F1. Kinetics Study of the Reaction OH + NO_2 + AIR → Products

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The OH + NO_2 association reaction is one of the most important gas phase chemical transformations in atmospheric chemistry.

$$OH + NO_2 + Air \rightarrow HONO_2 + Air \quad (1a)$$

$$\rightarrow HOONO + Air \quad (1b)$$

Because reaction (1a) converts highly reactive HO_x and NO_x radicals into relatively unreactive nitric acid ($HONO_2$), models of urban air quality are more sensitive to the rate coefficient for this reaction (k_{1a}) than to any other single rate coefficient. Reaction (1a) also plays an important role in controlling radical levels in low temperature environments like the upper troposphere and lower stratosphere. Because of its importance in atmospheric chemistry, the OH + NO_2 reaction has been studied many times over the last 3 decades. Nonetheless, uncertainties in both the overall rate coefficient for OH removal ($k_1 \equiv k_{1a} + k_{1b}$) as well as the temperature and pressure dependence of the $HONO_2$ and HOONO product yields remain undesirably high. Peroxynitrous acid (HOONO) is a relatively weakly bound chemical species that is expected to dissociate to HO_2 + NO relatively rapidly in all but the coldest atmospheric environments. Hence, unlike reaction (1a), reaction (1b) is probably not a sink or long-term reservoir for HO_x and NO_x radicals in most atmospheric environments.

We are employing a laser flash photolysis − pulsed laser induced fluorescence technique to make high accuracy measurements of k_1 as a function of temperature (220 − 320 K) and pressure (20 − 800 Torr) in air bath gas. The improvement over earlier work in our approach is the use of sensitive multipass absorption spectroscopy to quantitatively measure the NO_2 concentration both upstream and downstream from the reaction cell in the flowing gas mixture that contains NO_2, air, and a photolytic source for OH (H_2O_2, $HONO_2$, or acetyl acetone). This approach, which employs narrow-band radiation from an argon ion laser as the light source (457 nm line) allowed us to make the most accurate measurements available of temperature-dependent rate coefficients for the key stratospheric reaction O + NO_2 → NO + O_2 [1]. Having demonstrated to our satisfaction that the NO_2 absorption cross section for the 457 nm narrow-band radiation is pressure-independent up to P ~ 900 Torr, we believe that our rate coefficient measurements are accurate to better than ±10%. The room-temperature falloff curve obtained from our data is shown and compared with current NASA and IUPAC panel evaluations [2,3] in Figure 1. Temperature dependent data are being acquired and will be presented.

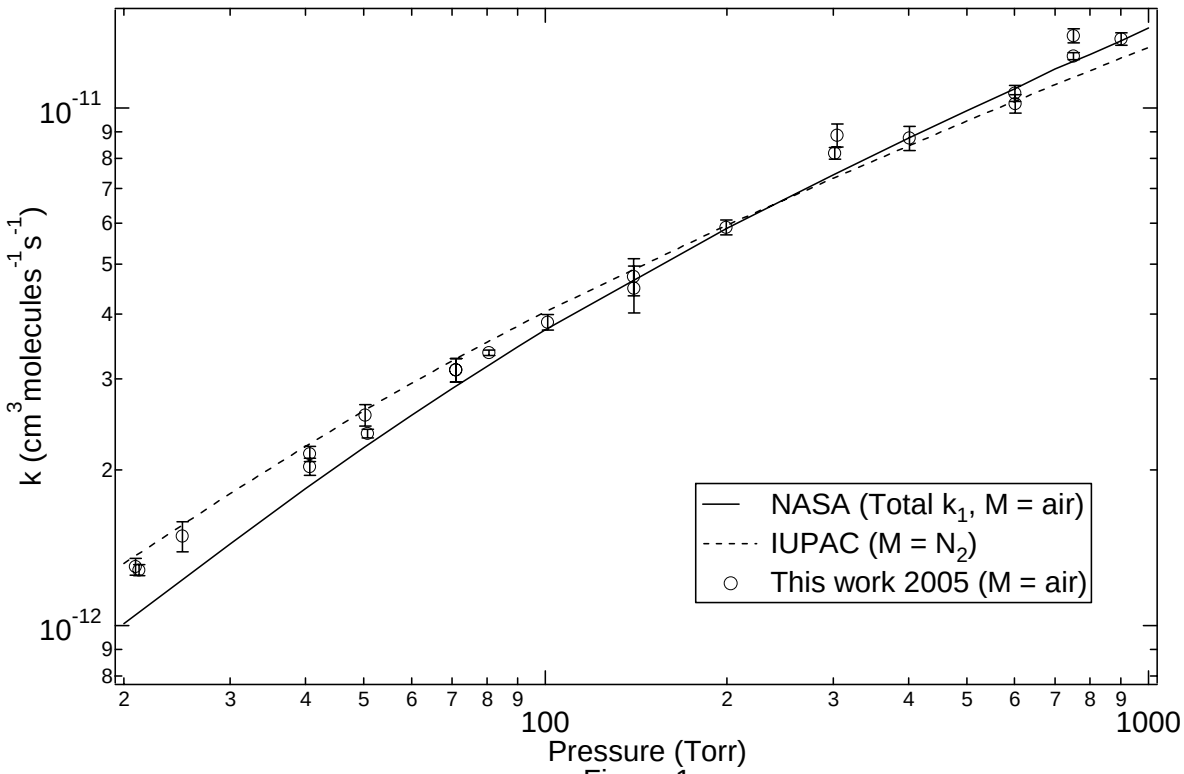

Figure 1

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F2. Elementary Reaction Mechanism Formulation for the Hydroxylamine-Nitric Acid-Nitrous Acid System

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An elementary reaction mechanism for the autocatalytic and scavenging reactions of hydroxylamine in an aqueous nitric acid medium was developed from first principle quantum chemical calculations and previously published insights into the system. An improved understanding of the titled reactions is needed to determine the "stability boundary of hydroxylamine" for safe operations of the Plutonium-Uranium Reduction Extraction (PUREX) process. Under the operating conditions of the PUREX process, namely 6M nitric acid, the reactive forms of hydroxylamine are NH_2OH, NH_3OH^+, and the complex $NH_3OH{\cdot}NO_3$, and those of nitrous acid are NO^+, H_2ONO^+, N_2O_4, N_2O_3, NO_2, and NO. High level CBSQB3/IEFPCM and CBSQB3/COSMO calculations were performed using GAUSSIAN03 to investigate the energy landscape and to explore a large number of possible ion-ion, ion-radical, ion-molecule, radical-radical, radical-molecule, and molecule-molecule pathways available to the reactive forms of the reactants in solution. An elementary reaction scheme has been proposed and rate constants for the reactions were estimated using transition state theory and other traditional techniques. Estimates of the thermochemical data for the species and reactions of interest were also performed to allow for the prediction of reaction equilibria and temperature effects. This systematic exploration of reactions in solution and mechanism development for a solution phase process based on SCRF results is likely to be one of the first of its kind. Analysis of modeling results yielded insights into the titled reactions, and into how well modern computational chemistry techniques can predict the complex thermochemistry and reaction kinetics of ionic, radical, and neutral species in highly polar media.

F3. Intramolecular Vibrational Energy Redistribution within 1,1,1-Trifluoroethane: A Molecular Dynamics Study

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Recently Kiefer et al.[1] (KKSST) studied HF elimination from 1,1,1-trifluoroethane (TFE) using a shock-tube, laser schlieren setup. KKSST report unimolecular rate constants, vibrational relaxation and incubation times, and their attempts to model the data using a strong collision version of RRKM theory. Several results of this study are of interest: 1) The vibrational relaxation displays two distinct time constants. 2) The unimolecular rate constants show little pressure dependence when compared to the pressure dependence predicted by RRKM theory. 3) Modeling the reaction using RRKM theory did not reproduce the dual vibrational relaxation times. KKSST suggest that slow intramolecular vibrational energy redistribution (IVR) out of the torsional mode might be responsible for these unusual observations.

Although difficult to measure experimentally, IVR can in principle be investigated using molecular dynamics simulation provided an accurate potential energy surface exists for the system of interest. In order to study IVR within TFE we have developed a potential energy function for use in the molecular dynamics program VENUS96[2]. Our potential energy function employs Morse oscillators to describe bond stretching and harmonic functions to describe bond bending. Functions to describe the three-fold symmetric torsional potential are also included. Additionally, non-diagonal stretch-stretch, bend-bend and stretch-bend interactions are included in the potential energy function. The adjustable parameters in the potential energy function were chosen so that the vibrational frequencies and geometry defined by the potential energy surface are in good agreement with these properties calculated at the B3LYP/cc-pVTZ level of theory.

With our potential energy function we are using VENUS96 to study IVR within TFE for energies below the threshold energy for the HF elimination reaction. In particular, our efforts focus on determining the time required for energy initially localized in the torsional mode to redistribute to other vibrational modes in the molecule, both for the isolated molecule and for molecules perturbed by collisions. These calculations are still underway, and preliminary results will be presented.

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F4. Formation Of Nanoparticles By Rapid Expansion Of Supercritical Solutions: *In Situ* Characterization By Laser Scattering

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A technique for *in situ* characterization of the RESS process (Rapid Expansion of Supercritical Solutions) was developed and applied to RDX (cyclotrimethylenetrinitramine) nanoparticle formation. An excimer laser (248 nm) was used in combination with a fast gated ICCD camera. Calibrations of the ICCD camera were done using Rayleigh scattering from air and Mie scattering from standard latex particles. The results of these two calibrations agreed within 20 %, which results in less than 5 % error in the RDX particle size.

The technique was applied to study the evolution of the particle size distribution function downstream the RESS jet of RDX-CO_2 supercritical solutions. The ICCD images of a small area of the jet were accumulated for the different sampling positions. The spots, which correspond to scattering from individual nanoparticles, were identified, and the spot intensities were converted to the particle size using the calibrated sensitivity. An example of the ICCD frame is given in Figure 1. The dependence of the size distribution function on the distance from the nozzle is illustrated in Figure 2. The particle size at the maximum of the distribution functions is 82 ± 2 nm over the range 6 - 43 mm from the nozzle. It is apparent that at 6 mm the process of particle formation is almost completed and there is mainly reduction of the particle concentration due to air entrainment.

Somewhat different behavior is observed for large particles (larger than 120 nm) were the number of particles initially increased and then decreased downstream the jet. This is tentatively interpreted as due to condensation of carbon dioxide with subsequent evaporation.

The experimental results were compared with numerical simulations using a complete reversible kinetic model and the end-product characterization using scanning electron microscopy.

Figure 1. An example of the ICCD frame. Distance from the nozzle 3 mm. Pressure before expansion 180 bar. Nozzle temperature 140 °C.

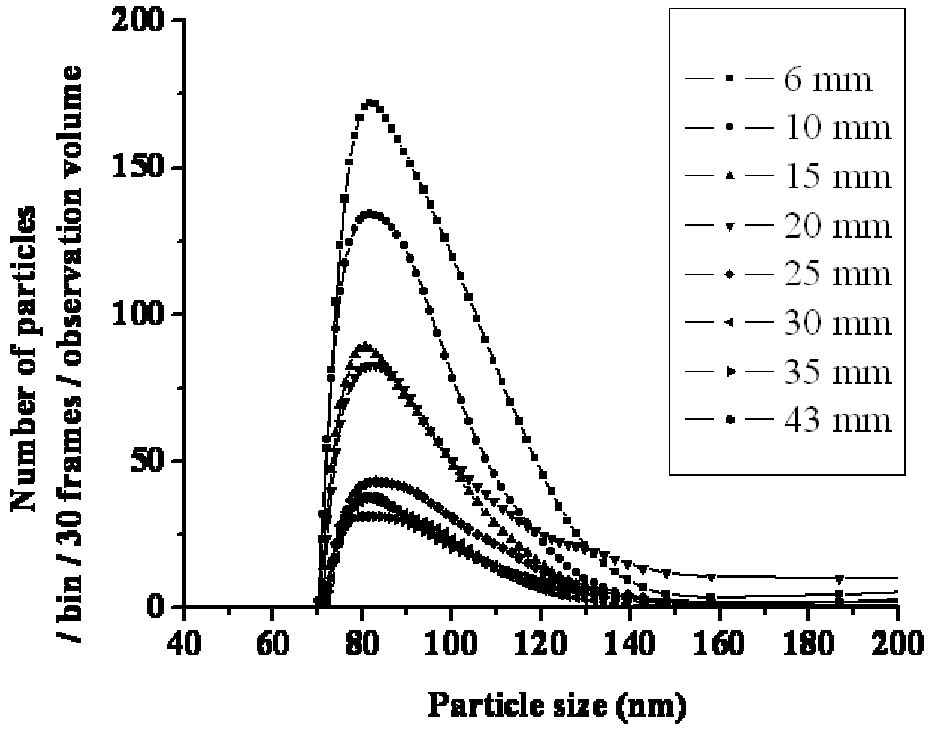

Figure 2. The dependence of the size distribution function on the distance from the nozzle

F5. From Potential Energy Surface to the High Pressure Rate Constant: CH_2 + H Recombination Reaction

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The accurate theoretical value of the high pressure rate constant for unimolecular dissociation/free radical recombination reactions is governed by properties of the potential energy surface (PES). The minimum energy path (MEP) for reaction, eigenvalues (frequencies of the normal modes orthogonal to the reaction path) along the MEP, and anharmonic regions well away from the MEP all contribute to the high pressure rate constant but in ways that depend on which of several statistical theories is selected to calculate the rate.

In order to study the ways PES information is consumed by several popular statistical rate theories and in order to compare to experiment, we are studying the CH_2 + H recombination reaction. In this work we use a new global analytic potential surface for CH_3 based on CAS+1+2/ aug-cc-pvtz calculations at 77000 discrete points on the surface. We calculated the recombination rate constant using three different methods: the canonical variational transition state theory (CVTST) [1], simplified statistical adiabatic channel model (simplified SACM) [2], and exact statistical adiabatic channel model (exact SACM). Based on a proposal by Quack and Troe [3], exact SACM evaluates the rate constant by determining the maximum for all energetically accessible adiabatic channels. Each model is free from any adjustable parameter.

We inspect the influence of several details of the models on the rate constants over a wide temperature range. The results will be presented and discussed.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under Contract No. W-31-109-Eng-38.

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F6. *Ab Initio* Study on the Decomposition and Isomerization of CH_3NO_2 and CH_3ONO

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The mechanisms for CH_3 + NO_2 and its reverse reactions have been investigated by *ab initio* molecular orbital and transition-state theory calculations. The species involved have been optimized at the B3LYP/6-311+G(3df, 2p) level and their energies refined by single-point calculations at the CCSD(T)/6-311+G(3df,2p) level. The energy diagram for the low energy channels is shown in Figure 1. Thermal decomposition rate constants for CH_3NO_2 and CH_3ONO in the experimental pressure ranges were predicted and compared with experimental values, as shown in Figs. 2 - 3. The predicted rate constants are in good agreement with experimental values.

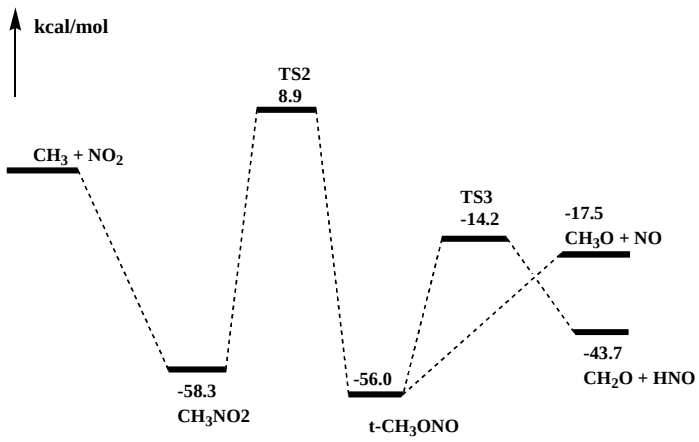

Figure1. PES diagram of CH_3 + NO_2 reaction calculated at the CCSD(T)/6-311+G(3df,2p)//B3LYP/6-311+G(3df,2p) level.

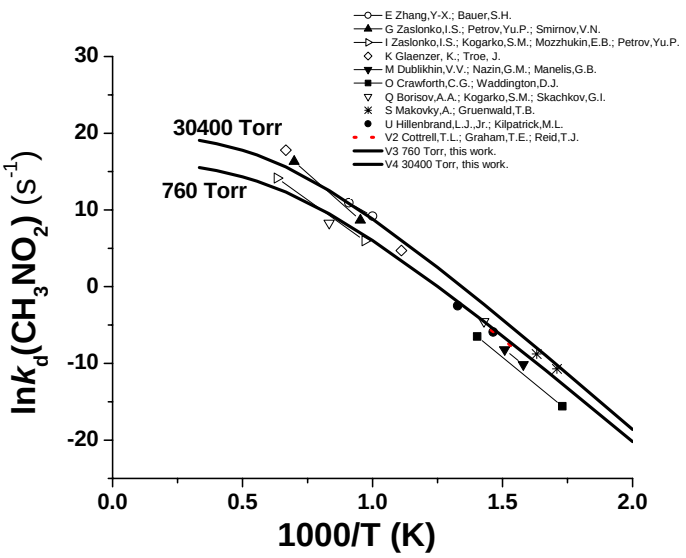

Figure 2. Comparison of the predicted and experimental thermal decomposition rate constants for CH_3NO_2

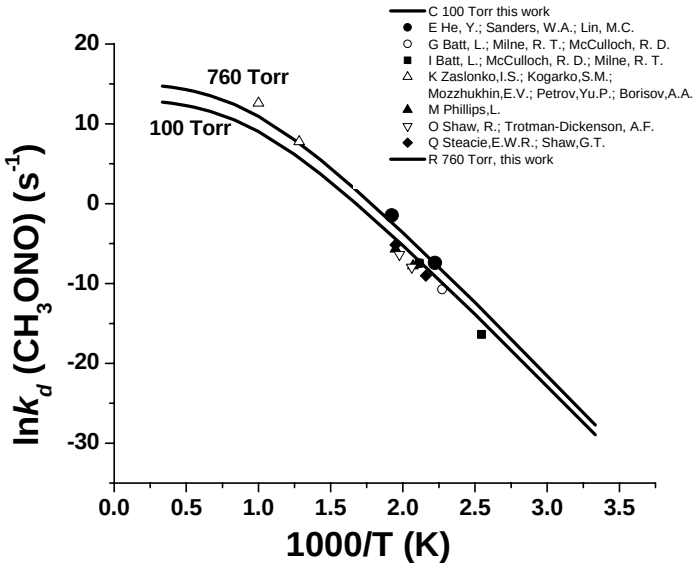

Figure 3. Comparison of the predicted and experimental thermal decomposition rate constants for CH_3ONO

F7. Kinetics And Mechanism Of The Reaction Between Propargyl And Molecular Oxygen

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Propargyl, C_3H_3, is the smallest unsaturated hydrocarbon radical to be resonance stabilized. This resonance stabilization accounts for the formation of weak bonds with stable molecules such as molecular oxygen and for its resistance to pyrolysis. As a result, propargyl is unreactive in a combustion environment, relative to other radical species, enabling large concentrations to exist in flames. The importance of propargyl in combustion comes from its ability to react with itself and form cyclic species such as benzene or phenyl. These initial aromatic species form polyaromatic hydrocarbons (PAH), which are the major components of soot. Consequently, the soot producing capacity of the propargyl radical resides in the ratio of its self-reaction rate to other oxidation and pyrolysis rates. The reaction of propargyl with O_2 is a very important competing step and it is the focus of the present work.

Infrared laser absorption spectroscopy is used to measure the time-resolved decay of propargyl radicals and the time-resolved production of products over the temperature range of 295-450 K. Propargyl radicals are formed by 193 nm photolysis of propargyl chloride. Reactant disappearance and product formation are monitored in the infrared region by either direct absorption spectroscopy or by frequency modulation spectroscopy. Special emphasis is placed on the "intermediate temperature regime" (~380-430 K) where previous experimental and theoretical studies suggest that $C_3H_3 + O_2 \leftrightarrow C_3H_3O_2$ equilibrates. Measured profiles are compared to a kinetic model taken from time-resolved master equations results based on *ab initio* characterizations of the relevant stationary points on the potential energy surface which allows testing and refinement of the theory.

This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, U. S. Department of Energy. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the National Nuclear Security Administration under contract DE-AC04-94-AL85000.

F8. Modeling of Nitric Oxide Formation in Methane – Oxygen – Nitrogen (Carbon Dioxide) Flames Doped with Ammonia

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The goal of this work was to analyze formation of NOx from fuel-N under well-controlled conditions. Probe sampling measurements of the concentrations of nitric oxide in the post-flame zone of methane – oxygen – nitrogen flames doped with ammonia (0.5 % of the fuel) are reported. A Heat Flux method was used for stabilization of non-stretched flames on a perforated plate burner at atmospheric pressure. Dilution ratios of oxygen, $O_2/(O_2+N_2)$, were varied from 0.16 to 0.209. The concentrations of O_2, CO, CO_2 and NOx were measured by means of a non-cooled quartz probe at different axial distances from the burner. Measured burning velocities for these flames and concentrations of the major species (O_2, CO, CO_2) agree well with those of the flames of methane – oxygen – nitrogen within an experimental accuracy. The concentrations of NOx in the post-flame zone have a maximum near the stoichiometry.

These measurements were compared to similar experiments in flames of methane – oxygen – carbon dioxide doped with ammonia [1] and to predictions of two detailed kinetic mechanisms [2, 3]. In CH_4 (NH_3) - O_2 - CO_2 mixtures the modeling over-predicts the measured concentrations of NOx however the experimental data trends are well reproduced. Including the downstream heat losses to the modeling does not remarkably alter the predicted concentrations of NOx.

In CH_4 (NH_3) - O_2 - N_2 mixtures the plots of the concentrations of NOx in the post-flame zone as a function of the stoichiometric ratio differ qualitatively from that in CH_4 (NH_3) - O_2 - CO_2 mixtures. The modeling is in satisfactory agreement with the experiments in lean flames, while in rich flames it is not. Present results are compared with the data from the literature, and possible reasons of discrepancy are discussed.

This work was partially supported by the European Commission within the “Safekinex” Project EVG1-CT-2002-00072.

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F9. Theoretical and Experimental Studies of the C_2H_4 + $O(^3P)$ and C_2F_4 + $O(^3P)$ Reactions: Non-Adiabatic Reaction Mechanisms

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The potential energy surface for the $O(^3P)$ + C_2H_4 reaction, which plays an important role in C_2H_4/O_2 flames and in hydrocarbon combustion in general, was theoretically re-investigated using B3LYP, G2M(CC,MP2), CBS-QB3, G3, CASSCF, CASPT2 and MRCI methods in combination with various basis sets such as 6-31G(d), 6-311++G(3df,2p), cc-pVDZ and cc-pVTZ. The energy surfaces of both the lowest-lying triplet and singlet electronic states were constructed. The primary product distribution for the multi-well multi-channel reaction was then determined by RRKM statistical rate theory and weak-collision master equation analysis. Intersystem crossing of the "hot" CH_2CH_2O triplet adduct to the singlet surface, known to account for about half of the products, was estimated to proceed at a rate of $\approx 1.5\text{x}10^{11}$ s^{-1}. In addition, the thermal rate coefficients $k(O + C_2H_4)$ in the T = 200-2000 K range were computed using multi-state transition state theory and fitted by a modified-Arrhenius expression as $k(T) = 1.69 \times 10^{-16} \times T^{1.66} \times \exp(-331K/T)$. Our computed rates and product distributions agree well with the available experimental results. Product yields are found to show a monotonous dependence on temperature. The major products (with predicted yields at T = 300 K / 2000 K) are: CH_3 + CHO (48 / 37%), H + CH_2CHO (40 / 19%), and $CH_2(X^3B_1)$ + H_2CO (5 / 29%), whereas H + CH_3CO, H_2 + H_2CCO and CH_4 + CO are all minor (≤ 5%).

The $C_2F_4(X^1A_g)$ + $O(^3P)$ reaction was studied experimentally using molecular beam–threshold ionization mass spectrometry (MB-TIMS). The major primary products were established to be CF_3 (+ CFO) and CF_2O + (CF_2), with measured yields of 16^{+11}_{-7} % versus 84^{+7}_{-11} %, respectively, neglecting minor products. The reaction was also investigated theoretically, using the same levels of theory as above. Based on the potential energy surfaces obtained, microcanonical rate constants were computed using RRKM theory, followed by product distribution calculations for various reaction conditions by weak-collision master equation analysis. It was thus found that fast intersystem crossing (ISC) from the triplet to the singlet surface must occur, at a rate of *ca*. 3×10^{12} s^{-1}, in order to explain the observed production of $CF_3(X^2A_1)$. The combination of experimental data with theoretical calculations shows that the yield of triplet $CF_2(\tilde{a}^3B_1)$, resulting from reaction on the triplet surface prior to ISC, is most likely <25%, whereas the major primary product channel is $CF_2(X^1A_1)$ + CF_2O, with yield >60%. In addition, the thermal rate coefficients

$k(O + C_2F_4)$ in the T = 150-1500 K range were computed using multi-state transition state theory and fitted by a modified-Arrhenius expression as $k(T) = 1.64 \times 10^{-16} \times T^{1.48} \times \exp(+6K/T)$, in good agreement with the available experimental results in the T = 298-500 K range.

F10. High Temperature Oxidation of Cyclopentadiene and its Radical

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Cyclic hydrocarbons, in particular C_5 compounds, play an important role as intermediates in the combustion of aromatic hydrocarbons which are mostly toxic and considered as important soot precursors. For example, phenyl (C_6H_5) reactions with molecular oxygen lead to phenoxy (C_6H_5O) and in a further fast decay of phenoxy to cyclopentadienyl radicals (C_5H_5) and CO [1]. Phenol (C_6H_5OH) which is an intermediate appearing on the route of benzene oxidation can also easily be converted to cyclopentadiene (C_5H_6) and CO [2]. According to theoretical work [3] there might exist a route leading by the association of two cyclopentadienyl radicals to either naphthalene ($C_{10}H_8$) or to naphthyl radicals ($C_{10}H_7$) + H-atoms. This route, if existing, can, under certain fuel to oxygen ratios in a flame, contribute to the formation of PAH's. Till now, a simulation of measured concentration profiles in a cyclopentadiene flame has not been very successfully (see e.g. [4]-[5]). In earlier investigations, we reported on pyrolysis reactions of the C_5H_6/C_5H_5 species [6-7] and of the association reaction of $C_5H_5+H \rightarrow C_5H_6$ [8]. However, reaction mechanisms of cyclic, especially aromatic hydrocarbons are still far from being quantitatively understood, in particular experimental data on oxidation reactions of C_5H_6 and C_5H_5 are needed.

For a deeper insight into high temperature C_5 -reactions, the oxidation of cyclopentadiene has been investigated. The measurements were performed behind the reflected shock front in a high purity heatable stainless steel shock tube. ARAS and MRAS were used to monitor the time dependent concentration profiles of H-, and O-atoms, and of CO-molecules, respectively. As light sources for the absorption measurements, microwave-excited discharge lamps were used. The H-atom concentrations were measured at L_α (121.6 nm) and the O-atoms at λ = 130.2 nm, simultaneously. In a separate series of experiments, time dependent absorption pofiles of CO-molecules were recorded at λ = 151 nm. The initial concentrations for the experiments were 8-30 ppm cyclopentadiene and 160-300 ppm oxygen in the temperature range 1300-1800 K at total pressures of 0.7 to 5 bar.

The oxidation of cyclopentadiene occurs mainly via the cyclopentadienyl radical because under the experimental conditions of the present work, cyclopentadiene splits off rapidly H atoms which react with molecular oxygen leading to O and OH. Thus, a radical pool is build up. In the second phase of the oxidation process, reactions of cyclopentadienyl are important. Its oxidation reactions – with O and O_2 - lead to intermediate species such as C_4H_5 and C_5H_4O, besides CO as well as H and OH. Its thermal decomposition leads via the open-chained C_5H_5 radical to the formation of acetylene and propargyl radical (C_3H_3). However, using the above mentioned reaction model the measured absorption profiles were underpredicted considerably.

The experimental profiles, in particular of CO and O atoms, were modelled much better if subsequent reactions of decomposition products of C_5H_5 - namely acetylene and propargyl - were taken into account. These two species can undergo reactions with O_2, O and OH which are very important in particular for the CO production, e.g. via the following reaction sequences:

(i) for acetylene: $C_2H_2 + O \rightarrow HCCO + H$ *and* $HCCO + O_2 \rightarrow 2CO + OH$

(ii) for propargyl: $C_3H_3 + O \rightarrow C_3H_2 + OH$ *and* $C_3H_2 + O \rightarrow C_2H_2 + CO$.

However, no direct experimental determination of the rate coefficients and the product distribution exist till now.

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F11. Ab Initio Kinetics for The Decomposition and Isomerization of The C_2H_4OH Radicals.

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The decomposition and isomerization processes of the C_2H_4OH (C_2H_5O1) radicals have been investigated by ab initio molecular orbital theory. The species involved have been optimized at the MP2/cc-PVTZ level and their energies were refined at the PMP2/aug-cc-PVQZ level. The relative energy diagram (relative to C_2H_4OH) is shown in Figure 1. The results indicate that the most stable isomers is CH_3CHOH (LM4) which is 6.4 and 15.2 kcal/mol more stable than C_2H_4OH (LM2) and CH_3CH_2O (LM3), respectively. For CH_3CHOH, its decomposition to CH_3CHO + H is more favorable than its isomerization to C_2H_4OH; for the decomposition of CH_3CH_2O, production of CH_3 and CH_2O is dominant, this process needs to overcome 13.8 kcal/mol barrier, which is more than 10 kcal/mol lower than the isomerization from CH_3CH_2O to C_2H_4OH; for C_2H_4OH (LM2), the main decomposition products are C_2H_4 and OH, between the products and LM2, there is an OH--π complex (LM1) lying 29.3 kcal/mol above LM2. Decomposition of LM2 to CH_2CHOH + H needs to overcome 31.8 kcal/mol energy. The iomerization barriers from LM2 to LM1, LM3 and LM4 are 30.4, 33.9 and 37.6 kcal/mol, respectively. In addition, the processes for the decomposition of LM2 to C_2H_3 + H_2O via three- and four-center transition states have much high barrier heights, 75.1 and 72.6 kcal/mol. Apparently, these channels are unfavorable. The stationary points on the dominant channels of $C_2H_4OH \rightarrow C_2H_4$ + HO have also been calculated at the G2M(CC1), G3, G3B3, and CCSD(T)/6-311+G(3df,2p) levels. The best agreement with experimental results is found at the PMP2/aug-cc-PVQZ//MP2/cc-PVTZ level of theory. The rate constants for the low energy channels of the isomerization and decomposition processes will be calculated soon based on the energy diagram

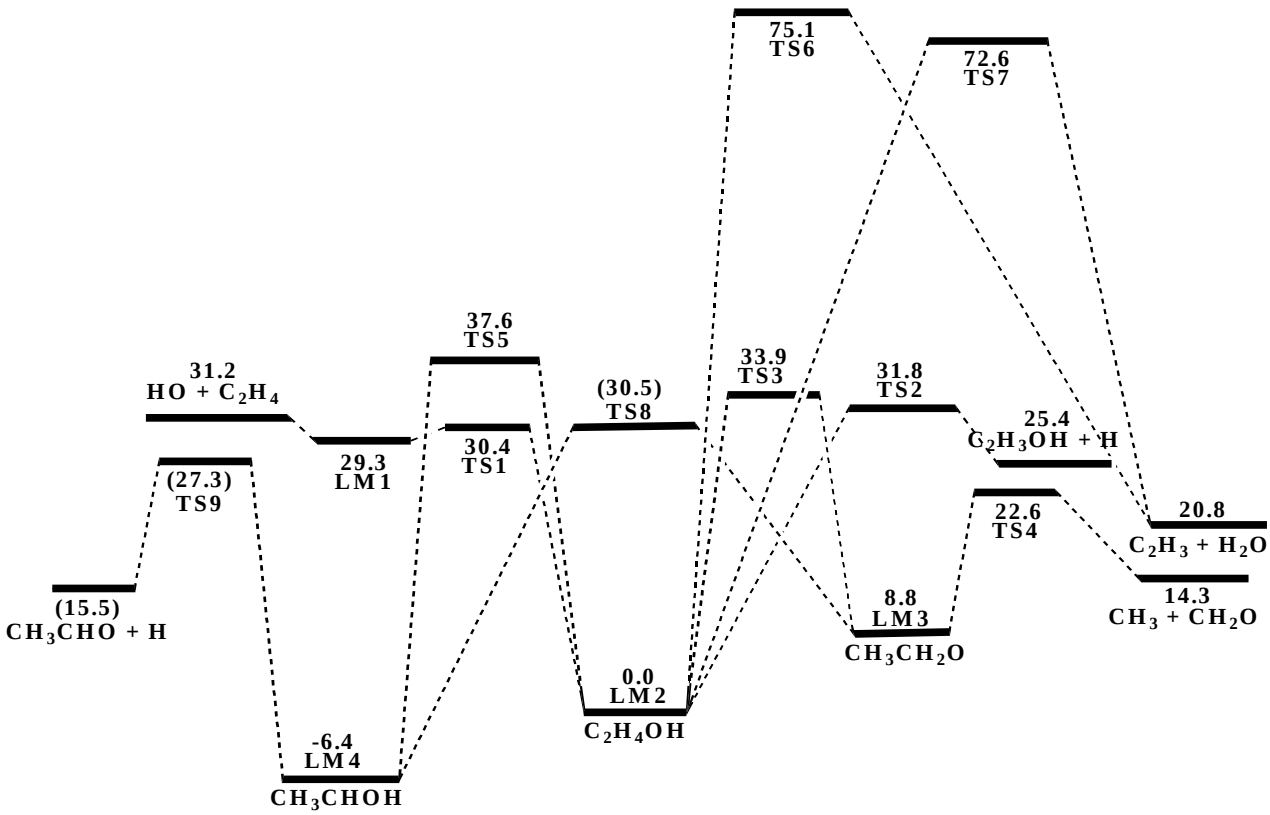

Figure 1. The PES for the decomposition and isomerization of C_2H_4OH radical computed at the PMP2/aug-cc-PVQZ//MP2/cc-PVTZ and G2M(rcc5)//B3LYP/6-311+G(*d*,*p*) (in parenthesis) levels.

F12. Reaction Paths to Gas Phase Perfluoropropene Formation: A CASMP2 and B3LYP Investigation

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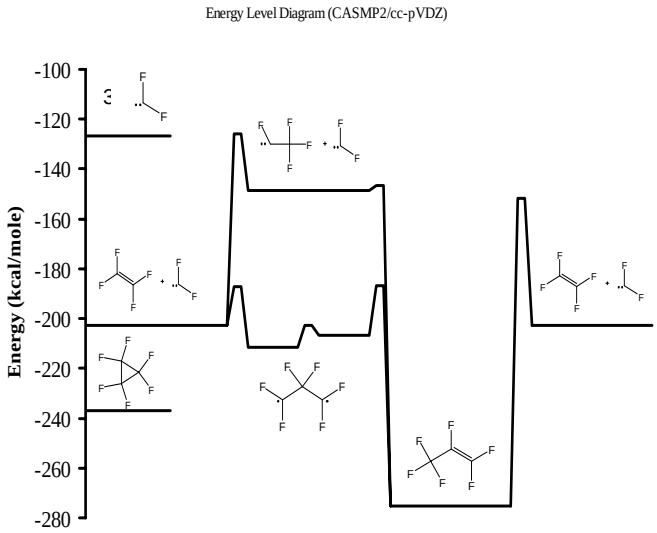
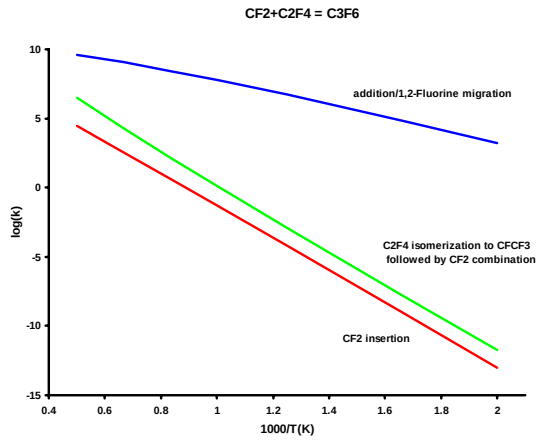
Calculations were performed at the CASMP2(6,6)/cc-pVDZ and B3LYP/cc-VTZ levels of theory on three pathways to perfluoropropene formation. The first pathway was a direct insertion of difluoromethylene into tetrafluoroethylene. The second pathway was addition of difluoromethylene to tetrafluoroethylene to form a singlet biradical with subsequent 1,2 fluorine migration to form perfluoropropene. The third pathway was a carbene combination pathway in which tetrafluoroethylene isomerizes to a C_2 carbene which subsequently combines with difluoromethylene. Calculations were performed using the Gaussian codes G98W and G03W. Transition states and internal rotations were animated using GaussView.

The hindered internal rotation contributions to the heat capacity and entropy were made using the methods of Shokhirev and Krasnoperov[1] and also Ayala and Schlegel[2] and were compared to treatment as a vibration.





An energy level diagram based on the CASMP2(6,6)/cc-pVDZ results is shown above. The barrier for the addition/1,2 flurorine migration is clearly the lowest energy reaction pathway. To compare the isomerization/combination rate constants we assume that C_2F_4 is in equilibrium with the C_2 carbene. This assumption would place an upper limit on the rate constant for this pathway. Even with this assumption, the addition/1,2 fluorine pathway to C_3F_6 appears to be at least three orders of magnitude faster than the isomerization/combination pathway at temperatures below 2000 K, as shown in the Arrhenius plot above. Similar conclusions are obtained for both levels of theory, despite small differences in the energy barriers for various reaction steps. The insertion pathway is 1/10 th to 1/100 th the rate of the

isomerization/combination pathway, making it the least favorable of the three pathways. A more detailed comparison or the CASMP2 and the B3LYP results will be presented.

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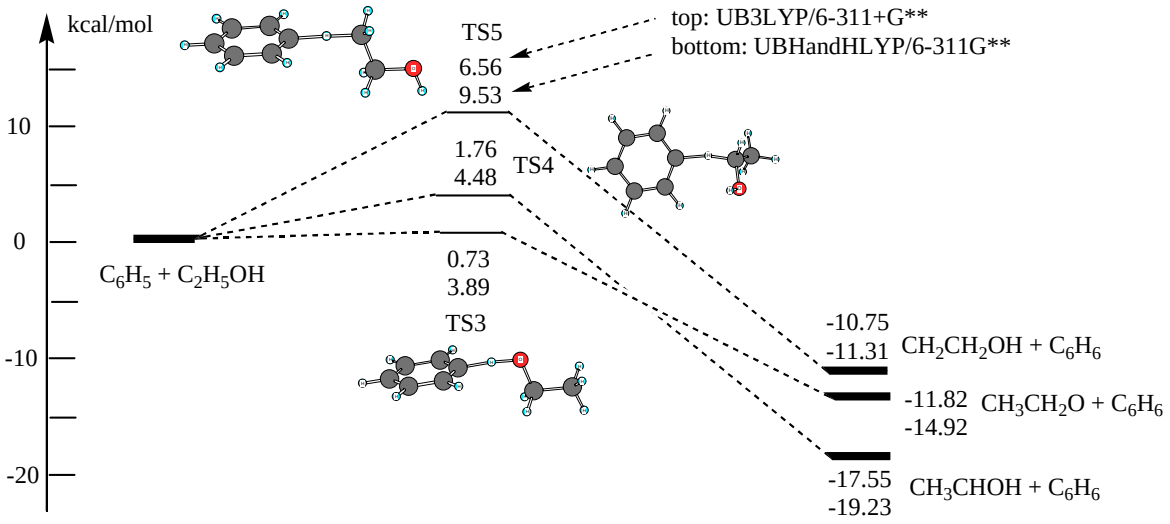
B. C_6H_5 + C_2H_5OH



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F13. Theoretical Study of the Kinetics and Mechanism for the Reaction of C_6H_5 with CH_3OH and C_2H_5OH

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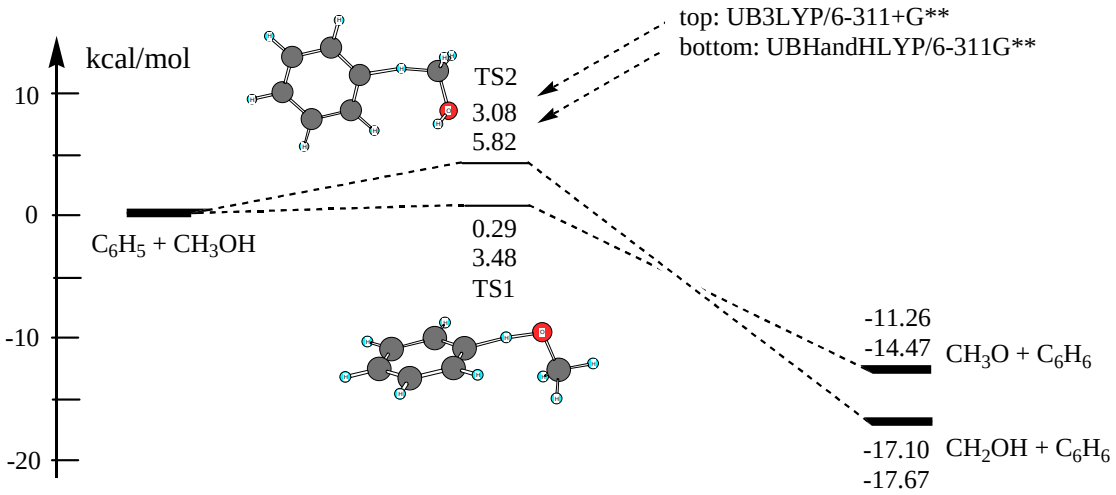
Phenyl radicals play an important role in the formation of polycyclic aromatic hydrocarbons and soots in hydrocarbon combustion under fuel rich conditions. The reactions of the C_6H_5 radical with methanol and ethanol have been studied theoretically in this work. Five possible reaction pathways are considered here:

$$C_6H_5 + CH_3OH \rightarrow C_6H_6 + CH_3O$$
$$\rightarrow C_6H_6 + CH_2OH$$
$$C_6H_5 + C_2H_5OH \rightarrow C_6H_6 + CH_3CH_2O$$
$$\rightarrow C_6H_6 + CH_3CHOH$$
$$\rightarrow C_6H_6 + CH_2CH_2OH$$

The geometries of the reactants, products, and transition states on the ground electronic doublet state potential energy surfaces (PESs) were optimized by the density functional theory at both B3LYP/6-31+G(d, p) and BH&HLYP/6-31G(d, p) levels of theory. The rate constant for each of reaction channels in the temperature range 300 – 2000 K will be calculated by the transition state rate theory with tunneling corrections after a further refinement in energy has been carried out at a higher level of theory.

A. $C_6H_5 + CH_3OH$



F14. Experimental and Modeling Study of Autoignition of Liquid Fuels in Flow Reactor

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In recent years, stringent emission standards have made lean-premix, prevaporized combustion more popular in industrial applications than ever before. However, the difficulty often encountered in practical combustion devices is the early auto-ignition of fuel/air mixture before it reaches the main combustion zone. This is especially true with the higher order hydrocarbon fuels, such as kerosene and diesel, which have lower ignition delay times compared to natural gas.

Since there is a scarcity of experimental measurements of the autoignition behavior of 'real' fuels such as kerosene and diesel, a flow reactor experimental set-up is used to measure the ignition delay time at conditions relevant to the premixing of fuel and air in a gas turbine. The experiments were performed in an atmospheric pressure flow reactor using heptane and kerosene (*i.e.* fuel oil #1). The flow reactor consists of a premixing section and a plug-flow test section. The fuel was prevaporized before mixing with air in the premixing section, which is located at the entrance to the reactor. Figure 1 shows the schematics of the premixing section. The test section is a 52" x 2" alumina tube placed in a furnace with independently controlled three-zone heaters. A schematic of the mixing section of the flow reactor apparatus is shown in Figure 1. One of the difficulties of any flow reactor experiment is to mix the fuel and oxidant quickly at the entrance to the reactor [1]. In this work, rapid premixing of the prevaporized fuel and air is achieved by using a swirler followed by an expanding duct, which opens into the test section. A photo-multiplier coupled with a narrow band filter is placed at the end of the test section to detect CH* emissions. The time between the injection of fuel vapor into the mixing section and the detection of CH* emission signal is the ignition delay time. The plug-flow test section is maintained at iso-thermal condition for a given reactor temperature. The premixer temperature is maintained at 600 K in order to simulate the conditions in a gas turbine premixing situation.

Figure 2 shows a typical ignition delay time measurements for heptane at 865 K as function of equivalence ratio. The fuel flow rate was changed while keeping the inlet O_2 at 10 mole%. Figure 2 also compares the model predictions with experimental data. The model predictions of the detailed n-heptane kinetic mechanism of Curran *et al.* [2] agree very well with the experimental measurements. It can be observed that the fuel lean mixtures have higher ignition delay time compared to rich mixtures. Also, ignition delay time for mixtures higher than 2.0 equivalence ratio tends to become constant. Figure 3 shows the ignition delay time measurement of kerosene (77.6 vol% parafins, 20.0 vol% aromatics and 2.5 vol% olefins; H/C ratio–1.91) as function of equivalence ratio at 900 K and 17 mole% O_2. The experimental measurements are compared with the model predictions of Gokulakrishnan *et al.* [3] in Figure 3. The model under predicts the ignition delay time at higher equivalence ratios. The original

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kerosene mechanism of Gokulakrishnan *et al.* [3] was validated against aviation grade fuels such as JP-8 and Jet-A. Thus, the model needs improvement to accommodate the chemical constituents of the commercial grade kerosene used in the experiments shown in Figure 3.

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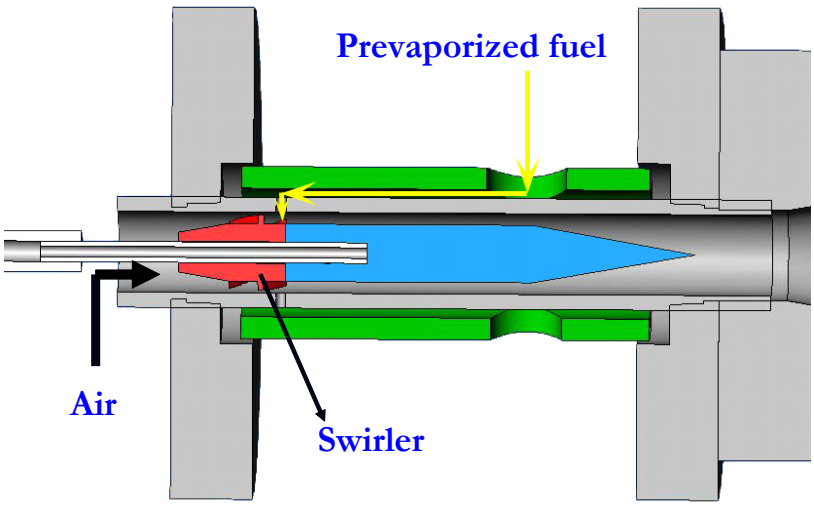

Figure 1: The cross-sectional view of the premixing section of the flow reactor. The yellow line indicates the fuel injection path.

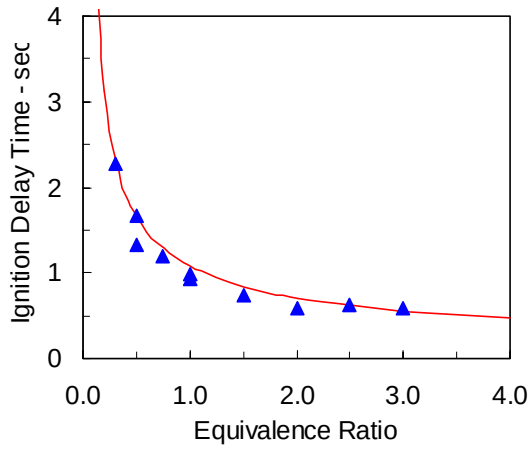

Figure 2: n-heptane ignition delay time measurement as a function of equivalence ratio at 865 K and 10 mole% O_2. Key: symbols – experiments; line – model prediction of Curran *et al*. (1998)

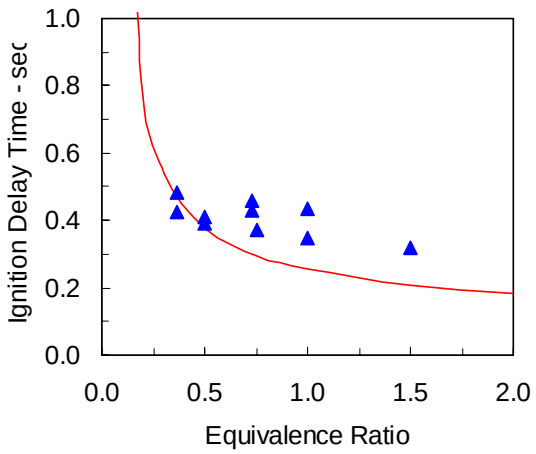

Figure 3: Ignition delay time of kerosene as function of equivalence ratio at 900 K and 17 mole% O_2. Key: symbols – experiments; line – model prediction of Gokulakrishnan *et al*. (2005)

F15. Laboratory and Modelling Studies of Peroxy Radical Cross Reactions

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This study aims to acquire experimental kinetic and mechanistic data on natural tropospheric photochemical cycles involving peroxy radicals (HO_2 and RO_2), concentrations of which are strongly influential upon O_3, NO_x, NO_y and HO_x budgets throughout the troposphere. The importance of these families in determining atmospheric composition, Earth's radiative balance and future climate change is well documented. However, as our knowledge of the complex interplay between these important families of species has been augmented by field measurements and their comparison with ever more sophisticated computer models, it emerges that certain peroxy radical cross reactions warrant further examination.[1-4]

The study of peroxy radical cross-reactions with hydroperoxy radicals requires an accurate knowledge of both the [RO_2] and [HO_2]. The majority of previous work has determined the peroxy radical concentrations by UV absorption. While UV absorption detection is well suited for the detection of species with banded structures, peroxy radicals are broad band structureless absorbers. This presents a limitation on the flash photolysis technique in that it is difficult to distinguish species from each other. Therefore, it is difficult to deconvolute the contributions of each individual peroxy radicals from the raw experimental spectrum. As a result this can seriously limit the accuracy of the experimentally determined peroxy radical concentrations.

Quantitative kinetic and mechanistic data will be obtained for systems involving the above mentioned species using a turbulent flow-tube chemical ionization mass spectrometer (TF-CIMS). The benefits of this apparatus are manifold,[5,6] enabling the user to operate at a variety of pressures and temperatures, whilst maintaining thorough mixing of gaseous components in the system and at very low radical concentrations. The turbulent flow-CIMS system will allow all peroxy radical concentrations to be determined without interference and thus greatly reduce the errors associated with the measured rate parameters at conditions that pertain to the whole of the troposphere. A turbulent flow chemical ionisation mass spectrometer has been used to provide kinetic and mechanistic data on the reactions of RO_2 (where R = C_2H_5 or CH_3) with HO_2 over the pressure range 70 – 700 Torr and temperature range 180 – 300 K.

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F16. Modeling Soot Inception and PAH Formation in Rich Ethylene/air Combustion

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Soot is a common by-product in many combustion processes yet the mechanisms of soot formation are poorly understood. Of the major steps in soot formation: fuel pyrolysis, polycyclic aromatic hydrocarbon (PAH) formation, particle inception, coagulation, surface growth, carbonization, agglomeration, and oxidation [1], the processes of PAH formation and particle inception are the least understood. These two processes are being studied using a plug flow reactor (PFR), coupled to the output of a well stirred reactor (WSR).

Rich mixtures of ethylene/air are partially combusted in a toroidal WSR. The products of this partial combustion are introduced into a PFR where they continue to react. Residence times in the WSR and PFR are approximately 10 ms and 60 ms, respectively. The relatively long residence times of the PFR extend the region over which PAH formation and particle inception occur. This improves physical access to the combustion products and permits finer resolution of the different stages of the soot formation process.

Sampling of the combustion products is through fixed ports located at several heights along the length of the PFR. Gas samples are extracted at these sampling ports, filtered to capture bulk particulate matter, and then sent to a gas chromatograph for compositional analysis. Gas chromatography (GC/FID) is used to quantify hydrocarbon concentrations in the PFR gas samples. Species ranging in size from methane through naphthalene are quantified (future work will expand quantification to include PAHs of up to six rings in size). Gas concentrations are measured over equivalence ratios ranging from near sooting ($\phi = 1.8$) to heavily sooting ($\phi = 2.2$). Combustion in the reactor is modeled using the CHEMKIN 4.0 software suite and the light hydrocarbon/soot formation mechanisms of Wang-Frenklach [2] and Babushok-Tsang [3]. Experimental results are compared to the modeling predictions and performance of the two mechanisms evaluated against the experimental data.

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F17. Estimate of Thermochemical Properties of Cyclic Molecules

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When constructing a large kinetic model, it is often necessary to rapidly but accurately estimate the thermochemical properties of thousands of different molecules, most of which have never been studied experimentally. These estimates are usually done using Benson's group additivity method [1], using groups derived both from experimental data and from quantum chemistry calculations on a small number of reference molecules[2]. This method works very well for non-cyclic molecules in which significant interaction between different functional groups is not present. However, as shown here, Benson's group-additivity method is not very accurate for cyclic species. Recently, Yu et al. proposed an extension of Benson's method to bond-centered groups that gives accurate predictions for the thermochemical properties of Polycyclic Aromatic Hydrocarbons (PAH) [3]. However, this method also does not work very well for non-aromatic cyclic compounds. It appears that these failures of group-additivity methods based on "2-d" molecular connectivity are due to the fact that ring strain is sensitive to the three-dimensional structure of the ring and its substituents; this is particularly important for nonplanar fused ring systems. Using more accurate methods (such as quantum chemistry, semi-empirical methods, and molecular mechanics) would require estimating the 3-d geometries of thousands of new species and reactive intermediates while the reaction mechanism is being constructed, posing several challenges. While some programs exists for converting 2-d connectivities to 3-d geometries exist [4, 5] it is not clear whether these programs are reliable enough for use without a human individually checking each proposed structure. The state of the art in this area will be reviewed, and a proposed path forward is outlined.

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F18. Experimental and Numerical Studies of Primary Reference Fuels Oxidation: Flow Reactor Experiments and Model Comparison

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Robust chemical kinetic models are needed for understanding the complicated chemical and physical processes occurring in advanced internal combustion (IC) engines. Since practical fuels, such as gasoline, are mixtures of very large numbers of different hydrocarbons, extensive efforts have been focused on studying the kinetic model of single component or simple mixtures of components that represent gasoline fuels. Primary reference fuel (PRF) mixtures of *iso*-octane and *n*-heptane have been widely used as a surrogate fuel for gasoline combustion research. New experimental data have been obtained in the Princeton variable pressure flow reactor for further validation of detailed kinetic models. These experiments are performed at high pressure (p=12.5 atm), with initial temperatures spanning from 635K to 900K, and an array of equivalence ratios (ϕ=0.35-1.0). These experiments not only provide information on the reactivity of each fuel but also identify the major intermediate products formed during the oxidation process. The newly obtained data, along with previously available literature data, have been used as a basis to test existing models in the literature. The models tested included a comprehensive detailed mechanism as well as other mechanisms produced to achieve smaller dimensional representations of the reaction chemistry. Comparisons of experimentally measured profiles of O_2, CO, CO_2, H_2O and temperature rise with the model predictions are presented. Intermediates identified in the flow reactor are compared with those present in the computations.

F19. 248 nm Laser Photolysis of $CHBr_3$/O-Atom Mixtures: Kinetic Evidence for UV CO(A)-Chemiluminescence in The Reaction of Methylidyne Radicals with Atomic Oxygen

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4th Positive and Cameron band emissions from electronically excited CO have been observed for the first time in 248-nm pulsed laser photolysis of a trace amount of $CHBr_3$ vapor in an excess of O-atoms. O-atoms were produced by dissociation of N_2O (or O_2) in a cw-microwave discharge cavity in 2.0 torr of He at 298 K. The CO emission intensity in these bands showed a quadratic dependence on the laser fluence employed. Temporal profiles of the CO(A) and other excited state products that formed in the photo-produced precursor + O-atom reactions were measured by recording their time-resolved chemiluminescence in discrete vibronic bands. The CO 4th Positive transition ($A^1\Pi$, v'=0 $\rightarrow$ $X^1\Sigma^+$, v"=2) near 165.7 nm was monitored in this work to deduce the pseudo-first-order decay kinetics of the CO(A)-chemiluminescence in the presence of various added substrates (CH_4, NO, N_2O, H_2, and O_2). From this, the second-order rate coefficient values were determined for reactions of these substrates with the photo-produced precursors. The measured reactivity trends suggest that the prominent precursors responsible for the CO(A)-chemiluminescence are the methylidyne radicals, CH($X^2\Pi$) and CH($a^4\Sigma^-$), whose production requires the absorption of at least 2 laser photons by the photolysis mixture. The O-atom reactions with brominated precursors (CBr, CHBr and CBr_2), which also form in the photolysis, are shown to play a minor role in the production of the CO(A or a)-chemiluminescence. However, the CBr_2 + O-atom reaction was identified as a significant source for the 289.9-nm Br_2-chemiluminescence that was also observed in this work. The 282.2-nm OH- and the 336.2-nm NH-chemiluminescences were also monitored to deduce the kinetics of CH($X^2\Pi$) and CH($a^4\Sigma^-$) reactions when excess O_2 and NO were present.

This laboratory work provides evidence that supports the idea that the interaction of thermospheric O-atoms with carbonaceous species like CH that are present in Space Shuttle plumes could be responsible for part of the far-field ultraviolet emissions observed there.

F20. Influence of Weight of Third Body on Probability of Recombination in The System $Cs^+ + Br^- + R \rightarrow Csbr^* + R$

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The method of trajectory simulation was applied to investigation of dynamics of recombination in the system $Cs^+ + Br^- + R \rightarrow CsBr^* + R$, where R=Hg, Xe, Kr. Calculations carried out on potential energy surfaces, which describe quantitatively reverse process of collision induced dissociation [1-3]. Initial distance between ions Cs^+ and Br^- was set 250 a.u., and atom R reached the center of mass of all system simultaneously with ionic pair, moving perpendicularly a line of their approach. Impact parameter of atom R relatively center of mass of the pair Cs^+ - Br^- was chosen by Monte-Carlo method. The termination of a trajectory corresponding to recombination was fixed if distance between ions Cs^+ and Br^- does not exceed 30 a.u., total energy of this pair is negative, and distances of each of ions up to atom R exceed 250 a.u..

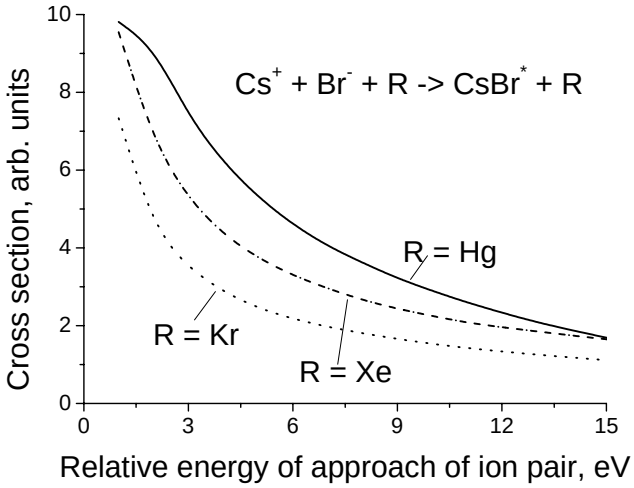

Figure represents dependence of cross sections of recombination on relative energy of approach of ion pair in the reaction $Cs^+ + Br^- + R \rightarrow CsBr^* + R$ for three atoms R with different masses. Cross sections of recombination decrease with the growth of energy, but for every value of energy the more weight of atom, the higher total cross section.

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F21. Kinetic Modeling Study of The Laser-Induced Breakdown Spectroscopy Plume from Metallic Lead in Argon

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A kinetic model of the laser-induced breakdown spectroscopy (LIBS) plume of lead in argon has been developed for analysis of the physical and chemical factors controlling the LIBS signature. The model includes processes involving ion chemistry, excitation, ionization, and other processes affecting the concentrations of argon and lead atoms (in 9 different electronic states) and their ions. A total of 15 chemical species and 90 reactions are included in the model. Experimental measurements of the temporal dependence of a number of lead emission lines in the LIBS plume of metallic lead have been made in argon and air.

It was demonstrated that the process of generation of emitting Pb atomic states can be considered as a two-stage process. The first stage corresponds to a fast approach to quasi-stationary species concentrations, while in the second stage the quasistationary concentrations change because of the falloff in the temperature. Experimental results demonstrate that the LIBS spectrum of lead for argon buffer gas is more intense than for air under identical conditions. The decay lifetimes for low-energy emitting Pb I levels were slightly longer in argon than in air. For high-energy Pb I levels and emitting lead ion levels, the lifetimes were substantially longer for argon buffer gas in comparison with air.

The computed concentrations of emitting levels of the lead atom were also higher for argon than for air buffer gas. In comparison to LIBS of Pb in air, the main processes generating electronically excited, emitting Pb atoms in an argon atmosphere are electron-impact processes. The period over which atomic emission is occurring is related to electron excitation processes in the plasma. Thus larger rates of production of emitting species will occur in buffer gases which have a greater propensity for formation of electrons. The main contributor to the production of electrons in an argon atmosphere is the stepwise cascade ionization through metastable states. The modeling results are compared with experimental results.

F22. Vibrationally Driven D-atom Abstraction Reactions of Highly Excited Pyridine-d_5 (E_{vib}=38,000 cm^{-1}) and Cl

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High resolution transient IR absorption probing is used to study the influence of large amounts of internal energy on D-atom abstraction reactions of pyridine-d_5 with Cl radicals in the gas phase. The goal of these studies is to learn how vibrational energy influences reactivity under high temperature reaction conditions. Our results reveal that randomized vibrational energy enhances rates for D-atom reactions. These studies also show that reaction products have surprisingly small amounts of energy compared to the total energy of the reactant molecules.

In these studies, vibrationally excited pyridine-d_5 molecules with E_{vib}=108 kcal/mol are prepared using 266 nm pulsed excitation, followed by rapid radiationless decay to the ground electronic state. The internal energy of the pyridine-d_5 molecules corresponds to the average energy of an equilibrium system at T_{vib}~3700 K. Cl radicals are generated by photodissociation of Cl_2 at 355 nm and have a relative kinetic energy of E_{trans}=10 kcal/mol. This corresponds to a translational temperature of T_{trans} ~3300 K. The appearance of individual quantum states of the DCl products is monitored using high resolution IR diode laser transient absorption probing at 4.9 μm. State-resolved population measurements yield information about the rotational energy of the DCl products and Doppler broadened linewidths are used to determine the relative kinetic energy of the DCl and pyridinium-d_4 radical products. Absolute rate measurements are determined from the early time appearance of reaction products under low pressure conditions.

The influence of internal excitation is investigated by comparing the following reactions:

Reaction **(1)**: Pyr-d_5 + Cl (vel) → pyr-d_4 + DCl (v=0, J)
Thermal pyridine-d_5 with chlorine radicals

Reaction **(2)**: Pyr-d_5 (E_{vib}) + Cl (vel) → pyr-d_4 + DCl (v=0, J)
Vibrationally excited pyridine-d_5 with chlorine radicals

The D-atom abstraction reaction is endothermic by ΔH=8.7 kcal/mol and the translational energy of the Cl atom is sufficient to overcome the reaction endothermicity. We observe appearance of DCl reaction products for Reaction **(1)** and determine that the rate constant for production of DCl in the J=4 state is $k_1^{J=4}$ ~$(1\pm0.7)\times10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}. Transient absorption signals for Reaction **(1)** are too small to obtain reliable translational energy measurements, but we expect the translational energy content of the products to be small based on the available energy.

For Reaction **(2)**, we have measured rotational populations and linewidths for the J=2, 4, 5, 8 and 13 states of DCl. The linewidth data for Reaction **(2)** indicate that nascent DCl molecules have translational energy, but very little rotational energy. For Reaction **(2)**, the J=4 state of DCl has a translational energy of T_{trans} =1300 K and population measurements for the J=4, 5 and 8 states indicate that T_{rot}~200 K for DCl. The relatively small product energy (~1.1 kcal/mol) is surprising given the large amount of available energy. The dynamics are consistent with a direct reaction mechanism that does not involve formation of a long-lived pyridine-d_5:Cl complex. Rate measurements for Reaction **(2)** yield a rate constant of $k_2^{J=4}$ ~$(1.5\pm0.5)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, corresponding to a rate enhancement of ~150 due to vibrational energy in the pyridine-d_5 reactant. Phase space theory calculations are underway to determine whether the observed rate enhancement is consistent with a statistical distribution of reactant energy.