{-1}$ s^{-1}):

$$k_1 = (8.3 \pm 0.8) \times 10^{-11} \exp\{-(6.5 \pm 0.2 kcal/mol)/RT\} \qquad \text{(OH + benzene: 908–1736 K)}$$
$$k_2 = (8.9 \pm 1.2) \times 10^{-11} \exp\{-(4.7 \pm 0.3 kcal/mol)/RT\} \qquad \text{(OH + toluene: 919–1481 K)}$$

The results were analyzed by quantum chemical / TST calculations. These calculations indicate that the hydrogen abstraction channels are dominant in high-temperature.

J5. Deuterium Kinetic Isotope Effects in Hydroperoxyl Radical Formation from Ethyl + O_2 And Propyl + O_2 Reactions

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The reaction between alkyl radicals, R, and molecular oxygen plays a pivotal role in the oxidation mechanism of alkanes at low temperature. Complete understanding of the R + O_2 mechanism has implications in diverse areas such as combustion chemistry (including autoignition and engine knock), atmospheric chemistry, and radical reaction chemistry. The properties of these reactions cause the change in oxidation mechanism of alkanes between approximately 500 K and 800 K, which results in the "negative temperature coefficient" (NTC) behavior in hydrocarbon oxidation.

Time-resolved production of HO_2 and DO_2 from the reactions of normal and deuterated ethyl and propyl radicals with O_2 have been measured as a function of temperature and pressure in the "transition region" between 623 and 703 K. Experimental measurements, using both pulsed-photolytic Cl-atom initiated oxidation of ethane and propane and direct photolysis of ethyl, *n*-propyl and *i*-propyl iodides, are compared to kinetic models based on the results of time-dependent master equation calculations with *ab initio* characterization of stationary points. The *ab initio* energies are adjusted to produce agreement with the present experimental data and with available literature studies. The isomer-specificity of the present studies enables refinement of the model for *i*-C_3H_7 + O_2 and improved agreement with experimental measurements of HO_2 and DO_2 production in propane oxidation. The observed kinetic isotope effect (expected to be a convolution of kinetic isotope effects for the stabilization, redissociation, and elimination pathways) places additional demands on the theoretical description of the ethyl and propyl potential energy surfaces. Isotope effects in elementary steps can be rationalized based on the nature of reaction coordinate. Results from this work suggest that a reinvestigation of the high temperature kinetics of the *i*-C_3H_7 + O_2 reaction is warranted. Recommendations toward a general model for alkyl + O_2 reactions will be discussed.

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J6. Formation of $C_7H_7^+$ Ions from Ethylbenzene and o-Xylene Ions: Fragmentation vs. Isomerization

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The $C_7H_7^+$ ion, existing in three major isomeric forms (tropylium, benzylium and tolylium), is one of the most fascinating species in organic mass spectrometry [1]. Yet the properties of the three isomers are still under some debate [2]. In a recent experiment we have measured the rate constants for the formation of $C_7H_7^+$ from energy-selected ethylbenzene and o-xylene ions [3]. The rate constant curves k(E) obtained for the two precursors were clearly different and, more over, the respective slopes (k versus E) were different. However, the role of isomerization in the precursor ions remained unclear. In the current work we present an extended kinetic analysis taking into account competition of isomerization and fragmentation in both ethylbenzene and o-xylene ions [4]. A schematic energy diagram including the relevant specific rate constants is depicted in fig. 1. Based upon this scheme we have setup a set of six coupled differential equations, which were solved numerically.

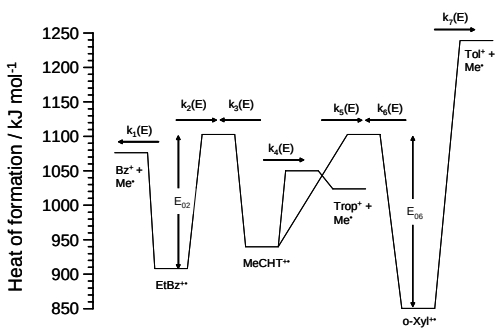

Fig. 1 Energy scheme for the isomerization and fragmentation of ethylbenzene and o-xylene ions.

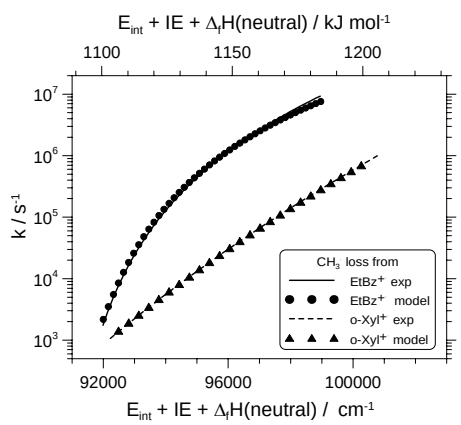

Fig. 2 Comparison of effective rate constants for $Me^{\bullet}$ loss from $EtBz^{+\bullet}$ and o-$Xyl^{+\bullet}$. Symbols: this work; lines: experimental data from [3].

Ultimately the calculated effective rate constants for methyl loss have been compared to the experimental data as shown in fig. 2. The comparison of the kinetic model with experimental data suggests that the barriers for isomerization of the precursors are significantly higher than the thermochemical onset of fragmentation. This indicates that isomerization of the precursors to a

common intermediate (the methyl-cycloheptatriene ion) prior to fragmentation does not play an important role in the threshold region.

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J7. Experimental and Computational Studies of the Kinetics of Chlorinated Hydrocarbon Radicals

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A series of reactions involving chlorinated hydrocarbon radicals (C_2Cl_3, CCl_2, CH_2CClCH_2, CH_2Cl, $CHCl_2$, CCl_3) were studied experimentally in the gas phase using the laser photolysis – photoionization mass spectrometry technique. Reactions of several types were investigated: radical – radical reactions, radical – closed shell molecule reactions, and reactions of unimolecular decomposition. Rate constants of these reactions were obtained in direct real-time experiments as functions of temperature and pressure. Experimental studies were complemented by computational investigations of the potential energy surfaces using quantum chemical methods and transition state theory and RRKM/master equation calculations of the rate constants. Experimental and computational results were used for extrapolation of the rate constant values to conditions outside the experimental ranges of conditions.

Experimental and computational results demonstrate that many of the reactions of chlorinated hydrocarbon species possess mechanisms and kinetic parameters that are qualitatively different from those of the reactions of corresponding non-chlorinated species. In particular, this includes reactions involving singlet CCl_2 biradical, reaction pathways involving Cl atom migration, and Cl atom interaction with π bonds in addition-decomposition reactions.

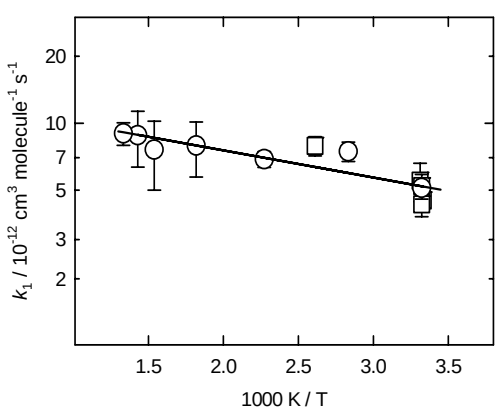

Figure 1. Temperature dependence of the rate constant of the $CCl_2 + Cl_2 \rightarrow CCl_3 + Cl$ reaction.

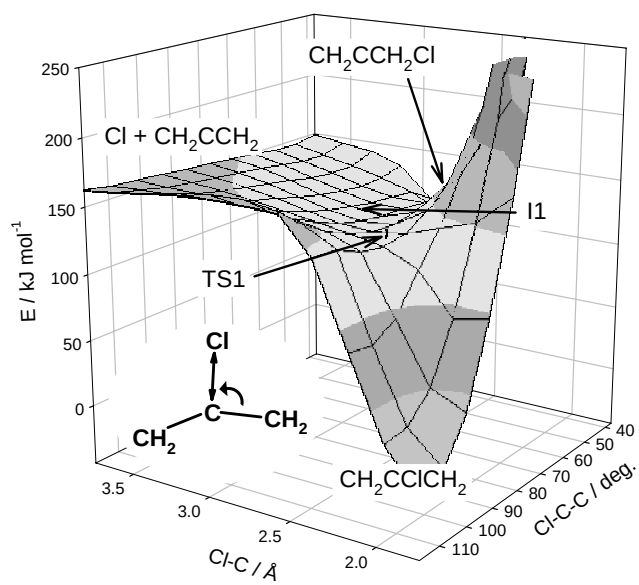

Figure 2. 3-dimensional potential energy surface (relaxed PES scan) of the reaction of thermal decomposition of 2-chloroallyl radical. The minimum energy path of the CH_2CClCH_2

dissociation to Cl + CH_2CCH_2 proceeds from the CH_2CClCH_2 equilibrium structure through the saddle point TS1 and the I1 plateau (a weakly bound complex formed due to the interaction of Cl atom with the π bond of allene).

J8. Shock Tube Measurements of the Reaction HCO + O_2 Using the Photolysis of Glyoxal as an Efficient HCO Source

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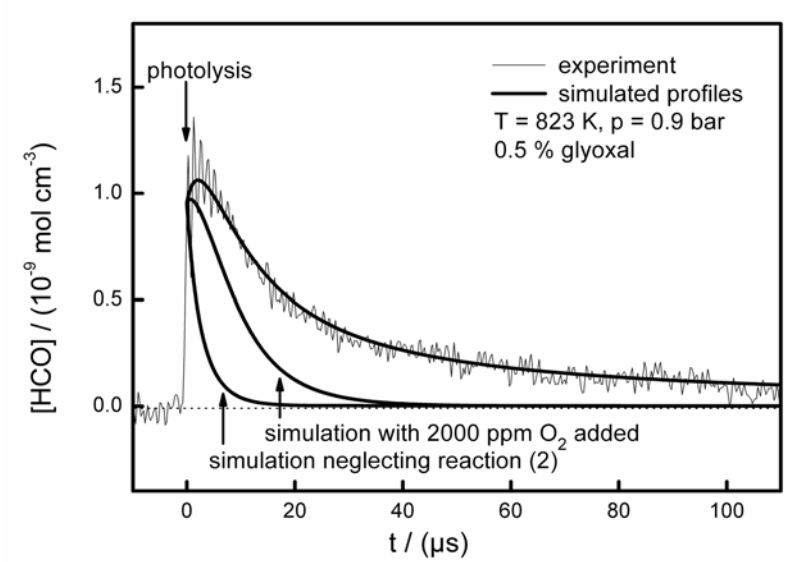
The reaction of the formyl radical with molecular oxygen

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (1)$$

is a major source of hydroperoxy radicals both in hydrocarbon combustion and atmospheric chemistry. Whereas there have been many direct studies of the room temperature rate constant, no direct measurements of the rate constant at temperatures T > 700 K have been reported so far. Studies in the intermediate temperature range, however, revealed a slightly negative [1], positive [2], or negligible [3] temperature dependence, thus resulting in considerably uncertainty of the high temperature rate constant. The investigation of HCO reactions at high temperatures is difficult due to the high reactivity and thermal instability of HCO, which causes its lifetime to be short and the observable concentration levels to be low. Whereas the problem of low intermediate concentrations can be overcome by a sensitive detection method – frequency modulation (FM) spectroscopy in our case – suitable HCO sources for high temperature kinetic measurements are not readily available. We employed the photolysis of glyoxal, $(HCO)_2$, as a new high temperature source for shock tube measurements. At a wavelength of λ = 193 nm, the photolysis next to HCO radicals also generates hydrogen atoms. The subsequent abstraction reaction of the H atoms with glyoxal initially yields the unstable (HCO)CO radical, which decomposes to form HCO radicals within the time resolution of the experiments.

$$H + (HCO)_2 \rightarrow H_2 + (HCO)CO \rightarrow H_2 + HCO + CO \qquad (2)$$

At high temperatures, HCO rapidly decays (HCO $\rightarrow$ H + CO) but is steadily regained by reaction (2). This chain mechanism results in HCO observation times sufficiently long to investigate other HCO reactions by a perturbation approach (see figure). In this work, the photolysis of glyoxal was investigated at room temperature and at temperatures of 750 K < T < 1000 K behind shock waves. From experiments with mixtures of glyoxal in argon, the rate constant of reaction (2) and the H atom photolysis yield were determined. The observed HCO profiles can be described by a consistent mechanism. Observed differences between HCO profiles measured with and without controlled levels of O_2 added to the reaction mixture could be attributed almost exclusively to reaction (1). These measurements represent the first sensitive determination of the rate constant of reaction (1) at temperatures T > 700K and indicate a slightly positive temperature dependence.



HCO profile obtained by the photolysis of a glyoxal/argon mixture behind a reflected shock wave together with three different simulations: (i) the best fit, (ii) a simulation neglecting reaction (2), and (iii) a simulation that demonstrates a measurement of the rate of the reaction HCO + O_2 by a perturbation approach, i.e. addition of 2000 ppm O_2 to the reaction mixture ($k_1 = 6 \times 10^{12}$ $cm^3mol^{-1}s^{-1}$).

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