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INVESTIGATION OF REACTIONS AND SPECIES DOMINATING LOW TEMPERATURE COMBUSTION

Schlussbericht

Ausgearbeitet durch

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Zusammenfassung

Peroxy Radikale bestimmen das Zündverhalten und beeinflussen die Speziation der anfänglich vorhandenen Zwischenprodukte und somit die Entwicklung weiterer Reaktionen. Trotz intensiven Studien ist die quantitative Beschreibung der Prozesse im Zündvorgang noch nicht gesichert. Vielmehr beruht die Beschreibungen auf zwar recht glaubwürdigen aber letztlich unbewiesenen Modellen. Diese Situation kann nur geändert werden indem die Peroxy Radikale auf molekularer Ebene genau beschreiben werden können.

Für die Darstellung von Peroxy Radikalen wurde in der PSI Gruppe “Molekulare Dynamik” eine neue Molekularstrahl Apparatur konstruiert und in Betrieb genommen. Eine neuartige Radikalen-Quelle wurde installiert. Mit Hilfe einer elektrischen Gasentladung können unter günstigen Umständen spezielle Radikale gezielt dargestellt werden. Nach der Entladung kann dem aus der Entladungskammer strömenden Gas ein weiteres Gasgemisch beigefügt werden. Damit ist es möglich, kurz vorher erzeugte Radikale mit neutralen Molekülen reagieren zu lassen. Die neue Versuchseinrichtung erlaubt, lineare und nichtlinearen spektroskopische Messungen gleichzeitig an Molekülen in einem Molekularstrahl durchzuführen.

Massenspektrometrische Versuche wurden durchgeführt, um ionisierte Alkyl-Peroxy Radikale nachzuweisen, bisher erfolglos. Evtl. gelingt dieser Nachweis nicht, da Peroxy-Ionen, wie vermutet wird, keinen stabilen Ionenzustand aufweisen. Der Beweis für diese Vermutung oder deren Gegenteil konnte noch nicht schlüssig erbracht werden. Versuche mit erweiterten spektroskopischen Methoden, die wir an der Chemical Dynamics Beamline am SLS-Synchrotron durchführen werden, sollen Klarheit schaffen. Femtosekunden-Spektroskopien wurden auf di-Terbutyl Peroxy angewandt. Die erhaltenen Signale können auf Anhieb noch nicht schlüssig interpretiert werden. Wir rechnen mit einem grösseren Aufwand, um die involvierten Dissoziationsprozesse zustandsspezifisch angehen zu können.

Die nun zur Reife gebrachte Photo-Fragmentation-Excitation (PHOFEX) sowie die fs-Vierwellen-Methode (fs-CARS) werden weiterhin auf H_2CO und HCO angewendet. Diese Messmethoden werden im Hinblick auf die kommenden Peroxyl Untersuchungen weiterentwickelt und modifiziert. Die auf H_2CO bezogenen Arbeiten, die ihrerseits für die Beschreibung von Zündprozessen relevant sind, werden im Rahmen von zwei Doktorandenarbeiten vom SNF unterstützt.

Resumé

Peroxy radicals determine ignition and speciation of the initially present intermediates and thereby the progress of subsequent reactions. In spite of intensive studies, the quantitative description of ignition is not yet complete. Current modelling of ignition still incorporates quite plausible though unsecured approximations. This situation is only to change if peroxy radicals can be described exactly on a molecular level.

For the preparation of peroxy radicals a dedicated molecular beam apparatus has been built by the PSI group "molecular dynamics". A novel radical sources comprising an electrical discharge is operational. In favourite cases, specific radicals can be prepared with high selectivity. After a discharge took place, the gas coming from the discharge chamber can be mixed with gas provided in a second gas stream, thus allowing reactions of just formed radicals with neutral molecules. The new experimental set up allows application of linear and non-linear spectroscopic measurement techniques to molecules prepared in a molecular beam.

Mass spectrometric measurements were performed to monitor ionized alkyl-peroxy radicals, without success. As the peroxy ions may be unstable such measurements may prove to be impossible. The stability of peroxy ions is the subject of current research. Experiments comprising other spectroscopic techniques carried out at the Chemical Dynamics beamline at SLS-Synchrotron may shed more light on this subject. Femto-second spectroscopies were applied to di-terbutyl-peroxy. The measured transients can not yet be interpreted conclusively. More achievements are necessary to assess the underlying dissociation processes state specifically.

The now ripe Photo-Fragmentation-Excitation (PHOFEX) and fs-Four Wave Mixing (fs-CARS) measurement techniques are continuously applied to H_2CO und HCO. The measurement methods are currently refined and will be applied after modification in the upcoming investigations of peroxy radicals. The H_2CO related experiments that are relevant for the description of ignitions processes, too, are supported by SNF in the frame of two PhD-studies.

Abstract

The description of flame chemistry is not yet sufficiently developed to reliably predict the speciation of intermediate products during ignition. Laser based measurement techniques, especially Photo-Fragmentation-Excitation (PHOFEX) and fs-Four Wave Mixing spectroscopies are applied at PSI to measure static and dynamical properties of alkyl peroxy radicals in order to accurately describe their reaction behaviour in combustion processes. Currently, a dedicated synchrotron beamline is installed at the Swiss light Source (SLS) that extends the available range of spectroscopic measurements into the VUV (Vacuum-Ultraviolet) wavelength domain.

1. **Introduction**

In recent research reports [1] the need of a better experimental data base for combustion processes at low to medium temperatures was pointed out. For the establishment of a kinetic model, all possible elementary reaction paths have, a priori, to be taken into account together with their appropriate reaction rates. Only the numerical evaluation of the rate equations for each species allows, on a scientific base, to exclude unimportant reactions. Minority species may then be omitted and other species that lead to comparable amounts of products independent of the specific path via different intermediates may be treated as a group described by one common rate equation. Up to now, many models were constructed intuitively relaying on a guess which species and reactions might be important. Such models suffer from shortcuts that can not be rationalized, a posteriori, by a comparison with experiment [S. Tomlin et al. (Chapt IV) in [2]].

The generation of a kinetic equation system is a huge "bookkeeping" task. Codes are developed that can generate, in a combinatorial way, a description according to the initial ingredients. The effort is to some extent mitigated as a novel kinetic model may comprise sub-models developed and tested earlier for simpler systems, i.e., the H_2/O_2 and $CO/O_2/H_2O$ kinetics are basic subsystems of all other hydrocarbon combustion models.

Whereas the automatic generation of rate equations for a combustion model is feasible, the ab initio derivations of the associated rate constants are not. Though it is possible to calculate single rates for some species with increasingly better accuracy, it is up to now out of computer capacity to calculate hundreds of them. Moreover, the ab initio- or molecular model- calculations do not provide lower or upper error limits [1]. A more practicable way is to use rates measured for some species and to derive rates for other similar species by analogy, as for instance by group additivity (GA) rules [3]. GA is a powerful tool that in many cases seems quite appropriate. However, for whole classes of molecules GA is not yet satisfactorily developed, mainly due to the lack of corresponding experimental verifications.

The experimental determination of rate constants is very delicate. Kinetic experiments suffer from the fact that in order to realize, e.g., a radical reaction, intermediate educts have to be prepared by other reactions from suitable precursors. The amount of educts for a specific reaction thus depends on the reaction channels and reaction speeds involving precursors. For quantitative measurements these preceding reactions should be known with high precision, what often is not the case. Moreover, the persistently encountered lack of selectivity may result in unwanted species that interfere either by reactions with the species to be prepared or hamper the optical- or mass- spectrometric measurements of the reaction educts and products.

In many recent publications the lack of experimental data for the quantitative assessment of low temperature reactions becomes evident [4, 5]. Especially, the fate of peroxy radicals, - the first radical in a flame giving rise to branching-, is not yet sufficiently investigated. The figures used in current models to describe overall reaction rates, are often known within an order of magnitude only. The detailed reaction paths and the corresponding branching efficiencies are mostly not verified experimentally.

Peroxy radicals $RO_2\bullet$ are the key species in low temperature combustion and ignition of alkanes. Start point of ignition is the attack of alkanes RH by a radical, typically OH, producing an alkyl radical R.

$RH + OH \rightarrow R\bullet + H_2O$

$R\bullet$ is then consumed in three types of reactions

$R\bullet \rightarrow \text{alken} + R'\bullet$ (Propagation, $R'\bullet < R\bullet$)

$\rightarrow RO_2\bullet$ (Propagation)

$\rightarrow \text{alken} + HO_2\bullet$ (Termination)

Though $HO_2\bullet$ is a radical, it is not very reactive. In a typical combustion environment the last reaction is therefore considered to be a termination- rather than a propagation reaction. $RO_2\bullet$ can isomerize to a compound, usually denoted as $\bullet QOOH$ that either undergoes a cyclization after loss of an $OH\bullet$ radical, or reacts again with O_2 to $\bullet O_2QOOH$, eventually ending up as a hydroperoxide R'OOH.

$RO_2\bullet \rightarrow \text{Cycloether} + OH\bullet$ (Propagation)

$RO_2\bullet \rightarrow R'OOH$ (Propagation)

Hydroperoxide and $RO_2\bullet$ can thermally dissociate, splitting off an OH radical, to alkoxy and aldehydes, respectively, and are thus the first species in the chain leading to a branching reaction, necessary for combustion to start.

$RO_2\bullet \rightarrow R'CHO + OH\bullet \rightarrow$ products (Branching)

$ROOH \rightarrow RO\bullet + OH\bullet$ (Branching)

In this scheme, at least one adduct reaction forming an $RO_2\bullet$ species is required to produce the first branching species. All other reactions are terminating or at best propagating. Ignition is therefore dependent on pressure. It is promoted with an increasing amount of $RO_2\bullet$, an adduct formed in a pressure dependent three body collision. The availability of $RO_2\bullet$ is determined by the equilibrium of the reaction $R\bullet + O_2 \Leftrightarrow RO_2\bullet$. With increasing temperature, the equilibrium shifts to the alkyl radical side and ignition is held up. This fact is responsible for the phenomenon called cold combustion: A range of combustible gas mixtures can ignite, heat up and extinguish again. Only when substantial temperatures are reached in this transition phase, high temperature reactions can take over to develop a self-supporting flame.

To assess the role of peroxy radicals molecular data have to be worked out by spectroscopic means. The spectroscopic features of peroxy radicals are yet rather poorly developed. In spite of that, the absorption on the transition $B^2A" - X^2A"$ was extensively exploited for monitoring purposes in kinetic experiments. The transition $B^2A" - X^2A"$ is a bound - free transition exhibiting a broad unstructured band with a peak around 235 ± 10 nm for all hydrocarbonperoxy radicals investigated so far. For the use as a quantitative measurement tool a lot of work concentrated on the determination of the absorption cross sections. In two comprehensive reviews [6, 7] the experimental methods and the results are compiled. There is no possibility to distinguish between radicals with different R and substituted R moieties. Moreover other species can interfere in this wavelength region, e.g. ethyl used to produce ethylperoxyl. The absorption cross section is temperature dependent, due to excited vibrational levels in the ground state. It proved difficult to determine the absolute value of the cross section even at room temperature. For these reasons there is no evident way to observe peroxy radicals in a real environment quantitatively. In a first approach the absorption band shape can approximately be described with a Gaussian in accordance with spectroscopic rules for a transition from a single vibrational ground state to a dissociative state. A more refined assessment of the band shape depending on temperature was performed by Maric´ et al. [8]. Still, the debate on the accuracy of the experimentally determined absorption cross section is going on.

The ground- and first excited state of methyl peroxyl radicals were theoretically determined by Jafri and Philipps, [9]. In the X^2A"ground state dissociation energies of 2.01 eV and 3.37 eV were inferred for separation along the CH_3–O_2• and CH_3O–O• coordinates, respectively. The first excited state, A^2A', is bound, too, and lies about 1 eV above the ground state, in good agreement with infrared spectroscopic experiments performed by Hunziker and Wendt [10]. In a recent study 10 of 12 possible vibrational bands in CH_3O_2• were monitored with Fourier transform spectroscopy [11], refining and extending the information on vibrational frequencies this research group inferred earlier from the energy measurements of electrons detached from the anion [12].

The ionization threshold of the peroxy radicals lies around 11 eV above the neutral ground state. It seems that ionizing transitions are hardly exploited for kinetic and dynamical studies, nor was the potential of the B state and possible higher lying states determined experimentally.

An open question is, whether more states can be found in some peroxy radicals, - states which up to now were hidden behind the obviously dissociative B state, or which have energies above the up to now explored spectral domain. The discovery of high lying states would enable to develop nonlinear spectroscopic methods, e.g. Two Colour Four Wave Mixing schemes (TCFWM), which in the laser laboratory could serve as a monitoring tool for specific peroxy species. Ab initio calculation for some peroxy radicals predict that there may be other bound states than the X and A state. Such predictions are questionable and have to be verified in an experiment.

In summary, the peroxy system was investigated up to now in an enormous effort by mainly kinetic experiments and theoretical derivations [13]. The reaction paths are sought to be comprehensive and reduced to elementary reactions. The spectroscopic measuring techniques used in the kinetic experiments are discussable. Either well proven techniques were used to monitor product species, like OH, that do not provide direct, unambiguous information. Or, the measurements aimed directly at peroxy radicals, but employed, faute de mieux, an absorption method that can not distinguish between different peroxy radicals, and, the measurements in the UV region around 240 nm, can interfere with other species.

The result is, that the derived rate equations did not yet reach a level of robustness that would stop someone to adjust them pragmatically in a model intended to fit a real combustion process, [14].

2. Aims

Our investigations point at the direct measurement of formation and dissociation energies that up to now were only indirectly inferred from kinetic experiments or derived in model calculations. The intended experiments will concentrate on methyl- and ethylperoxy radicals and should provide information about dissociation thresholds, i.e., the energy of transition states.

3. Methods

For the monitoring of products resulting from peroxy radical dissociation, optical- and mass spectrometric techniques have to be set up. In earlier studies we prepared tools to measure state selectively fragments like OH, O, aldehydes and ethene. To exclude ambiguities due to branching reactions it will be necessary to identify now the more specific fragments HO_2, ethyl, oxirane etc. For these tasks new spectroscopies have to be made available.

The neat and ample preparation of a species decides on success or failure of a molecular dynamical experiment. A chemical compound, stable or intermediate, has to be prepared, selectively, in sufficient quantities. Precursor- molecules and their accidentally co-produced unwanted fragments should not infer with the applied measurement method. Therefore, molecular beam concepts and radical sources have to be developed. Photolytical-, pyrolytical and discharge driven radical sources have to be realized and tested in order to obtain and optimal approach to the measurement task.

Spectroscopic methods, especially nonlinear spectroscopies, are pushed further to allow monitoring of the dynamics of peroxy radicals. With TCFWM techniques (Two colour Four Wave Mixing) exhibiting high temporal resolution an important breakthrough in identifying intermediate states along the reaction path could be achieved. A proof for the existence of the assumed elementary reaction paths and a characterization of the involved intermediate states would be gained. The only spectroscopic techniques applied to peroxy radicals were up to now absorption spectroscopy on the UV band $B^2A'' - X^2A''$ and on the IR band $A^2A' - X^2A''$. These techniques probe ensemble averages and do not provide the time resolution nor the sensitivity to monitor molecular dynamics.

Degenerate and two-colour four-wave mixing (DFWM and TC-RFWM, respectively) are nonlinear spectroscopic tools exhibiting high signal-to-noise (S/N) ratios resulting from a fully resonant process. As a consequence, the methods are applicable to species that are present in low concentrations. These nonlinear techniques are complementary to linear spectroscopic methods and offer frequently advantageous capabilities [15]. The simultaneous use of resonant four-wave mixing together with one or more linear techniques provides a powerful spectroscopy approach. In a pioneering work by Germann and Rakestraw, DFWM and absorption spectroscopy have been combined to measure transition dipole moments and absolute concentrations of molecular species [16]. The method relies on the fact that both spectroscopic techniques produce the same results but exhibit a different functional dependency on the two involved parameters, i.e. transition dipole moment, μ_{12}, and the population difference in the ground and excited state, ΔN. In a similar way, DFWM and laser-induced fluorescence (LIF) can be combined to measure quantum-state specific quenching rates. The different dependence on μ_{12} and ΔN for DFWM and LIF signal intensities has been exploited for multiplex spectroscopy of NO_2 in a molecular beam and yield relative line strength factors and the ratio of populations in different energy levels [17]. Also, the multiplexing of DFWM and LIF provided information on the transition dipole moment dependence of the DFWM process, even when the level populations are not accurately known.

Electron energy spectrometers will be implemented in our test rigs to enable energy level mapping via ionic states of molecules. Detection of zero kinetic energy electrons (ZEKE) together with Time of Flight (ToF) - mass spectrometry of the associated ions will be used to characterize ionization and fragmentation processes during the ionization step in mass spectrometry, in order to remove ambiguities. The development of electron spectrometry will be performed in close synergy with a novel endstation to be built for gas phase chemical dynamics investigations at the Vacuum Ultraviolett Beamline at SLS.

By upgrading our TOF-Instruments with spatially resolving detectors a base will be established for translational mass spectrometry. This technique is able to detect the excess energy of fragments emanating from an excited complex.

4. Results

Peroxy radicals can be produced by three body reactions, according to

$R\bullet + O_2 + M \rightarrow RO_2\bullet^* + M$ 1)

where R• is a hydrocarbon radical and M the third collision partner.

The high pressure rate of this reaction is 10^{-12} cm^3/sec, and above 10 mbar pressure reaction 1) is the dominant loss mechanism of radicals R• [7]. Any source able to selectively produce radicals R• in the presence of oxygen is thus suited for the generation of peroxy radicals. Three types or radical sources are available in our laboratory by the end of the contract period. Each source exhibits strengths and drawbacks. The suitability of a source for production of a specific species R• has to be evaluated by tests.

All of our radical sources comprise a fast solenoid valve discharging a pulse of gas into a vacuum. Typical opening times of the valve are in the order of a few 10 µs and gas pulse durations of a few hundreds of micro-seconds can be achieved. Precursor molecules entrained with the gas pulse can be dissociated to yield R• radicals by photoexcitation (photolysis), or rapid heating (pyrolyis) or by collisions with electrons produced in a discharge prior free expansion into vacuum.

Photolytic source

A photolytic radical source has been constructed and combined with the molecular beam apparatus (Fig.1). The source mainly consists of a suprasil-quartz tube (4cm length and 1mm Ø), which is attached to a fast valve (Jota, 1mm opening). The 4'th harmonic of a Nd:YAG laser at 266 nm is used to photo-dissociate various precursor molecules producing alkyl radicals that can associate with O_2 to alkyl peroxy radicals. The dissociation laser output (~ 20 mJ, 9 ns duration) is focused on the quartz tube with a cylindrical lens (f=30 cm). A gas volume of 10 mm x 0.75 mm^2 within the tube is irradiated with a power density of ~7 10^8 W/cm^2. The gas pulse expanding from the tube-end is skimmed forming a pulsed beam of molecules that fly into the interaction region of a Time Of Flight Mass Spectrometer (TOF-MS). The duration of the gas pulse has been measured to be about 400 μs. The gas pulse is only partly illuminated by the dissociation laser. Assuming a gas velocity of about 500 m/s the irradiated part of the gas pulse persists in the interaction region for about 20 μs.

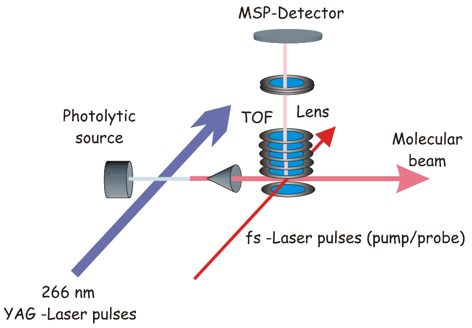

Fig.1: Experimental setup of the photolysis radical source and subsequent mass spectrometry.

The ionization step for mass spectrometry is performed with a femtosecond laser pulse. The fs-multi-photon ionization is not really selective and individual molecular species with comparable ionization potentials (IP) are in general ionized at comparable rates. Mass selectivity is achieved by accelerating the ions towards the detector in a time of flight assembly (TOF) and measuring the different arrival times.

The precursor molecules for the photo induced production of radicals in the source were ethyl iodine or 3-pentanone (di-ethyl ketone) in accordance to successful photolytic cell experiments performed by Pusharsky *et al.* [18] and di-tert-butyl peroxide. All of them exhibit a significant absorption in the 266 nm spectral region. The actual precursors available in liquid form were filled into a stainless steel bubbler-assembly. The applied high pressure gas mixture passes the 'bubbler' and saturates with the vapour of precursor molecules before filling the back volume of the valve. The content of precursor molecules in the gas pulse depends on the temperature of the bubbler content and approaches the saturation vapor pressure of the actual material. A calculation [19, 20] indicates precursor densities in the order of 10^{15} to 10^{16} molecules/cm^3.

The absorption cross section of ethyl iodine at 266 nm is ~10^{-18} cm^2/molecule [21]. C_2H_5I directly dissociates after the excitation to the electronic A-state, yielding about 10^{12} molecules/cm^3 ground state C_2H_5 radicals and ground state or excited iodine atoms. The reaction between ethyl radicals and molecular oxygen is expected to yield 100% ethyl peroxide radicals at 298 K in the recations

$C_2H_5I + h\nu \rightarrow C_2H_5 + I$

$C_2H_5 + O_2$ □ $C_2H_5O_2^*$.

The $C_2H_5O_2$ adduct can stabilize ($C_2H_5O_2^* + M$ □ $C_2H_5O_2$) in collisions. Unfortunately, the production of iodine atoms can interfere with the reaction system in an unpredictable way. We tried to compensate for fast Iodine reactions by adding ethane into the gas mixture with the intention to yield an increased formation of ethyl by H-abstraction: $C_2H_6 + I$ □ $C_2H_5 + IH$ [22].

Figure 2 shows on a logarithmic scale the yield of masses obtained with a C_2H_5I(4%) / O_2(2%) / C_2H_6(12%) / Ar(82%) gas mixture. The total gas pressure in the valve was 2.5 bar. The spectrum mainly depicts well known fragments, such as the ICH_n series around 140 amu, I and IH at 127 and 128 amu and strong peaks from 26 to 29 amu, i.e. mainly fragements of the precursor molecule. However, in this spectrum no ethyl peroxyl (61 amu) appears. Neither the addition of ethane nor the change of the O_2 content from (1% to ~4%) did show a significant change at the peroxyl mass position.

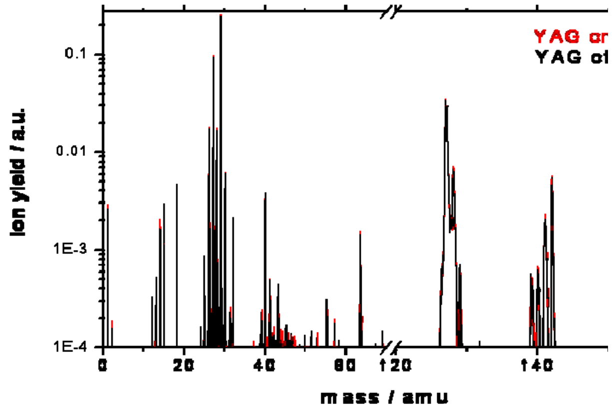

Fig.2: Multi photon ionization mass spectrum using C_2H_5I as precursor

Because of a strong ion state fragmentation of ehthyl iodine upon the fs multi photon excitation we couldn't clearly distinguish between the production of ethyl radicals in the preceding phototdissociation- or in the ionization step, even if the intensity of the ionization laser was reduced to the detectability limit of the precursor molecule. The only observable effect depending on the dissociation laser timing, and hence verifying the functionality of the photolysis, was a decrease of oxygen in the mass spectrum when the dissociation laser was turned on (Fig. 3). A loss of oxygen would be expected due to the production of oxygenated species. Our experiment so far is interpretable and further measurements are needed for a clear analysis.

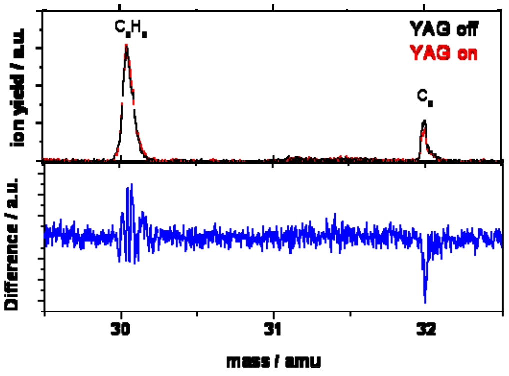

Fig.3: Difference spectrum: Dissociation laser on and off. Reduction of O_2 observed.

The photolysis of ketones of type R-CO-R has been proposed as alternative to the alkyl halogenides. Diethyl-ketone (3-pentanone) dissociates after photo-excitation to C_2H_5 and CO.

C_2H_5-CO- C_2H_5 + $h\nu$ $\rightarrow$ C_2H_5-CO + C_2H_5 $\rightarrow$2 C_2H_5 + CO

Two ethyl radicals are produced upon photo excitation. Moreover, CO is, in respect to the expected radical pool, chemically quite inert [18]. However, the absorption cross section of $(C_2H_5)_2CO$ is two orders of magnitude lower (~60^{-20} cm^2/molecule) compared to ethyl iodine and the dissociation occurs not exclusively at the C-C bond of the ketone-group [23], complicating the experiment. The problem may be overcome with an ArF-excimer-laser providing up to 200 mJ @ 193 nm. Experiments with our current setup gave no evidence for the production of ethyl peroxyls by photolysis of di-ethyl ketone in the presence of oxygen.

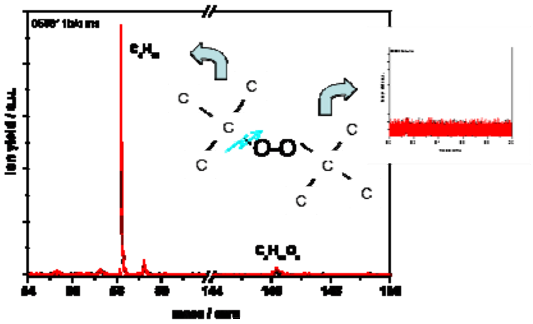

Fig.4: Fragmentation of Di-tert-butyl-peroxide upon

The peroxyl ion states are not known and their stability has been questioned many times (Recent discussion in [24]). Therefore, it is possible that alkylperoxyls are formed but can not be detected as ions that possibly dissociate immediately after the fs ionization step. This suspicion is supported by the photolyis of di-tert butyl peroxide ($C_8H_{18}O_2$). The fragmentation pattern of the stable $C_8H_{18}O_2$ molecule (Fig.4) shows a strong peak at the C_4H_{10} instance but no observable signal for butyl peroxyl ($C_4O_2H_n$) (insert of Fig. 4). This experiment indicates that though $C_4H_{10}O_2$ radicals most likely are produced, they dissociate as neutrals or do not survive the ionization step. Interestingly, the ion signal of the parent molecule is also much weaker than that of the isobutane (C_4H_{10}) fragment, even though the ionization potential (IP) of the mother molecule is relatively low at 8.78 eV [25] compared to iso-butane at 10.57 eV [26].

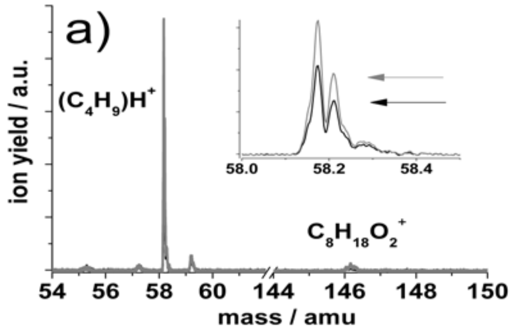

Fig.5 Fragmentation products of di-tert-butyl upon fs multiphoton ionization, with (grey) and without (black) 266 nm photolysis

In nano-second ionization experiments di-tert-butyl peroxide dissociates in a range of fragments. Fs-ionization methods is more selective as the process is too fast to allow fragmentation via neutral dissociative intermediate states. However, dissociation is not totally avoided as dissociative ionic states may be excited. Figure 5. shows that $(C_4H_9)H^+$ at mass 58u is the main fragment showing up when we try to ionize di-tert-butyl peroxide. The 'mother' molecule signal is rather weak indicating that most di-tert-butyl peroxide ions dissociate. The ionic bond cleavage presumably occurs between the C and O atoms with simultaneous abstraction of an H atom yielding a neutral fragment and protonated tert-butyl ion. This is in contrast to the dissociation of neutral di-alkyl peroxide, for which an excitation to the first excited singlet states yields an O-O rupture [27-29], and in agreement with the observed change of ion production when the 266 nm photolysis laser has been switched on (grey curve). In this case a reduction of the O_2^+ peak occurred, while the $(C_4H_9)H^+$ signal increased. We believe that the photolysis produces tert-butoxy radicals, which upon ionization still fragment to tert-butyl radicals by breaking the C-O bond. The free oxygen atoms seem to form C_2O^+

as it has been evidenced as the only additional increasing signal in the mass spectrum at photolysis conditions.

An interesting feature can be observed in the ionization spectrum of di-tert-butyl peroxide. The main fragmentation product $(C_4H_9)H^+$ shows a double peak structure, which indicates a high kinetic energy release to the dissociating fragments. Ion fragments, ejected in opposite direction along the time of flight axis will arrive at different times at the detector. Ions dissociating in an orthogonal direction will arrive within this time interval. A broadened TOF peak would then be expected. The appearance of a double peak in Fig. 5. may be due to a loss of orthogonally departing ions that are no longer accepted by the aperture of the TOF-MS ion optics.

So far no alkyl-peroxides or stable peroxide ions have been observed in the time of flight mass spectra. This has directed our attention to ‘pure’ spectroscopic investigations of neutrals instead of ion detection methods.

Pyrolytical Source

Though photolysis, due to its experimental ease, is often the method of choice, it does not provide in all circumstances a clear-cut production of the desired species. Strong side effects were observed in the case of photolytic ethyl production from ethyl-iodide, which could not easily be worked around [30]. In addition to photolysis, concurrent photo-excitation occurs producing radicals not only in their electronic ground state but in excited states, too. These excited molecules exhibit an own spectrum of photonic transitions that may interfere with the applied spectroscopic monitoring, or lead to further dissociation increasing the variety of species.

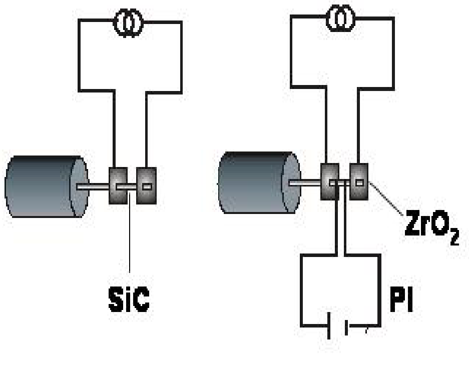

Fig. 6: Pyrolytical radical source

A different concept for radical production are the two pyrolytical radical sources shown in Figure 6. This type of sources has been described in detail by Chen et al. [31]. A tube, made out of a semi-conducting material, is directly heated by an electric current along its length. The main difference between the arrangements shown in the figure is the tube material, SiC or ZrO_2. In the case of ZrO_2, the tube has to be initially preheated with an ancillary heater, e.g. a platinum coil. Gas containing a precursor dissociating to a specific radical is flown through the hot tube. Efficient pyrolytic dissociation often requires temperatures up to the realistically feasible limit around 2100 K.

In preliminary measurements we have operated a Siliciumcarbid (SiC) source in a molecular beam experimental set up. The source has been aligned to the 1mm diameter outlet of a valve, pulsed at 10 Hz. Again, ethyl -iodide served as a precursor. After selection of a molecular beam from the gas pulse by skimming, intermediates contained in the beam were multiphoton ionized and analyzed in a linear TOF-spectrometer, yielding the speciation of the gas. It could be shown that the precursor ethyl-iodide is totally consumed and no longer appears in the mass spectrum when the tube is heated (pyrolysis on). However the measurement does not yet give a definitive answer, whether ethyl-iodide dissociates exclusively to ethyl and atomic iodine. Actually, ethyl also appears when the pyrolysis is off, indicating that ethyl is formed by potodissociation in the ionization step. If ethyl-iodide dissociates pyrolytically mainly to ethyl, the ethyl-ion yield should increase when the SiC tube is heated up. However, it is difficult to quantitatively compare the two measurements with a hot and cold source. The flow through the tube changes with temperature influencing the expansion characteristics of the gas and thereby its cooling rate prior to be skimmed as molecular beam. The density of molecules in the beam may change and a different level population due to a hotter or cooler beam affects the ionization efficiency. Though the pyrolytic source proved in other contexts to be a valuable instrument to produce specific molecular beams it seems to be less suited for the production of alkyl-peroxyl radicals.

Discharge Source

Yet another approach to generate hydrocarbon radicals are sources comprising a discharge excitation. In a gas containing suitable precursors a pulsed electric discharge is established between two electrodes in the channel through which the gas flows prior to expansion into vacuum. These source are especially useful if ionic intermediates are desired. Actually, another approach to the creation of peroxy radicals is the “ion” channel. An alkyl kation combines with a diatomic oxygen anion according to equation 2, exemplified for ethylperoxyl.

$$C_2H_5^+ + O_2^- + M \rightarrow CH_3CH_2OO^* + M \qquad (2)$$

Pulsed discharges with fast voltage rise times provide a means of generating non-equilibrium ion-molecular plasmas. Hence, a variety of intermediate charged and neutral molecules can be generated in post discharge chemistry. Discharges in hydrocarbon containing mixtures have been the focus of a number of recent studies with a variety of potential applications [32-35] (e.g., transformation of methane into larger C_n hydrocarbons, organic synthesis in electric discharges). In some cases species production can be very selective [34]. The discharge activates a molecular precursor by electron collisions. The activation efficiency depends on an energy dependent cross section characteristic for a specific molecule and the electron energy distribution of the available electrons. By varying the discharge characteristics (current, pulse duration) and the gas mixture, optimal conditions for enhanced generation of a particular species may be found.

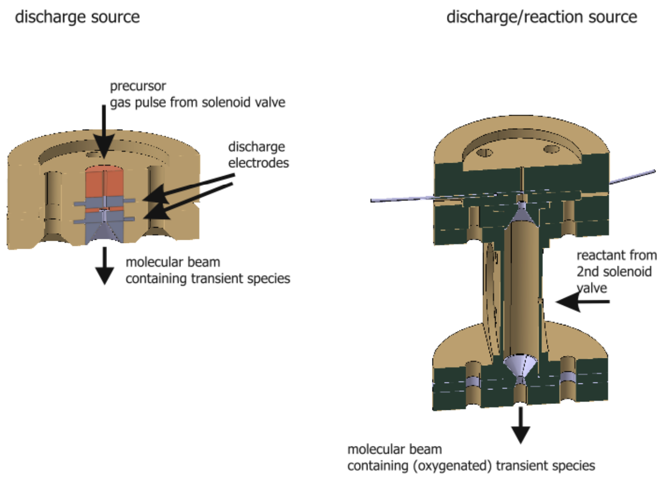

Fig. 7: Production of transient species in a molecular beam. Left: Discharge source. Right: Design of the discharge/reaction source. A pulse containing a reactant, like O_2 or NO_2, is added after the discharge. Reaction products are then supersonically expanded into the vacuum and cooled to ≈ 5-20 K.

In general the chemical processes induced by discharges would end up in the production of the most stable molecules. The combination of a discharge and a molecular beam technique enables the control of the plasma chemistry. The species produced in the discharge pass a so-called reaction channel before they expand with the gas pulse into vacuum. After the expansion collisions do no longer occur and all binary reactions stop. The length of the reaction channel can be chosen such that reactions stops when a specific intermediate species reached its maximum concentration.

Fig. 7 depicts the discharge source. It contains a set of electrically isolated stainless steel disc electrodes mounted on the valve body by glass ceramic spacers (MACOR). Radical production starts with a trigger applied to the solenoid valve producing a gas pulse containing about 5 % of a precursor, e.g. methane diluted in Ar. At a variable time after the initial trigger for the valve, a high voltage pulse of ~ 800 V and adjustable duration is applied to the discharge electrodes. A careful optimization of the voltage, trigger delay, trigger duration and polarity yields an intense and remarkably stable molecular beam.

Unfortunately, oxygen containing precursor molecules have generally a deteriorating effect on the discharge. As a consequence, we have designed a novel source for oxygenated transient species, like peroxy-radicals. A gas pulse from a second valve providing an oxygenated precursor (O_2, NO_2 etc) starts after an adjustable delay relative to the precursor gas pulse and discharge trigger. Radicals and other reactive species are allowed to react for a few μs prior to supersonic expansion. Up to now the discharge source was thoroughly tested for the production of C_3 – trimers using 5 % acetylene or cyclo-propane as precursor diluted in Ar. Initial experiments aiming at the production of oxygenated radical species are planned for early 2007 in the context of the follow up project.

Mass spectrometric experiments were carried out with methane and ethane diluted in rare gases (e.g., argon) or rare gas/O_2 mixtures. In addition discharges with the oxygen containing precursor molecules methanol and di-ethyl ketone were performed. For preparation of gas mixtures starting with liquid precursors the same bubbler assembly was used as for the photolytic setup.

One advantage of a discharge source is the use of small precursor molecules that form bigger compounds by reactions. There are then no direct precursor fragments that interfere at higher masses. The smallest precursor for hydrocarbon radical production is methane (CH_4). Figure 8 shows the difference between two mass spectra, which were detected under the same experimental conditions but with and without discharge. Positive peaks in Fig. 8 indicate thus production of and negative peaks destruction of molecules in the applied discharge. The precursor molecule is methane (4%) in He and the total pressure was 2.5 bar. The mass spectrum shows efficient methane fragmentation with the discharge on. The negative peak at 44 amu indicates destruction of butane that was introduced by the precursor gas as contamination.

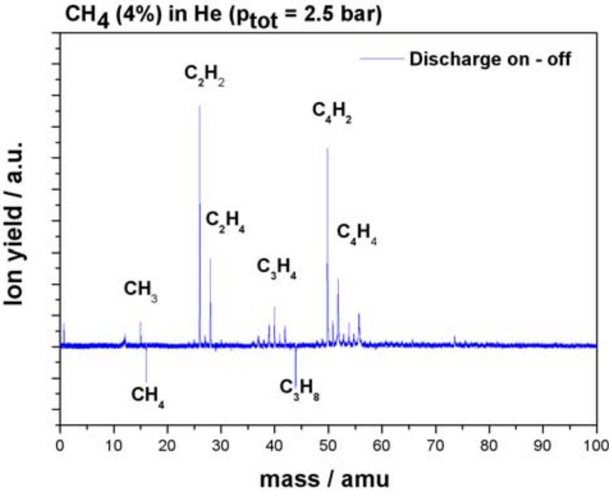

Fig. 8: Difference mass spectra of methane. Positive peaks indicate the production and negative peaks destruction of detected species by the applied discharge.

Besides the series of hydrocarbon radicals with various numbers of H atoms the very stable closed shell molecules like acetylene, diacetylene, and triacetylene are clearly observed. Most important for our investigation is the production of methyl radicals. Methyl reacts to methyl peroxyl in the presence of O_2 similar to the former discussed ethyl radical. Methyl peroxyl should be observable in mass spectrometry as its ion has found to be stable in an experiment performed by I. Slagle [36]. Adding oxygen to the gas indeed produced a range of new peaks in the mass spectra (Fig. 9). However, a clear identification of oxygen containing compounds was not yet feasible. Moreover no evidence for the production of methyl peroxide at mass 47 (CH_3O_2) was found in the measurements performed so far.

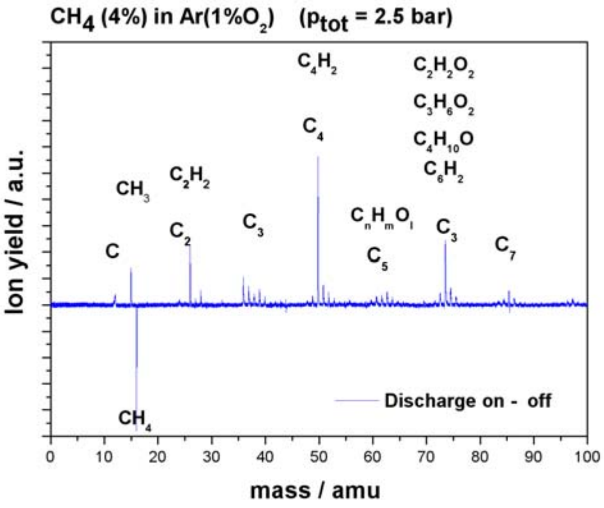

Fig. 9: Difference mass spectra of 4% methane in argon and 1% O_2.

Up to now we could prove that a discharge in hydrocarbon loaded rare gases efficiently produces alkyl radicals (that themselves are of high interest). The addition of O_2 does produce additional species which, however, could not yet unambiguously be assigned to oxygen containing molecules.

The discharge experiments are far from complete, but already now show a great experimental potential. Optimization towards the production of oxygenated compounds comprise a range of measurements with different precursors and a variation of experimental parameters such as pressures, mixture ratios, discharge current and discharge duration. As a high abundance of alkyl radicals could already be demonstrated with the discharge source.

Fast Dynamics by fs- Spectroscopy

The fast dissociation reaction of photo excited peroxides, suggest that ultra-fast spectroscopic investigations of the short-living and unstable species can be advantageous. We therefore aim to develop and to apply ultrafast spectroscopic methods to investigate alkyl peroxides (R-OO*), di-alkyl-peroxides (R-OO-R) or peroxide precursor molecules (e.g. R-I) by means of time resolved four wave mixing (FWM) methods. Even though the main targets of the proposed investigations are the R-OO* radicals, the R-OO-R peroxide species are often more stable at standard conditions and therefore can serve as a preliminary system.

Because all molecules of our interest have their electronic resonances in the UV frequency range, a UV–fs-FWM setup has been assembled. The 800 nm output of Ti Sapphire regenerative amplified

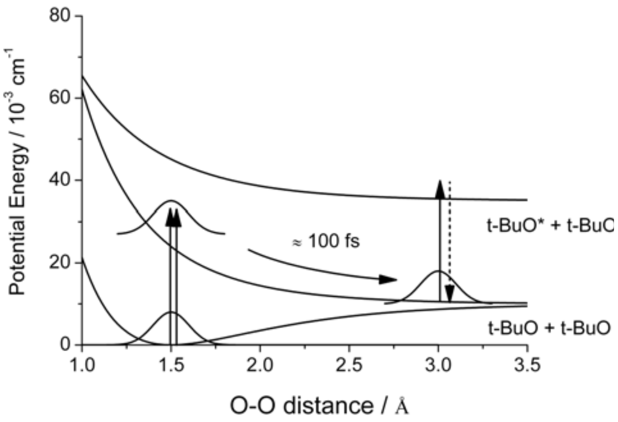

Fig.10 Potential energy surfaces and a possible excitation scheme of di-tert-butyl peroxide.

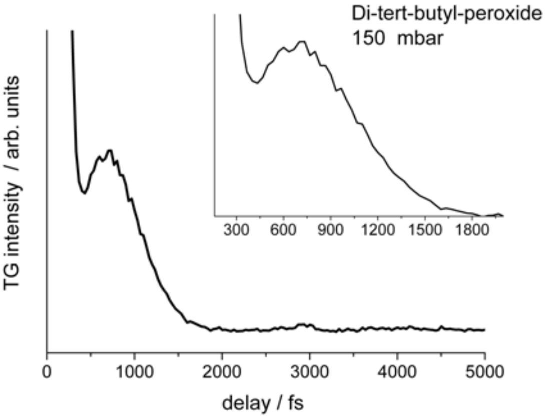

Fig.11 UV-resonant fs-transient signal of di-tert-butyl peroxide, according to the excitation scheme shown in Fig.6

Laser system (Clark MXR 1000) is converted by two homebuilt OPA systems into the infrared and visible wavelength region. The visible laser pulses are converted to ultraviolet pulses by second harmonic generation using BBO crystals. The obtained pulse energies and duration have been approximately 1 µJ to 3 µJ and ~ 220 fs FWHM at the sample position.

The UV absorption spectrum of di-tert-butyl peroxide is unstructured, but can be divided into two regions; one above and one below λ~230 nm. Transitions from 340 nm to 230 nm presumably correspond to a $\pi^* \rightarrow \sigma^*$ excitation to a non bonding orbital configuration and break the molecule symmetrically at the O-O bond, producing vibrationally 'hot' tert-butoxy radicals with unity quantum efficiency [29]. The potential energy profiles for the cleavage of the O-O bond in di-tert-butyl -OO have been outlined as very coarse approximations in Figure 10 to provide a basis for a mechanistic discussion. The approximations are based on thermo chemical data and semi-empirical potential energy curves of the HOOH molecule. Figure 10 displays a possible excitation scheme which would yield a delayed signal that could be exploited to determine the potential curves. The ensemble of excited molecules, which has been created by the coherent interaction with the initial light pulses, evolves in time along the O-O distance coordinate. If the probe pulse energy and the timing matches an optimal optical transition to a third electronic state, the signal intensity is expected to increase again.

The measurement were performed with 80 - 200 mbar di-tert-butyl peroxide prepared in a cell. The cell consists of a cylindrical stainless steel main body with four large aperture quartz windows for optical access. A photolysis laser beam can enter the cell through one the four quartz windows. A 305 nm excitation is at resonance with the repulsive excited state. Figure 11 depicts the measured transient. Next to a strong non-resonant contribution at zero time delay, di-tert-butyl peroxide provides a signal, which peaks at ~1 ps and decays within 2 ps. In addition a small contribution, most probably from a residual O_2 content, is observed at ~ 3 ps delay time.

The measurement most probably does not show the feature searched for. The dissociation energy of the O-O bond has been measured to be approx. 14700 cm^{-1} and the time it takes for increasing the distance of the O atoms from their equilibrium position at 1.467 Å to 3.5 Å along the repulsive excited state surface can be estimated to be ~100 fs. This is in contrast to the observed signal behaviour shown in Fig. 11, which indicates a signal recurrence only after about one picosecond. The observed signal has another origin, possibly it is due to rotational effects or ro-vibrational coupling from low lying vibrations. The exclusion of such ambiguous interpretations and the search for a signal depending on the dissociation along a defined potential curve needs further measurements and simulations of the behaviour of photoexcited di-tert-butyl peroxide.

5. Conlusions

The envisaged project on peroxy radicals is very ambitious and still bears many risks. The technical effort to achieve a suitable experimental environment is considerable and time consuming. A lot of our effort has to be spent in the development of new methods and new experimental techniques. Our attempts to apply the available methods to peroxy radicals produce interesting and promising results. Yet, the findings are not unambiguous and more measurements have to be performed. At the same time the mass-spectrometric and laser-spectroscopic techniques are refined.

At our focus are the investigations on quantum state-resolved dissociation processes by photofragment excitation (PHOFEX) spectroscopy. The method invokes, simultaneously, resonant degenerate four-wave mixing (DFWM) and laser induced fluorescence (LIF) [38]. It yields state-specific information on dissociative energy levels of a parent molecule and the emerging fragments. We develop PHOFEX with test molecules, mainly formaldehyde. In fact, H_2CO represents one of the few polyatomic molecules with readily accessible, spectroscopically well characterized states [37]. At the same time H_2CO is of high relevance for combustion. The measrured data are important for combustion diagnostics as well as for accurate flame modelling Our measurements produced new information on the decomposition properties of this molecule.. In the time period of this project, we have measured more than 800 state-to-state quantum yields for the unimolecular dissociation reaction H_2CO (ν, J,K_a,K_c) → HCO (ν, J,N, K_a,K_c) + H. A comparison of these measurements with data obtained from statistical models shows inconsistencies and imply that a more detailed analysis eventually improving the dissociation models is still necessary. A newly established external cooperation will shed more light on the dissociation reaction by applying demanding *ab initio* structure calculations.

The recently established [39] cavity ring-down (CRD) technique bodes well to provide quantitative absorption spectra with a substantially increased sensitivity. Thus, extended spectroscopic investigations are accessible on cold molecules and radicals in the collision-free environment of a molecular beam. We demonstrate initial experiments on the 4051-Å band of C_3 and show, for the first time, the applicability of a discharge source for the nonlinear spectroscopy of transient species in a molecular beam [15].

Femtosecond pump probe methods, CRD- and PHOFEX-techniques will continuously applied to further scrutinize the dissociation paths of H_2CO leading to H_2 + CO and H + HCO, respectively. The experience gained with H_2CO will then be transferred to the spectroscopic assessment of peroxy radicals, HOO being the prime candidate to which not only our measurement techniques but also a lot of available theoretical work can be applied.

Currently we install the chemical dynamics beamline at Swiss Light Source (SLS). In 2007 first pilot experiments will be performed. This beamline providing unambiguous single VUV photo-ionization for mass spectrometry meets our demands for complementary techniques towards successful assessment of peroxy compounds.

In the frame of a new grant BFE supports our work towards assessing the role of peroxy radicals and other species dominating ignition. The search for suitable precursors for peroxy radicals production in our test rigs allowing fs-spectroscopic or mass spectrometric measurements will remain our prime focus in 2007. More experiments, including laser sepctroscopic and synchrotron based measurements, are needed for an unambiguous spectroscopic and mass spectrometric identification of intermediate species.

7. Internationale Cooperation

With the new activity at SLS and with the establishment of a VUV beamline dedicated for molecular dynamics, a lot of knowledge and experience is brought to us by external groups with whom we are going to perform experiments. In a close cooperation with Tom Baer from University of North Carolina we will establish a Photo-Electron Photo-Ion Coincidence (PEPICO) apparatus to measure the formation enthalpies of a range of organometallic complexes The applied techniques can and will be applied to our objectives, peroxy radicals, as well.

The success of the fs experiments has led to a cooperation with the International University of Bremen ('Group of Prof. Dr. Arnulf Materny'), where fs-CARS experiments have been performed on benzene to explore energy transfer processes and rotational effects in liquids and in the gas phase.

The interpretation of measured dissociation data needs more theoretical investigations on the potential curve of molecules as well as the refinement of existing dissociation models. With Prof. R. Marquardt from University of Strassbourg we plan to performe a comprehensive investigation of molecular state manifolds by sophisticated ab initio computations.

6. Referenzen

1. Sumathi, R. and W.H. Green, *Missing thermochemical groups for large unsaturated hydrocarbons: Contrasting predictions of G2 and CBS-Q.* Journal Of Physical Chemistry A, 2002. **106**(46): p. 11141-11149.
2. R. G. Compton, G.H., M. J. Pilling ed. *Low-temperature Combustion and Autoignition*. Comprehensive Chemical kinetics, ed. G.H. R. G. Compton. Vol. 35. 1997, Elsevier: Amsterdam.
3. R. Sumathi, W.H.G.J., *A priori rate constants for kinetic modeling.* Theor. Chem.Acc, 2002. **108**: p. 187-213.
4. Curran, H.J., et al., *A comprehensive modeling study of iso-octane oxidation.* Combustion and Flame, 2002. **129**(3): p. 253-280.
5. Curran, H.J., et al., *A comprehensive modeling study of n-heptane oxidation.* Combustion and Flame, 1998. **114**(1-2): p. 149-177.
6. Wallington, T.J., P. Dagaut, and M.J. Kurylo, *Ultraviolet-Absorption Cross-Sections And Reaction-Kinetics And Mechanisms For Peroxy-Radicals In The Gas-Phase.* Chemical Reviews, 1992. **92**(4): p. 667-710.
7. Lightfoot, P.D., et al., *Organic Peroxy-Radicals - Kinetics, Spectroscopy And Tropospheric Chemistry.* Atmospheric Environment Part A-General Topics, 1992. **26**(10): p. 1805-1961.
8. Maric, D., J.N. Crowley, and J.P. Burrows, *Application of a Gaussian distribution function to describe molecular UV-visible absorption continua .2. The UV spectra of RO(2)center dot radicals.* Journal of Physical Chemistry A, 1997. **101**(14): p. 2561-2567.
9. Jafri, J.A. and D.H. Phillips, *Ground and Lower Excited-States of Methyl Peroxy, Ch3o2, Radical - a Computational Investigation.* Journal of the American Chemical Society, 1990. **112**(7): p. 2586-2590.
10. Hunziker, H.E. and H.R. Wendt, *Electronic Absorption-Spectra of Organic Peroxyl Radicals in near-Infrared.* Journal of Chemical Physics, 1976. **64**(8): p. 3488-3490.
11. Nandi, S., et al., *Polarized infrared absorption spectrum of matrix-isolated methylperoxyl radicals, CH3OO (X)over-tilde 2A ".* Journal Of Physical Chemistry A, 2002. **106**(33): p. 7547-7556.
12. Blanksby, S.J., et al., *Negative-ion photoelectron spectroscopy, gas-phase acidity, and thermochemistry of the peroxyl radicals CH3OO and CH3CH2OO.* Journal of the American Chemical Society, 2001. **123**(39): p. 9585-9596.
13. Barckholtz, T., J.W. Bozzelli, and C.J. Chen, *Reactions of peroxy radicals: Calculations of elementary reaction paths important to ignition of hydrocarbons, comparisons with experiments.* Abstracts of Papers of the American Chemical Society, 2003. **226**: p. 287-PHYS.
14. H. J. Curran, P.G., W. J. Pitz and C. K. Westbrook, *A Comprehensive Modeling Study of iso-Octane Oxidation.* Combustion and Flame, 2002. **129**: p. 253-280.
15. Tulej, M., M. Meisinger, and P. Radi, *multiplex spectroscopy of stable and transient species in a molecular beam.* Journal of Raman Spectroscopy, 2007. **accepted**.
16. Germann, G.J. and D.J. Rakestraw, *Multiplex Spectroscopy - Determining the Transition Moments and Absolute Concentrations of Molecular-Species.* Science, 1994. **264**(5166): p. 1750-1753.
17. Tang, Y. and S.A. Reid, *Multiplex spectroscopy of jet-cooled NO2.* Chemical Physics Letters, 1998. **292**(4-6): p. 691-697.
18. Pushkarsky, M.B., S.J. Zalyubovsky, and T.A. Miller, *Detection and characterization of alkyl peroxy radicals using cavity ringdown spectroscopy.* Journal Of Chemical Physics, 2000. **112**(24): p. 10695-10698.
19. Miller, D.R., *Atomic and Molecular Beam methods*, ed. S. G. 1988, New York: Oxford University.
20. Ramsey, N.F., *Molecular Beams*. 1990: Oxford Univerity: New York
21. Giuliani, A., et al., *Electronic excitation and oscillator strength of ethyl iodide by VUV photoabsorption and electron energy loss spectroscopy.* Journal Of Chemical Physics, 1999. **110**(21): p. 10307-10315.
22. Hartley, D.B. and S.W. Benson, *Kinetics Of Reaction Of Hi With Ethyl Iodide And Heat Of Formation Of Ethyl Radical.* Journal Of Chemical Physics, 1963. **39**(1): p. 132-&.
23. Martinez, R.D., et al., *The Near Uv Absorption-Spectra Of Several Aliphatic-Aldehydes And Ketones At 300-K.* Atmospheric Environment Part A-General Topics, 1992. **26**(5): p. 785-792.

24. Meloni, G., et al., *Energy-resolved photoionization of alkylperoxy radicals and the stability of their cations.* Journal of the American Chemical Society, 2006. **128**(41): p. 13559-13567.
25. Coughlin, D.J., R.S. Brown, and R.G. Salomon, *Prostaglandin Endoperoxide Nucleus And Related Bicyclic Peroxides - Synthetic And Spectroscopic Studies.* Journal Of The American Chemical Society, 1979. **101**(6): p. 1533-1539.
26. Flesch, G.D. and H.J. Svec, *Fragmentation Reactions In Mass-Spectrometer For C2-C5 Alkanes.* Journal Of The Chemical Society-Faraday Transactions Ii, 1973. **69**(8): p. 1187-1199.
27. Scaiano, J.C. and G.G. Wubbels, *Photosensitized Dissociation of Di-Tert-Butyl Peroxide - Energy-Transfer to a Repulsive Excited-State.* Journal of the American Chemical Society, 1981. **103**(3): p. 640-645.
28. Evleth, E.M., *Ground and Excited-State Correlations in Rupture of Oxygen-Oxygen Bonds in Peroxides.* Journal of the American Chemical Society, 1976. **98**(6): p. 1637-1639.
29. Dorer, F.H. and S.N. Johnson, *Energy Partitioning on Photolysis of Di Tert Butyl Peroxide.* Journal of Physical Chemistry, 1971. **75**(24): p. 3651-&.
30. Knopp G. , B.P., Radi P. , Tulej M. , and Gerber T. , *Femtosecond Photodissociation of the Ethyl Radical C2H5.* Femtochemistry and Femtobiology: ultrafast dynamics in molecular science. 2002: world scientific 116.
31. Kohn, D.C., H; Chen, P, *Flash pyrolysis nozzle for generation of radicals in a supersonic jet expansion.* Review of Scientific Instruments, 1992. **63**(8): p. 4003-4005.
32. Yao, S.L., E. Suzuki, and A. Nakayama, Plasma Chem. Plasma Process., 2001. **21**: p. 651.
33. Yao, S.L., et al., Plasma Chem. Plasma Process., 2002. **22**: p. 225.
34. Kudryashov, S.V., et al., Russ. J. Appl. Chem., 2004. **77**: p. 1904.
35. Jianxun, H.E., et al., *Investigation on Methane Decomposition and the Formation of C2 Hydrocarbons in DC Discharge Plasma by Emission Spectroscopy.* Chinese J. Chem. Eng., 2004. **12**: p. 149-51.
36. Slagle, I.R., E. Ratajczak, and D. Gutman, *Study of the thermochemistry of the* $C_2H_5 + O_2 \leftrightarrow C_2H_5O_2$ *and* $T\text{-}C_4H_9 + O_2 \leftrightarrow T\text{-}C_4H_9O_2$ *reactions and of the trend in the alkylperoxy bond strengths.* Journal Of Physical Chemistry, 1986. **90**(3): p. 402-407.
37. Clouthier, D.J. and D.A. Ramsay, *The Spectroscopy of Formaldehyde and Thioformaldehyde.* Ann. Rev. Phys. Chem., 1983. **34**: p. 31-58.
38. Tulej, M., et al., *Photo-fragment excitation spectroscopy (PHOFEX) by DFWM and LIF: propensities for H2CO -> HCO+H near the S-o threshold.* Journal of Raman Spectroscopy, 2005. **36**(2): p. 109-115.
39. Tulej, M., et al., *Comparative study of degenerate four-wave mixing and cavity ringdown signal intensities of formaldehyde in a molecular beam.* Journal of Raman Spectroscopy, 2006. **37**(6): p. 680-688.