L1. Elementary Reactions in Cat(HW)-CVD Processes

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The Catalytic (or Hot-Wire)-CVD is one of the most promising technique to obtain hydrogenated amorphous silicon and microcrystalline silicon films at low substrate temperatures. The qualities of these films are determined by film growth conditions. The gas-phase and surface chemical kinetics are essential knowledge for controlling the film qualities. The first step of Cat-CVD is decomposition of source gases on the hot wire. It has been confirmed that Si and H atoms are the major products of the SiH_4 decomposition [1,2]. The second step is gas-phase reactions of these radicals, and the third step is surface reactions. However, there have been few experiments for the consecutive gas-phase and surface chemistry in silicon Cat-CVD. Experimental and theoretical studies were conducted to understand chemical kinetic mechanism of Cat-CVD processes of SiH_4.

A time of flight mass spectroscopy (TOF-MS) with a VUV (Vacuum Ultra Violet) single photon ionization technique was applied to detect the gas phase chemical species in Cat-CVD. Si_2H_6 and Si_3H_8 were identified as the main gas phase species. A small amount of Si_2H_2 was also detected. In the Cat-CVD, SiH_4 is decomposed to Si, H and SiH_3 on the catalyzer (a W-filament). The reaction of H atom with SiH_4 further produces SiH_3. Most important reactions of SiH_3 are the self-reactions as below [3].

$SiH_3 + SiH_3 \Rightarrow SiH_2 + SiH_4$

$SiH_3 + SiH_3 \Rightarrow HSiSiH_3 + H_2$

Further reactions proceed as below.

$SiH_2 + SiH_4 (+ M) \Rightarrow Si_2H_6 (+ M)$

$HSiSiH_3 + SiH_4 (+ M) \Rightarrow Si_3H_8 (+ M)$

$HSiSiH_3 + SiH_4 (+ M) \Rightarrow H_2 + HSiSi_2H_5 (+ M)$

$HSiSiH_3 + M \Rightarrow H_2SiSiH_2 + M$

Silylenes (SiH_2, $HSiSiH_3$ and $HSiSi_2H_5$) are very reactive. It is well known that silylenes are easily inserted into Si-H bond. Accordingly, silylenes are thought to have large sticking coefficient on film surface. On the other hand, surface reactions of H_2SiSiH_2 are not known. We investigated a stable structure of H_2SiSiH_2 on a surface using quantum mechanical

calculations (Gaussian 98). When a Si_9H_{14} cluster had was used as a model for a H-terminated Si(100)-2×1 surface, a stable structure was not found for absorbed H_2SiSiH_2. This result predicted small sticking coefficient of H_2SiSiH_2.

The products of the reaction of Si with SiH_4 are not well known. Quantum mechanical calculations and present TOF-MS experimental results indicated that main product of the reaction was Si_2H_2.

$$Si + SiH_4 \Rightarrow Si_2H_2 + H_2$$

Si_2H_2 has been assumed to have very large sticking coefficient. We investigated adsorption states and its energy of Si_2H_2 by Si_9H_{14} cluster model of Si surface. A stable structure of Si_2H_2 was found to be adsorbed on H-terminated surface with a stabilization energy of -25.3 kcal/mol, and an activation energy of 10.9 kcal/mol. On the other hand, no activation barrier was found for the adsorption of Si_2H_2 to the dangling bond (Si_9H_{12} cluster model), as shown in figure 1. These results show the possibility of large sticking coefficient of Si_2H_2 on Si surface.

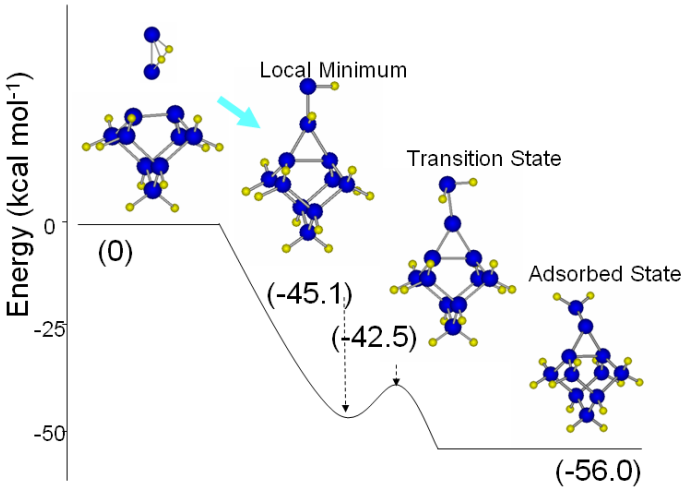

Fig.1 Potential energy diagram for Si_2H_2 adsorption

Based on these experimental and calculation results, a chemical reaction mechanism was developed. Our model consists of 4-parts, decomposition reactions on a hot wire (W-filament), gas-phase reactions, surface reactions on a substrate and surface reactions on a reactor wall. Chemical kinetic simulations were performed by using CHMKIN 4.0 program package. By assuming the reaction pathway of $Si+SiH_4 \Rightarrow Si_2H_2+H_2$ with a high reactivity of Si_2H_2 to the surface, the experimental product distribution of Si_2H_6 and Si_3H_8 could be reproduced. It is concluded that the major precursors for the film growth are SiH_3 and Si_2H_2.

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L2. The Reaction of OH with Acetaldehyde and Deuterated Acetaldehyde: Further Insight into The Reaction Mechanism at both Low and Elevated Temperatures

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The pulsed laser photolysis / laser-induced fluorescence technique has been used to conduct further measurements of the gas-phase CH_3CHO + OH reaction. These measurements were conducted to verify the complex temperature dependence previously observed by the authors [1] and to acquire mechanistic information about the reaction mechanism in the form of primary kinetic isotope effects. Primary kinetic isotope effect measurements at temperatures of 297, 383, 600, and 860 K indicate that H abstraction from the acetyl group dominates that of the methyl group at low to modest temperatures (≤600 K) and H abstraction from the methyl group dominates that from the acetyl group at higher temperatures (860 K). A bi-exponential fit to all experimental measurements of the CH_3CHO + OH reaction published since 1990, excluding our prior results [1] that were approximately 20-30% lower than the present results, resulted in the following expression (in units of cm^3 $molecule^{-1}$ s^{-1}):

$$k\ (202 – 860\ K) = 8.36 \times 10^{-11} \times \exp(-2410/T) + 4.34 \times 10^{-12} \times \exp(369/T).$$

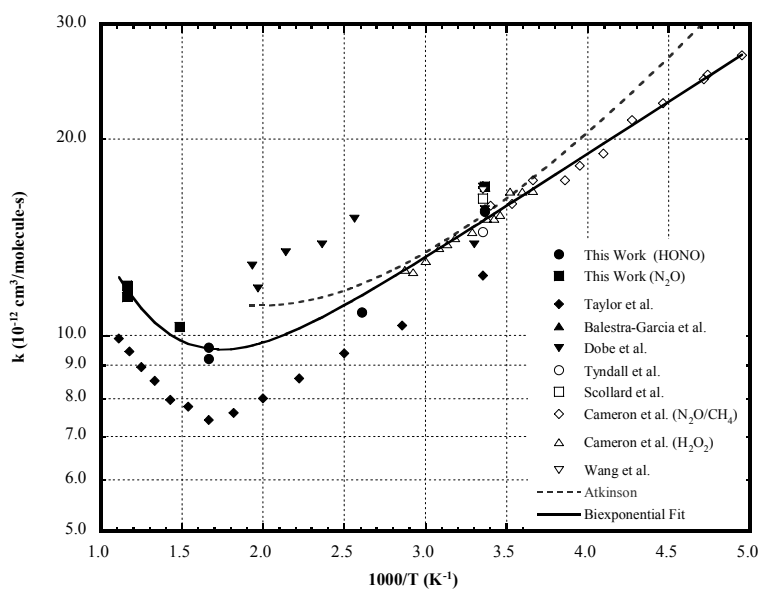

Figure 1. Comparison of measurements for OH + CH_3CHO

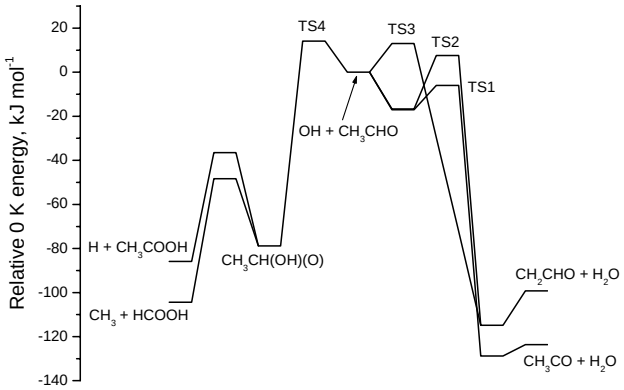

Figure 2. Potential energy diagram derived from CBS-QB3 theory

Ab initio calculations and transition state and unimolecular rate theories are used to evaluate four possible reaction paths: (1) addition to form a hydrogen-bonded adduct followed by abstraction of H from the CHO group, (2) direct abstraction from the CHO group, (3) addition to form a hydrogen-bonded adduct followed by abstraction of H from the CH_3 group, and (4) direct abstraction from the CH_3 group. It is argued that pathways via bound adducts, although energetically favorable, are entropically unfavorable and cannot account for the observed rate constants and kinetic isotope effects, contrary to previous claims.[2-3]

This work was supported by the Environmental Protection Agency (Grant R82-8175-01-0), the Robert A. Welch Foundation (Grant B-1174) and the UNT Faculty Research Fund. While this research has been supported by the US-EPA, it has not been subject to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. The authors thank Rajeshwar Ananthula and Jacinth Naidoo for assistance with some of the analysis.

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L3. Kinetics Study of The Reaction OH + NO_2 + M: Pressure- and Temperature-Dependent Falloff Parameters

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The reaction OH + NO_2 +M (1) is an important sink for HO_x and NO_x radicals in the troposphere. Global, regional and urban models of O_3 production are highly sensitive to rate constants for reaction.(1). There have been very few studies of reaction (1) under tropospheric conditions, especially near 1 atm. pressure with M = air. Published rate constants vary by a factor of two. We have studied the reaction (1) using an improved Pulsed Laser Photolysis - Pulsed Laser Induced Fluorescence technique augmented by *in situ* optical absorption measurements of NO_2. The pressure and temperature-dependent falloff parameters will be reported.

L4. Thermochemical Kinetic Analysis on Chain Branching in Alkyl Radical Reactions with O_2: *N*-Propyl and Hydroperoxide-Propyl Radicals

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Initial products from pyrolysis, oxidation, or photochemical reactions of saturated and unsaturated hydrocarbons are the corresponding radicals. Important reactions of these alkyl radicals in combustion and in atmospheric photochemistry are combination with molecular oxygen to form peroxy adducts which undergo further propagation and / or chain branching reactions through energized (chemical activation) and stabilized states. These reactions are complex, difficult to study experimentally and present a source of controversy with regard to both pathway and reaction rates. While these reactions often comprise the principal reaction paths of the hydrocarbon radical conversion in most hydrocarbon oxidation, combustion and atmospheric photochemistry, they are relatively slow in the combustion environment and are often rate controlling in ignition and hydrocarbon conversion studies[1-13].

Ab initio and density functional calculations are performed to determine thermochemical and kinetic parameters in analysis association reactions of the *n*-propyl (CCC•) and the hydroperoxide-propyl radicals, C•CCOOH and CC•COOH, with O_2. The CBS-Q//B3LYP/6-31G(d,p) composite method is utilized to calculate energies from the B3LYP/6-31G(d,p) optimized geometries. The *n*-propyl + O_2 reaction forms an energized peroxy adduct with a calculated well depth of 36 kcal mol^{-1}. The transition states of direct molecular elimination to C=CC + HO_2, 1,5 H-shift isomerization to form a hydroperoxide-propan-1-yl adduct (C•CCOOH), 1,4 H-shift isomerization to hydroperoxide-propan-2-yl adduct (CC•COOH), and products of C=CC + HO_2 and CYCOC + OH all have energy barriers below the reactants (Figure 1).

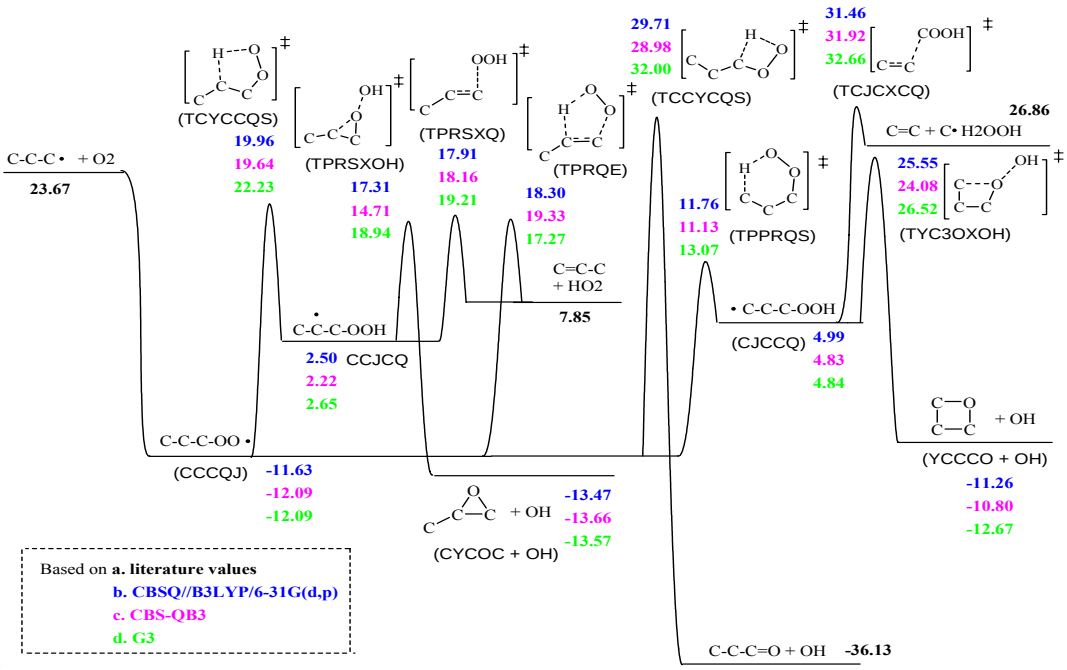

Figure 1

The hydroperoxide-propan-1-yl radical (C•CCOOH) + O_2 system (Figure2) has three reaction paths, which have lower energies than the entrance channel; two of which lead to chain branching. The hydroperoxide-propan-2-yl adduct (CC•COOH) + O_2 system is more complex; but intramolecular reactions of the peroxy adduct have higher barriers then that of (C•CCOOH) + O_2.

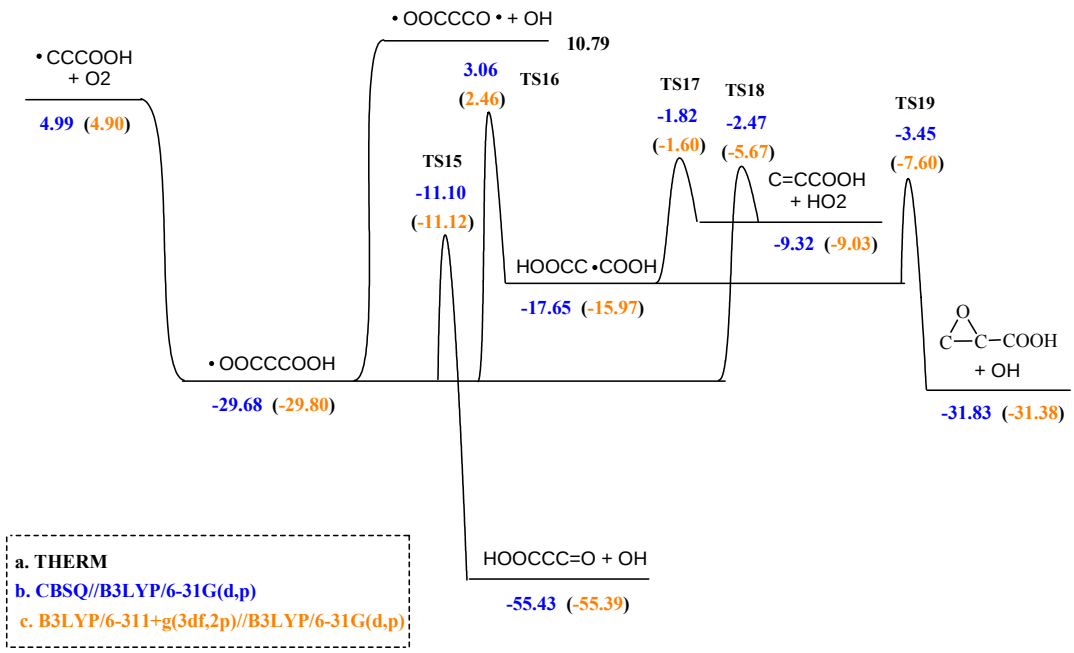

Figure 2

High- pressure limit kinetic parameters are obtained from the calculation results using canonical Transition State Theory. Quantum RRK analysis is utilized to obtain k(E) and master equation analysis is used for evaluation of pressure fall-off. An elementary reaction mechanism is constructed to model experimental data on negative temperature behavior data in propane oxidation. The chain branching needed for the negative temperature coefficient (NTC) comes from the isomerization of the propyl peroxy radical CCCOO• to C•CCOOH, with subsequent addition of another O_2 to produce •OCCC=O + 2 OH and from chemical activation reaction to •OOCCCO• + OH products. A small amount of chain branching comes from propyl-hydroperoxide, dissociation.

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L5. Laser Photolysis / Long-Path Absorption Measurement of the Rate Coefficient for Vinyl Radical Self-Reaction between 300 and 700 K

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Vinyl radicals (C_2H_3) are important intermediates in both atmospheric and combustion chemistry. Despite the kinetic importance of this radical, relatively few experimental studies have been reported. This is primarily due to the difficulty in generating and detecting a clean source of vinyl radicals. In addition, determination of the self reaction rate constant requires an accurate determination of the initial radical concentration. In this work, vinyl iodide is photolyzed at 266nm with 15-20mJ from the fourth harmonic of a Nd:YAG laser to produce both vinyl radicals and iodine atoms. Temporal profiles of both the vinyl radicals and the iodine atoms are simultaneously monitored by absorption at 405 nm (vinyl) and 1315 nm (iodine). It is assumed that the initial vinyl radical concentration is equal to the initial I atom concentration, which can be deduced from the known absorption cross section and the measured spin-orbit branching ratio. The time-resolved vinyl radical concentration is fit to a second order kinetic equation to extract the self-reaction rate constant.

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L6. Experimental and Computational Study on HF Elimination from 1,1,1,3,3,3-Hexafluoropropane and 1,1,1,3,3-Pentafluorobutane

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1,1,1,3,3,3-Hexafluoropropane ($C_3H_2F_6$) and 1,1,1,3,3-pentafluorobutane ($C_4H_5F_5$) were pyrolzyed in separate flow tube studies at 1 atm total pressure and temperatures ranging from 973 – 1098K and 823-973K respectively. Initial reactant mole fractions of 1%, 2%, and 3% (with the balance N_2) were examined for reaction times ranging from 0.2 – 2 seconds. Reactants and products were identified using on-line GC/MS and quantified using on-line GC/FID. In both cases, reactant loss was observed to follow first order kinetics, and in both cases the observed rate constants were independent of initial reactant concentration. The major product from $C_3H_2F_6$ pyrolysis was 1,1,3,3,3-pentafluoro-1-propene, while $C_4H_5F_5$ produced a mixture of tetrafluorobutene isomers. These observations strongly suggest unimolecular HF elimination is the dominant decomposition pathway for both reactants under these conditions.

A computational study was performed for decomposition of 1,1,1,3,3,3-hexafluoropropane, 1,1,1,3,3-pentafluorobutane, and for comparison with literature, trifluoroethane. Unimolecular HF elimination pathways were examined using the complete basis set extrapolation method of Petersson and coworkers [1,2] (CBS-QB3) as implemented in the Gaussian 2003 for Windows (G03W) program. Transition states and internal rotations were animated using GaussView to ensure the correct saddle points had been identified. Corrections for tunneling were made using the Wigner tunneling correction [3]. The hindered internal rotation contributions to the heat capacity and entropy were made using the methods of Shokhirev and Krasnoperov[4] and also Ayala and Schlegel[5] and were compared to treatment as a vibration.

Figure 1 shows an energy level diagram for three decomposition paths for $C_3H_2F_6$ calculated at the CBS-QB3 level of theory. Unimolecular HF elimination is clearly most favorable. Similar results were obtained for the $C_4H_5F_5$ energy surface. However, in that case there are four competing HF elimination pathways. Figure 2 compares calculated and experimental Arrhenius behavior for both $C_3H_2F_6$ and $C_4H_5F_5$ unimolecular HF eliminations. The symbols represent the experimental data, while the lines are based on multi-channel QRRK and CBS-QB3 calculations where restricted internal rotations were simply treated as vibrations. In both cases there is very good agreement between the experiments and calculations. Treatment of the restricted internal rotations tends to reduce the calculated rate constants.

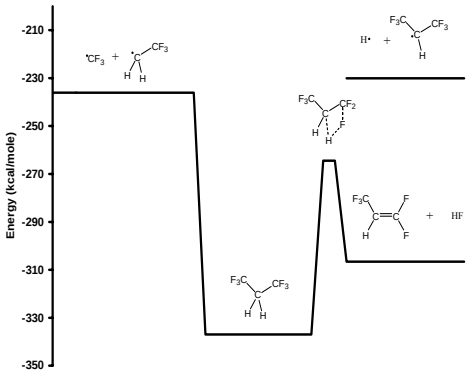

Figure 1. Energy level diagram for $C_3H_2F_6$

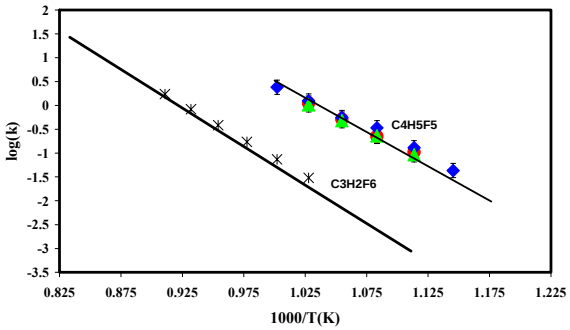

Figure 2. Arrhenius plot for $C_3H_2F_6$ and $C_4H_5F_5$ HF eliminations
Symbols – experimental, Lines – CBS-QB3

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L7. Reaction Pathways and Kinetic Analysis on Xylene Radicals

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Alkylated aromatics, including xylene, are an important component of fuels. Experimental studies show that meta-xyelene is signifigantly more resistant to ignition than ortho and para. Discovering the reason for this difference is the purpose of this study. We expect that the reason lies in the early stages of the decomposition of xylene, and other studies suggest that the stability of the xylenyl radicals leads to rapid disassociation of their oxygenated adducts, so we expect the combustion of meta benzyl (xylenyl) radical, after a benzyl H atom is abstracted, proceeds largely through unimolecular elimination reactions involving the loss of a second quasi benzyl hydrogen to produce a bis(methylene) cylclo-hexadiene product. We explored these reactions with computational chemistry, and discovered that these reactions are largely barrierless; the kinetics are therefore, determined primarily by the heats of formation of the products. We find that para-xylene has the lowest barrier to this elimination because the resulting 1,4 cyclohexadiene product has a stable quinoid-like structure. The ortho xylene cyclohexa 1,3 diene product is slightly higher in energy (approximately 7 kcal mol^{-1}), but because it can also form a stable bond-alternated structure, it is still significantly lower in energy than the comparible meta-isomer, which is geometrically incapable of forming a bond-alternated structure. The endothermicity for the H atom dissociation from the meta xylenyl radical thus lies substantially higher in energy than the ortho and para isomers. Energy level diagrams and reaction barriers to subsequent products of the xylenyl radical and H atom loss product reactions will be included.

L8. New Approaches for Collaborative Sharing of Chemical Model Data and Analysis Tools

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The urgent need for high-efficiency, low-emission energy utilization technologies for transportation, power generation, and manufacturing processes presents difficult challenges to the combustion research community. The needed predictive understanding requires systematic knowledge across the full range of physical scales involved in combustion processes – from the properties and interactions of individual molecules to the dynamics and products of turbulent multi-phase reacting flows. Innovative experimental techniques and computational approaches are revolutionizing the rate at which chemical science research can produce the new information necessary to advance our combustion knowledge. But the increased volume and complexity of this information often makes it even more difficult to derive the systems-level knowledge we need. Combustion researchers have responded by forming interdisciplinary communities' intent on sharing information and coordinating research priorities. Such efforts face many barriers, however, including lack of data accessibility and interoperability, missing metadata and pedigree information, efficient approaches for sharing data and analysis tools, and the challenges of working together across geography, disciplines, and a very diverse spectrum of applications and funding.

This challenge is especially difficult for those developing, sharing and/or using detailed chemical models of combustion to treat the oxidation of practical fuels. This is a very complex problem, and the development of new chemistry models requires a series of steps that involve acquiring and keeping track of a large amount of data and its pedigree. Also, this data is developed using a diverse range of codes and experiments spanning *ab initio* chemistry codes, laboratory kinetics and flame experiments, all the way to reacting flow simulations on massively parallel computers. Each of these processes typically requires different data formats, and often the data and/or analysis codes are only accessible by personally contacting the creator. Chemical models are usually shared in a legacy file format, such as Chemkin [1] or FlameMaster [2], often without needed metadata and pedigree information. Detailed reaction mechanisms are usually too large for efficient operation of chemical reacting flow solvers so there is also much work aimed at reducing number of species and reactions in a fashion consistent with the accuracy needs of the simulation. In the best of cases, this results in a proliferation of diverse models that are difficult to find or trace to their origins.

The Collaboratory for Multi-scale Chemical Science (CMCS) brings together leaders in scientific research and technological development across multiple DOE laboratories, other government laboratories and academic institutions to develop an informatics-based approach to

synthesizing multi-scale information to create knowledge in the chemical sciences. CMCS applies advanced collaboration and metadata-based data management technologies to develop an open source multi-scale informatics toolkit serving as the basis for a CMCS web portal. The portal enables cross-scale data discovery, viewing, comparison, transformation and exchange while facilitating community formation, communication, and data development. The portal also includes tools for browsing cross-scale data dependencies and mechanisms to integrate custom and community resources into active research projects. CMCS researchers are populating the portal with key chemistry data and integrating important chemistry applications. Additionally, several new chemical informatics applications supported by the project are being made available as portal-centric web services. These capabilities are being piloted internationally across several scales by interacting groups of leading researchers in combustion science.

Of particular interest here, is that the CMCS team is developing new approaches that facilitate collaborative sharing of chemical model data and analysis codes. In this paper, we will briefly describe the relevant CMCS infrastructure and tools in the context of an ongoing collaboration motivated by the desire to understand and control Homogenous Charge Compression Ignition (HCCI) in internal combustion engines. We will relate the issues and progress in developing XML based formats for large detailed chemical models [3], methods for documentation and viewing metadata, and implementations of translations to other useful formats. As an example of one way collaborative analysis codes can be implemented in CMCS, we will focus on the Range Identification and Optimization Tool (RIOT). RIOT is a software tool designed to reduce the number of reactions in a reaction mechanism to just those needed to maintain a specified chemical accuracy in the predictions of the resulting reduced mechanism [4, 5]. The approach for the ultimate use of such reduced models in HCCI research will also be briefly described. We intend to present in this way a vignette of how CMCS is providing new approaches to make research with practical combustion models easier, and to invite broader participation.

Acknowledgments

The authors wish to thank the team members of the Collaboratory for Multi-Scale Chemical Science (CMCS) for their many contributions to this work. This work was supported by the U.S. Department of Energy, Office of Science, Office of Advanced Scientific Computing Research, Mathematical, Information, and Computational Science National Collaboratory Program. The authors thank program manager Mary Anne Scott for her support of this work. This work was performed under the auspices of the U.S. Department of Energy by Livermore National Laboratory under contract No. W-7405-Eng-48, Sandia National Laboratories under Contract No. DE-AC04-94-AL85000, and Pacific North Pacific Northwest National Laboratory under Contract No. DE-AC06-76RLO 1830.

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L9. Kinetics of the Thermal Isomerizations of $(CH_3)_n$-Cyclopropanes: Methyl-, 1,1-Dimethyl-, 1,1,2-Trimethyl- and 1,1,2,2-Tetramethyl-Cyclopropane

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Cyclopropane (**CP**) is one of the most extensively studied molecules in the field of homogeneous gas phase kinetics. One reason is that **CP** is mechanistically complex, undergoing both structural (to propene) and geometric (cis ←→ trans) unimolecular isomerizations. Through isotopic labeling (^2H and/or ^{13}C) or substitution for H atoms (e.g. methyl, ethyl, phenyl, CN, Cl…) it is possible to measure the relative reaction rates of many competing reaction channels and to explore the effects of electron donation or withdrawal and stearic hindrance. A second reason is that the relative simplicity and high symmetry of **CP** make it attractive for high-level computational modeling of the energies of proposed transition state and/or reaction intermediate structures and the dynamics of approach to the top of the energy barrier(s). Reactions of **CP** and its relatives can serve as a good testing ground for the reliability of advanced theory, but this requires a solid body of reliable experimental rate data with which to compare the results of the computations.

We are measuring the rates of the homogeneous structural isomerizations of a family of alkylcyclopropanes over wide temperature ranges, in both static reactors and single-pulse shock tubes, to obtain accurate values of activation parameters and branching ratios for the formation of the various isomeric products. To date, we have completed the work on methyl-**CP** [1], 1,1-dimethyl-**CP** [2], 1,1,2-trimethyl-**CP** [3] and 1,1,2,2-tetramethyl-**CP** [4]; this paper will be a summary report of those results.

All four methylcyclopropanes considered in the present work have been studied and reported previously. Although each of the earlier studies covered a considerably smaller temperature range, much, indeed most, of the earlier work is reliable. Still, we have been able to resolve some inconsistencies in the earlier studies and discern definite trends in the activation parameters for these isomerizations; and we have found that some counterintuitive findings reported earlier are, in fact, correct.

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L10. Thermal Unimolecular Elimination of Water from *Tert*-Butyl Alcohol: Deuterium Kinetic Isotope Effects, Transition State Structure, Reaction Path and Mechanism

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The thermal elimination of water from *tert*-butanol (**TBA)** has long been considered a prototype homogeneous four-center elimination reaction. This reaction dominates the chemistry of gaseous **TBA** over a wide temperature range, as established by extensive experimental work in heated reactors and shock tubes [1, 2, 3]; and rates and activation parameters are well established: log (A, s^{-1}) = 14.6; E_a = 66.2 kcal/mol. Far less attention has been directed toward the dynamic and energetic details of the reaction. In the study reported here, we address those details – deuterium kinetic isotope effects, transition state structure, reaction path and mechanism – both experimentally and computationally [4].

Thermal decomposition of gaseous *tert*-butanol-1,1,1-d_3 (**TBA-d3**) was carried out in a static reactor (four runs, 436-481°C) and a single-pulse shock tube (four runs, 813-883°C). Product ratios [2-methylpropene-d_3]: [2-methylpropene-d_2], resulting from loss of H_2O or HDO respectively, were determined by gas phase 500 MHz NMR. The measured ratios give intra-molecular, symmetry-corrected k_H/k_D kinetic isotope effects for elimination of H_2O or HDO of 1.80 $\pm$ 0.08 at 436-481°C and 1.54 $\pm$0.12 at 813-883°C, which are comparable to values reported for other similar 1,2-elimination reactions. These two average values from runs at low and high temperatures -- different at the 99% confidence level -- also establish that the symmetry-corrected k_H/k_D ratio decreases slightly with increasing temperatures.

Gaussian 98W computations were performed to locate the transition structure for the elimination of H_2O from **TBA**, the internal reaction coordinate pathway linking it with **TBA** and the intra-molecular deuterium kinetic isotope effect for H_20/HDO elimination from **TBA-d$_3$**. The B3LYP/6-31G* density functional method, implementation and basis set were used. During the approach to the transition structure, changes in bond lengths are in part simultaneous and in part sequential. Early in the process the forming O-H (or O-D) bond shortens while the breaking C-O bond simultaneously lengthens, but the breaking C-H bond only begins to lengthen as the molecule nears the transition structure. Formation and shortening of the C=C bond occurs gradually throughout the process. The calculated activation energy is 63.4 kcal/mol, and

computed k_H/k_D ratios are 1.93 at 460°C and 1.44 at 860°C, all in good agreement with the experimental results.

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L11. A Time-Resolved Mass Spectrometry Study of the Reaction $HO_2 + C_2H_5$

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Reactions of HO_2 play an important role for the modeling of low temperature combustion processes, flame propagation and the self-ignition of fuels in internal combustion engines that cause engine knocking. For example, it is well known that the ignition of fuels at low temperatures is governed by the following (simplified) reaction sequence:

$$R + O_2 \leftrightarrow RO_2 \quad (1)$$
$$RO_2 \leftrightarrow R^{\bullet}OOH \quad (2)$$
$$R^{\bullet}OOH + O_2 \leftrightarrow \text{chain branching} \quad (3)$$

Recently, Carstensen et al. [1] have shown that in case of R = ethyl the concerted elimination reaction

$$C_2H_5O_2 \leftrightarrow C_2H_4 + HO_2 \quad (4)$$

effectively shuts down this chain-branching mechanism. Furthermore, via the title reaction

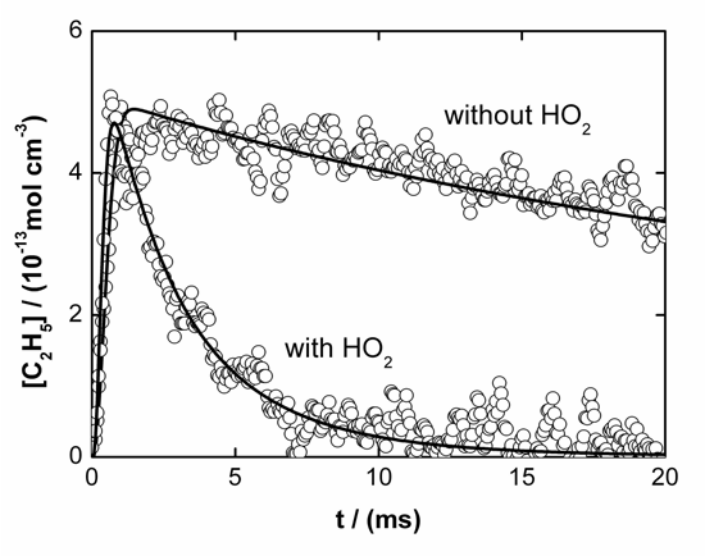
$$HO_2 + C_2H_5 \leftrightarrow C_2H_5O + OH \quad (5)$$

the HO_2 radicals generated in reaction (4) have a feedback on the equilibrium (1), which is responsible for the "negative temperature coefficient" observed in alkane ignition.

Generally speaking, the knowledge of HO_2 chemistry is rather limited, partly due to a lack of reliable HO_2 sources for kinetic measurements and partly due to the difficulties involved in a time-resolved HO_2 detection. In this study, the overall rate constant for the reaction $HO_2 + C_2H_5 \rightarrow$ products at room temperature has been determined for the first time by direct measurements of the concentration-vs.-time profiles of C_2H_5 and HO_2 radicals by means of time-resolved mass spectrometry in a laser photolysis / flow reactor combination. Excimer laser photolysis of reaction mixtures containing C_2H_6, H_2O_2 and oxalyl chloride provided experimental conditions such that the title reaction could be studied under nearly pseudo first-order conditions with HO_2 as the excess component (see figure). H_2O_2 was produced by the thermal decomposition of a urea hydrogenperoxide adduct as a new and reliable H_2O_2 source and the C_2H_5 and HO_2 radicals were generated by the fast H abstraction reactions of the primarily formed Cl atoms and OH radicals with C_2H_6 and H_2O_2. The rate constant for the title reaction was found to be

$$k_5(298\ \text{K}, 1\ \text{mbar}) = (3.1 \pm 0.9) \times 10^{13}\ \text{cm}^3/\ \text{mol s}$$

Moreover, C_2H_5O could be confirmed as a direct product of the reaction.



Example of a C_2H_5 profile measured with or without H_2O_2 and HO_2 present. $[C_2H_6]_0 = 2.7\times10^{-10}$ mol/cm^3, $[H_2O_2]_0 = 1.4\times10^{-9}$ mol/cm^3, $[Cl]_0 = 5.0\times10^{-13}$ mol/cm^3, $[HO_2]_0 = 1.8\times10^{-12}$ mol/cm^3, T = 298 K, p = 1 mbar.

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L12. A Chemically-Activated Cascade of Radical Reactions in Acetylene

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Acetylene was oligomerized in a flow system at pressures between 104 and 403 Torr and temperatures between 854 and 971 K. Products were analyzed by gas chromatography with flame ionization and mass spectrometric detection. In some experiments the reactor was placed in the chromatographic oven to limit condensation. Twenty-four products were detected, of which fifteen were found to be primary. Orders and Arrhenius parameters were found for thirteen products. The results were interpreted in terms of a radical mechanism with 24 reactions for pure acetylene. Radical addition to acetylene produced chemically activated radicals, which could either eliminate a hydrogen atom or add more acetylene. If the radical contained five or more atoms, cyclization to form cyclopentadiene or an aromatic compound, respectively, was also possible. It was suggested that radical recombination could produce chemically activated intermediates that could cyclize to form cyclohexadienes. Addition of neopentane introduced methyl radicals, which could participate in another series of seven chemically activated acetylene addition and hydrogen elimination reactions to form propyne, cyclopentadiene and toluene. Five quotents of rate constants were calculated for competitive reactions.

L13. Theoretical Study of the Kinetics and Mechanism for the Reaction of FCO with NO

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The radical FCO is one of the reactive intermediates in the atmospheric decomposition of hydrofluorocarbons (HFCs). One of the main removal processes for this radical is the reaction of FCO with NO.

In this work, the reaction mechanism of FCO + NO on the ground electronic state energy surface has been studied at the G2M level of theory based on the geometric parameters optimized at the B3LYP/6-311+G(d, p) level of theory. The two kinds of reaction paths include the direct fluorine abstraction channels producing CO + FNO and the association channels forming OC(F)NO complexes (c-LM1 and t-LM1), as shown in the following figure. The rate constant of this reaction system in the temperature range 200 – 1000 K has been calculated by the microcanonical RRKM and variational transition state theory. The theoretical result shows that the total rate constant has negative-temperature dependence and positive-pressure effect. The calculated total rate constant is in good agreement with the experimental ones.[1] The rate constants for individual reaction channels can be presented in the temperature range from 200 K to 1000 K by the following expressions:

Channel (1): FNO + CO → LM1

$k_1^{\infty} = 3.97 \times 10^{-11}\ T^{0.178} \exp(-19.4/T)$ cm^3 molecule^{-1} s^{-1}

k_1^{0} (He) $= 9.34 \times 10^{-13}\ T^{-6.80} \exp(-1009.7/T)$ cm^6 molecule^{-2} s^{-1}

k_1^{0} (N_2) $= 2.64 \times 10^{-13}\ T^{-6.47} \exp(-986.7/T)$ cm^6 molecule^{-2} s^{-1}

Channel (2): FNO + CO → (TS0) → NO + FNO

$k_2 = 7.94 \times 10^{-11}\ T^{0.077} \exp(-19.7/T)$ cm^3 molecule^{-1} s^{-1}

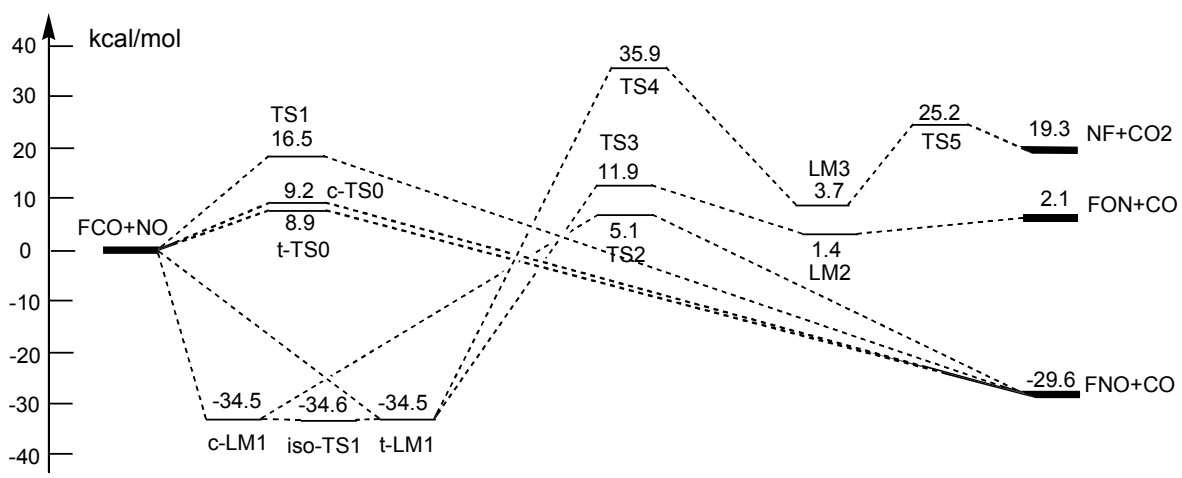

Figure 1. Potential energy diagram of the FCO-NO system

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L14. High Pressure Experiments on the Combustion of H_2/CO Mixtures

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The Mars In-Situ Propellants Rocket (MIPR) is a small vehicle proposed to fly autonomously on Mars, using in-situ propellant production [1]. The propulsion system will be fueled by carbon monoxide and oxygen. To achieve the maximum performance from the rocket engine, predictions or measurements of critical performance characteristics resulting from the use of carbon monoxide as fuel are necessary [2]. There are detailed models available for carbon monoxide oxidation, but they have never been validated by experiments conducted at the operating pressures of the proposed Martian vehicle rocket engine, 200-300 psi (13,7-20.4 atm) for pressure fed engines, 2000-3000 psi (137-204 atm) for turbopump fed engines. The most recent H_2/CO oxidation model by Davis et al. [3] has been validated against experimental data obtained at pressures up to 20 atm.

The high pressures at which the proposed engines operate cannot be easily accessed by the majority of experimental devices used to investigate chemical kinetics, but they are routinely accessed in the very high pressure single pulse shock tube operating at the University of Illinois at Chicago. Consequently the high pressure shock tube has been used in this work to study the combustion of CO/H_2 mixtures over a wide range of pressures and temperatures relevant to the operating conditions of the proposed engine. Standard GC and GC/MS techniques were used to analyze the stable species (CO, CO_2 and O_2) from the shock samples.

Six experimental data sets with more than 125 experiments spanning pressures from 25-550 bars over the temperature range 1000-1500 K were obtained. Nominal reaction times for these experiments were in the range 1.2-1.8 ms. Four sets of experiments were performed for stoichiometric oxidation (Φ=1) spanning pressures from 25 to 550 bars and two sets of experiments at 25 and 50 bars were performed using fuel lean (Φ=0.5) mixtures. Figure 1 is a compilation of the Φ=1 data sets showing the influence of pressure on the carbon monoxide conversion. No discernible difference is observed for the two highest pressure data sets at 300 and 550 bars but as the pressure is increased from 25-300 bars there is a 20% decrease in the CO conversion. The experimental data has been simulated using the recent Davis et al. [3] model. Figure 2a shows the predictions made by the model for the Φ=1, 50 bar data set. The CO trend is well described by the model but discrepancies can be seen for CO_2 and O_2 for this data set.

However for the higher pressure data sets the model does not a good job for all the three species as seen in Figure 2b for the 300 bar data set. The model is able to capture the qualitative trends observed in the higher pressure experiments but further work is required to improve the model predictions for the higher pressure data sets. The experimental data and the modeling work will be discussed in this presentation.

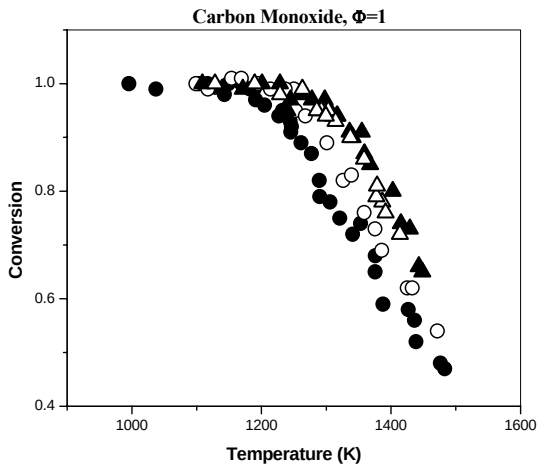
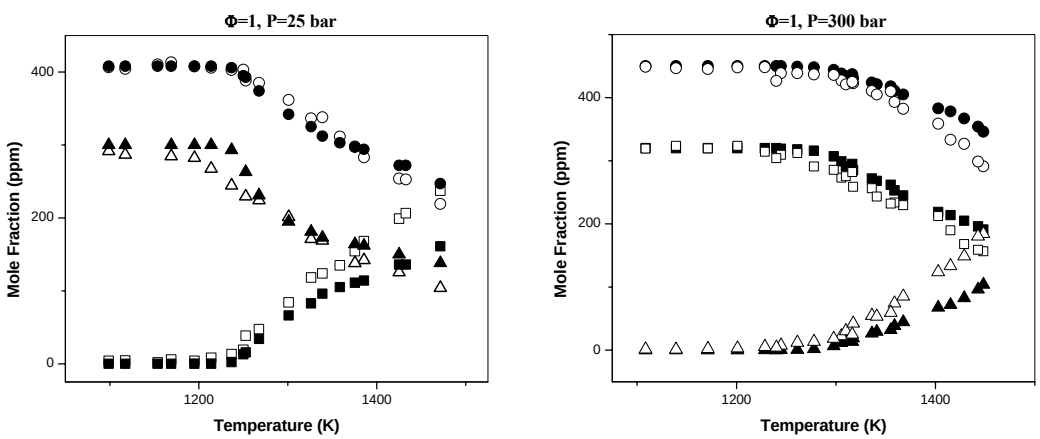


Figure 1. CO profiles. ●-25 bar; ○-50 bar; ▲-300 bar; Δ-600 bar. Φ=1.



Figures 2a & 2b. CO profiles: ●-simulations, ○-experiments; O_2 profiles: ▲-simulations, Δ-experiments; CO_2 profiles: ■-simulations, □-experiments.

Acknowledgements

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L15. Do We Understand How Two-Stage Hydrocarbon Ignition Mechanisms Work?

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Two-stage ignition (and related cool flame and negative temperature coefficient phenomena) during low-temperature oxidation of large hydrocarbon molecules is a well-established process [1, 2]. Initial phenomenological interpretations of these phenomena date back to 1940-50s [3, 4]; more detailed mechanistic rationale was suggested by Benson [5]. Detailed reaction mechanisms offering various levels of predictive ability for describing low-temperature oxidation of large hydrocarbons started to appear in late 1980s and are still under heavy development at present.
In spite of availability of detailed reaction schemes capable of quantitative predictions of various experimental observations related to two-stage ignition phenomena, the detailed and unambiguous interpretation of these model predictions is still incomplete and controversial [6]. This is primarily due to the complexity of the observed kinetic behavior as well as to the large size of the resulting detailed models, which makes them difficult to interpret using conventional tools of chemical kinetics (i.e, flux/sensitivity analysis). In this study, we use the methodology of Computational Singular Perturbation (CSP) [7] to interpret kinetic behavior related to two-stage ignition. While the most popular application of CSP is the generation of reduced kinetic models, this methodology also provides the means to directly analyze the complex kinetic systems and to identify specific processes/mechanisms responsible for the observed behavior [7]. Using an in-house CSP package, we analyzed the kinetic behavior of several popular *n*-heptane oxidation mechanisms of different complexity at the conditions where two-stage ignition and negative temperature coefficient phenomena were observed experimentally [8]. The results of this analysis are discussed and compared with the interpretations suggested in the literature [6].

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L16. Adsorption and Reaction of BCl_3 on TiO_2 Anatase (101) Surface by First -Principles Calculations

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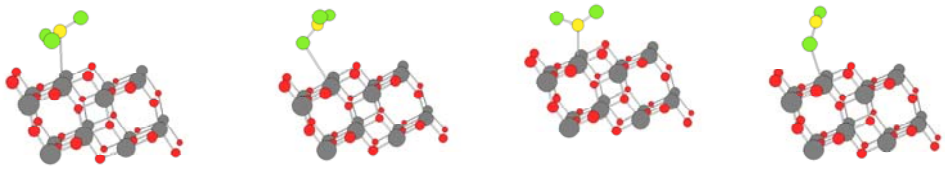
This study investigates the adsorption and reaction of boron trichloride (BCl_3) on the anatase TiO_2 (101) surface by first-principles calculations based on the density functional theory (DFT) with generalized gradient approximation (GGA) and the pseudopotential method with 400-eV plane-wave expansion. As shown in Figure 1, the geometrical structures and adsorption energies of BCl_3 and its fragments, BCl_2, BCl, Cl_2, B and Cl, adsorbed on either 5-fold-coordinate surface Ti atoms (5c-Ti) or on the 2-fold-coordinate surface O atoms (2c-O) have been optimized and computed by the VASP code. BCl_3 was found to adsorb weakly on a 5c-Ti atom with 3.5 and 5.7 kcal/mol binding energies for the Cl_3B-Ti and Cl_2BCl-Ti configurations, respectively. BCl_3 does not adsorb on a 2c- atom site, and no dual adsorptions involving two Cl atoms or one Cl and one B atom simultaneously bonding with O atoms, Ti atoms or one O and one Ti atom are found, however.

For potential plasma CVD modeling applications, we have computed the adsorption energies of the fragments of BCl_3 as listed above. Interestingly, most radical fragments were found to adsorb on both 2c-O and 5c-Ti sites forming species such as Cl_2B-O/Ti(a), Cl-O/Ti(a), ClBCl-Ti/O(a), Cl-Ti(a), etc. as summarized in Figures 1 and 2. In Figure 2, the adsorption energies of their stoichiometric product pairs are presented relative to that of the reactants, BCl_3(g) + TiO_2(101); the high energies of the dissociated products reflect the strong B-Cl bonds in BCl_3. Therefore, thermally BCl_3 cannot readily dissociate on the TiO_2 surface based on the current results. Alternatively, the dissociated BCl_2(a) + Cl(a) adsorption can be achieved by UV irradiation, electron-beam excitation or thermally decomposed, for example. We will compare the result of a similar calculation for the adsorption of BCl_3 and its fragments on a clean rutile surface in the near future.



1. Cl_3B-Ti(a): 3.5 2. Cl_2BCl-Ti(a): 5.7 3. Cl_2B-Ti(a): 9.0 4. ClBCl-Ti(a): 0.6

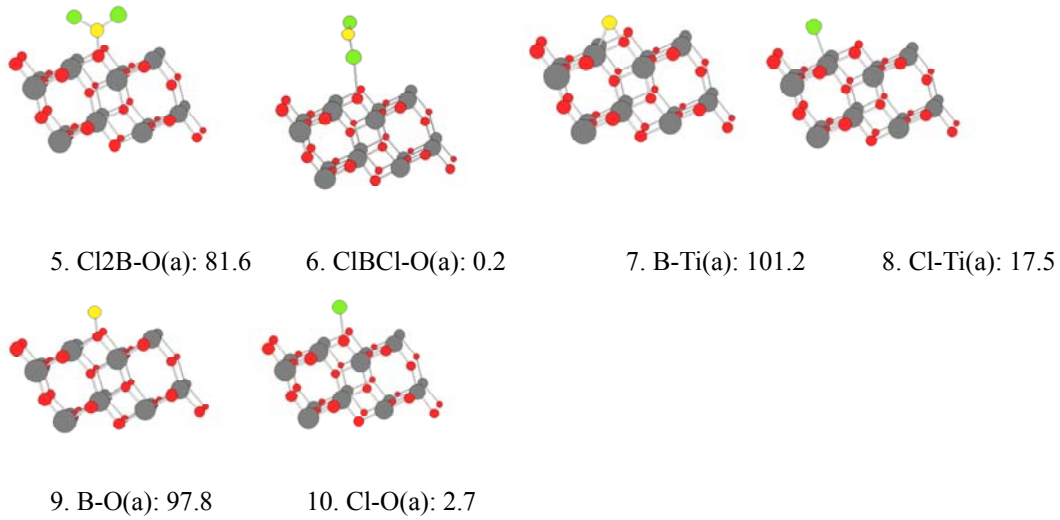


Figure1. Possible adsorption configurations of BCl_3 and its fragments

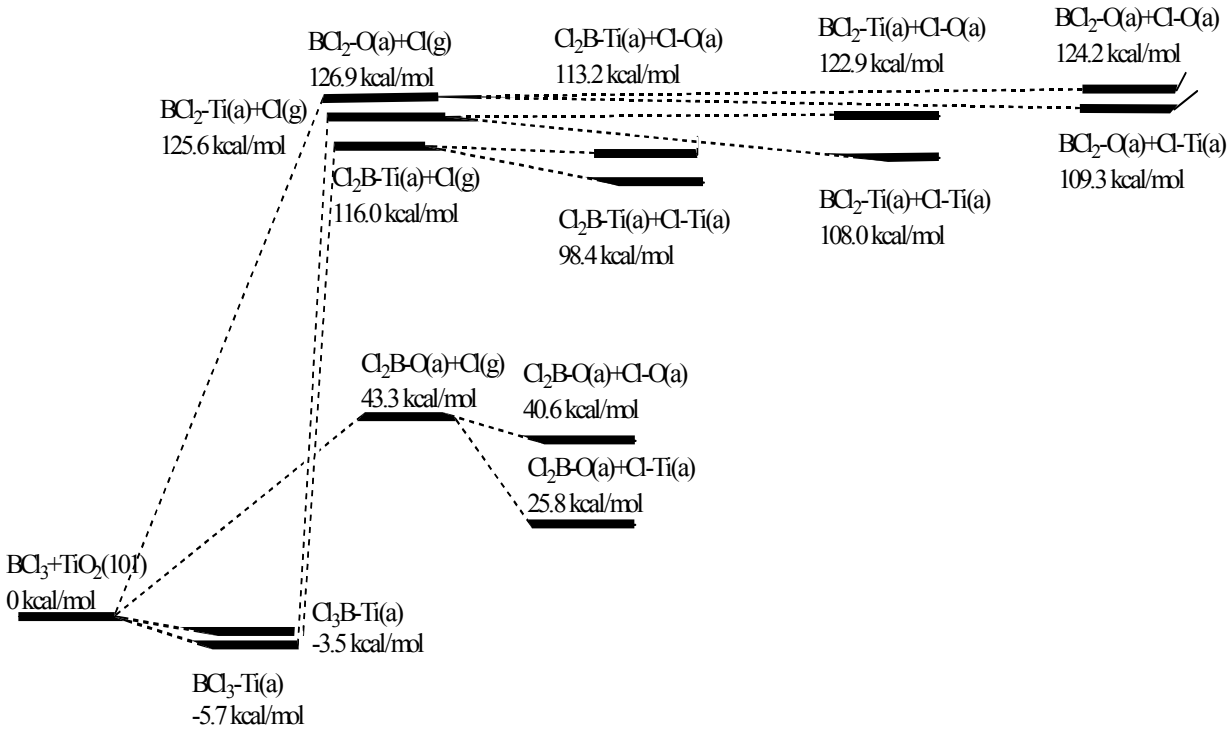


Figure 2. Potential energy diagram of BCl_3 and its dissociated product pairs on anatase $TiO_2(101)$

L17. Kinetic and Mechanistic Study of Cyclic and Aromatic Ketone Oxidation by Vandium (V) in Aqueous and Micellar Media.

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The pathway for the oxidation of cyclic ketone (Cyclohexanone) and aromatic ketone (Acetophenone) by vanadium (V) in sulphuric acid medium in presence of anionic surfactant (SLS) has been studied by following the formation of vanadium (V) spectrophometrically at 760 nm and at 313K. The oxidation displays a first order dependence on the vanadium (V) concentration, and fractional order with respect to the sulphuric acid concentration without and with SLS. The reaction is also first order with respect to the sulphuric acid concentration with no control, and an order oarger than one (1.2) at constant ionic strength, The reaction rate increases with increase of the dielectric constant. The reaction was studied at different temperature (308-323K) and activation parameters were computed with respect to the slow step of the proposed mechanism.

Vanadium (V) occurs in aqueous solution, in the activity region where it is a useful oxidant (pH < 1) as a cation of simplest formula VO_2^+. Considerable discussion has taken place as to whether or not this should be more correctly written $[V(OH)_4]^+$, or even $[V(OH)_4OH_2]^+$. It seems to be agreed, however, that a lower coordination number than six is probably correct for cations which are devoid of d-electron. The redox potential of the Vanadium (V) – Vanadium (IV) couple increases with acidity in the region from PH 1.5 to 2N acid (as would be expected if the species concerned are VO_2^+aq and VO^{2+} aq), but rather more steeply than this at higher acidities. Presumably the activity of water is reduced at higher acidities and so influences the redox equilibrium.

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$$

The prevalence of this type of kinetics can be rationalized by assuming the presence of small proportion of a further Vanadium species, $[V(OH)_3]^{2+}$aq, as the oxidant in the acid-catalyzed reaction. Though the kinetics themselves tell us nothing about the extent of formation of this cation, yet there is spectrophotometric evidence for ternary complex formation from VO_2^+, H_3O^+, and alcohol molecules; the shift of the charge-transfer spectrum of Vanadium (V) in this complex and general ideas of polarity, indicate that $[V(OH)_3]^{2+}$ must be a better oxidant than is VO_2^+ it self. we report here the kinetics and mechanism of oxidation of ketone by vanadium (V) in aqueous sulphuric acid medium inpresence and absence of SLS.

L18. Electronic Quenching Conveyed on Two Crossed States: A 6-D Time Dependent Wave Packet Study for the Collision of Two Electronically Excited $O_2(^1\Delta_g)$ Molecules

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We report a 6-dimension multiple state time dependent wave packet (TDWP) method to study the process of electronic quenching for the collision of

$$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow O_2(b^1\Sigma_g^+) + O_2(X^3\Sigma_g^-).$$

This involves two close by electronic states[1], and a spin orbit coupling term[1], assumed to be constant in this calculation. The multiple state TDWP method is developed based on the legendary single state TDWP program (Dynasol) of Prof. John Z. H. Zhang. We exactly follow all procedures of the original Dynasol code[2], and add a coupling matrix, expressed in an analytical form, to include the effect of nonadiabatic couplings between two electronic states. A same, but quite large, basis set is used to expand the nuclear wavefunctions for both of the ground and excited electronic states. As shown in Fig. 1, a wave packet analysis shows the quenching process proceeds more efficiently in the repulsive part of the potential energy surface (PES), near the curve crossing regions. This enhanced quenching process can be explained by the fact that the wave packet tends to spend more time (less kinetic energy) in the repulsive part of the PES, which happened to be close to the region, where two PESs cross.

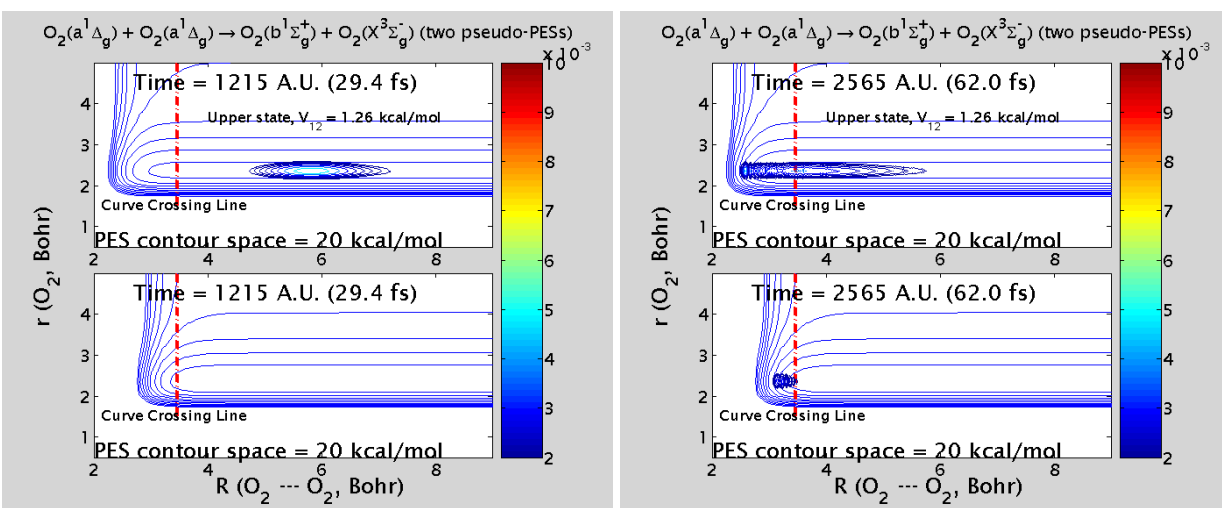

Fig. 1 Snapshots of time dependent wave packet propagated on two pseudo-PESs. (Left panel: T = 1215 A.U. Right panel: 2565 A.U.) The PESs are constructed by adding a repulsive term onto the O_2 diatomic potentials. The electronic quenching proceeds more efficiently on the repulsive part of the PES, close to the region where two PESs cross.

The population and stability of the electronic excited $O_2(^1\Delta_g)$ molecule control several key reactions in the electronic discharge chemical oxygen-iodine laser (ElectricCOIL) system[3]. For example, the near resonance energy transfer between the electronic excited $O_2(^1\Delta_g)$ molecule and the I atom ground state $I(^2P_{3/2})$ gives rise to the population inversion of I atom, $O_2(^1\Delta_g) + I(^2P_{3/2}) \Leftrightarrow O_2(^3\Sigma_g^-) + I^*(^2P_{1/2})$. The lasing of the ElectricCOIL is then coming from the electronic transition from the spin orbit excited state to the ground state of iodine atom at 1315 nm, $I^*(^2P_{1/2}) \rightarrow I(^2P_{3/2}) + h\nu$. Our study of the electronic quenching mechanism is the first of our many planned theoretical attempts to describe the reaction mechanisms of the ElectricCOIL, in details.

References:

1. J. Liu and K. Morokuma, to be published.
2. Dynasol, formerly called DynaSolver, is a software package for chemical reaction dynamics calculation with graphical user interface. http://p150.chem.nyu.edu/dynasolver/
3. D. L. Carroll, J. T. Verdeyen, D. M. King, J. W. Zimmerman, J. K. Laystrom, B. S. Woodard, G. F. Benavides, K. W. Kittell, W. C. Solomon, *IEEE J. Quantum. Elect.,* **41**, 213-223 (2005)

L19. Adsorption and Reaction of $SiCl_4$ on Hydroxylated TiO_2 Anatase (101) Surface by First -Principles Calculations

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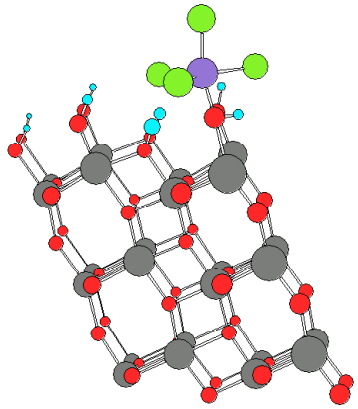
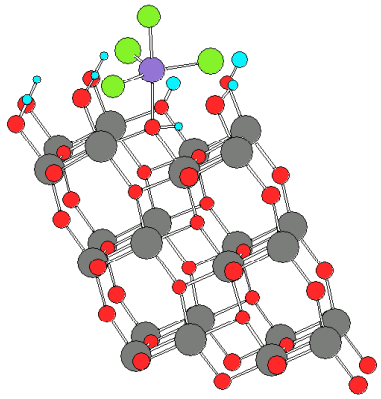
This study investigates the adsorption and reaction of silicon tetrachloride ($SiCl_4$) on the hydroxylated anatase TiO_2 (101) surface by first-principles calculations based on the density functional theory (DFT) with generalized gradient approximation (GGA) and the pseudopotential method with 500-eV plane-wave expansion. As shown in Figure 1, the geometrical structures and adsorption energies of $SiCl_4$ and its fragments, $SiCl_3$, $SiCl_2$ and Cl, adsorbed either on –$O(H)Ti_{5c}$ or on –$O_{2c}(H)$ have been optimized and computed by the VASP code; where T_{5c} and O_{2c} represent the 5-fold coordinated Ti and 2-fold coordinated O atoms, respectively.

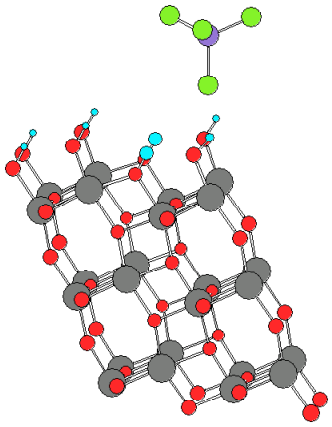
For preparation of self-assembled layers of $Cl_xSiOTi(a)$, we have computed the adsorption energies of $SiCl_x$ (x = 1 - 4) listed above. Preliminary results indicate that most radical fragments adsorb strongly on -$O_{2c}(H)$, -$O(H)Ti_{5c}$, -O_{2c}, and -OTi_{5c} as expected (where the latter two sites are bare sites without H atoms attached), forming species such as $SiCl_3$-$O(H)Ti_{5c}$/-$O_{2c}(H)(a)$, Cl_3Si-OTi_{5c}/-$O_{2c}(a)$, and $Cl_2Si(-OTi_{5c})_2(a)$ etc., as summarized in Figure 1. The results show unexpectedly that $SiCl_4$ cannot molecularly absorb on a hydroxylated surface site. On the other hand, $SiCl_x$ radicals can absorb on both OTi_{5c} and O_{2c} sites tightly. These strongly adsorbed Cl_3Si-$OTi_{5c}(a)$ and Cl_3Si-O_{2c} can be formed by highly exothermic reactions, $SiCl_4(g)$ + $HOTi_{5c}(a)/HO_{2c}(a)$ → $SiCl_3$-$OTi_{5c}(a)$/-$O_{2c}(a)$ + HCl(g), with the heats of reactions, -160 kcal/mol and -143 kcal/mol, respectively. Furthermore, subsequent HCl(g) elimination processes such as $SiCl_3$-OTi_{5c}/-$O_{2c}(a)$ + $HOTi_{5c}(a)/HO_{2c}(a)$ → $Cl_2Si(-OTi_{5c})_2/(-O_{2c})_2$ (a) + HCl(g) are also being investigated; the results of these reactions will be presented at the meeting.



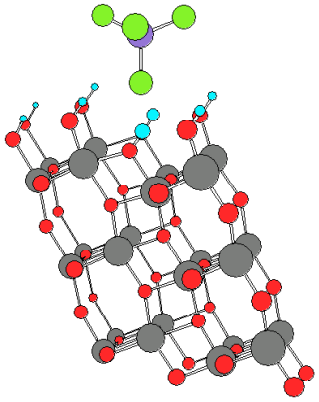
1.Cl_4Si-$O(H)Ti_{5c}$:N/A



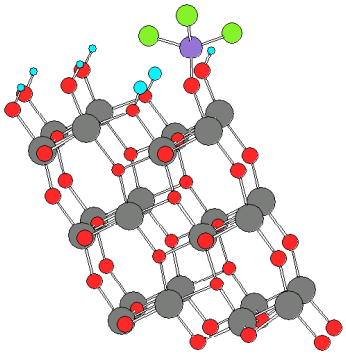
2.Cl_4Si-$O_{2c}(H)$:N/A



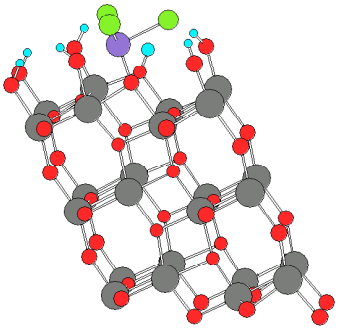
3.$SiCl_4$-$HOTi_{5c}$:N/A



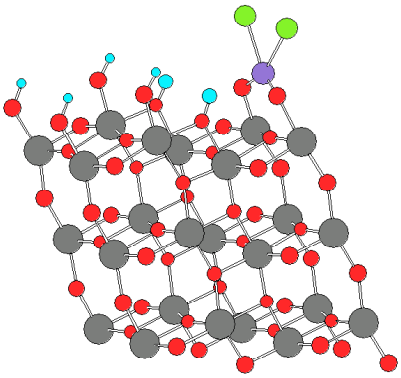
4.$SiCl_4$-HO_{2C}:N/A



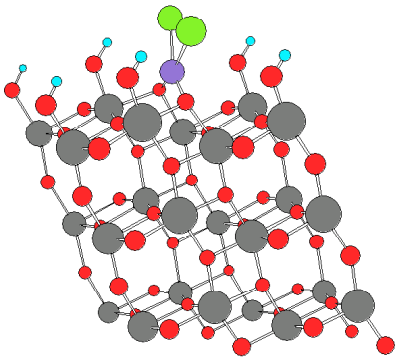
5.Cl_3Si-OTi_{5c}:160



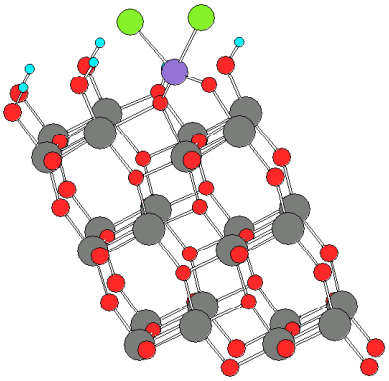
6.Cl_3Si-O_{2c}:143



7.$Cl_2Si(-OTi_{5C})$



8.$Cl_2Si(-O_{2c})_2$



9.$Cl_2Si(-O_{2c})(-OTi_{5c})$

Fig. 1 Possible Adsorption Configurations of $SiCl_x$ (xxx represnts energies under computation)

L20. Formation of HO_2 and OH in the Reaction of Methoxymethyl with Moleculer Oxygen at Room Temperature Using Near-IR and UV Spectroscopy

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Production of HO_2 and OH has been observed in 355 nm photolysis of CH_3OCH_3 / Cl_2 / O_2 mixture even at room temperature. Near-IR frequency modulation spectroscopy in a Herriott type multi-path cell was applied to detect HO_2 and OH.

Figure 1 shows HO_2 and OH profiles at 296 K. The HO_2 profile exhibits a rapid rise, in contrast with the slow rise at 600 K. The rapid rise of OH is similar to that at 600 K on the time constant, but with the less peak yield against the initial Cl concentration. Our model constructed to represent the HO_2 and OH profiles at 600 K has failed to reproduce the above experiments, particularly for HO_2 formation. According to an existing mechanism proposed by Jenkin et al. [1], HO_2 formation is expressed as:

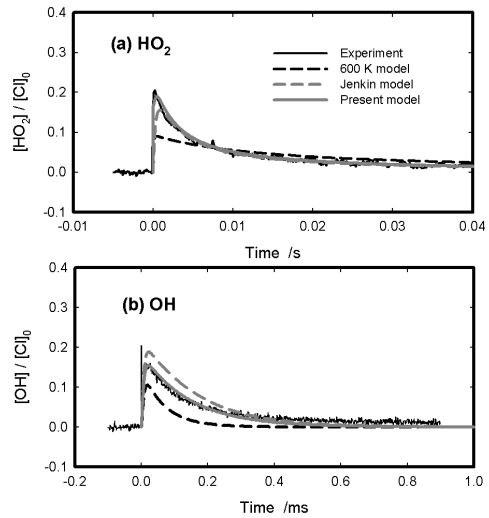

Fig.1 HO_2 and OH time profiles at 296 K in the. photolysis of CH_3OCH_3 / Cl_2 / O_2 (1.5 / 2.8 / 168 × 10^{15} molecule.cm^3).

$CH_3OCH_2 + O_2 \Leftrightarrow CH_3OCH_2O_2$ (R1)
$CH_3OCH_2O_2 + CH_3OCH_2O_2 \rightarrow CH_3OCHO + CH_3OCH_2OH + O_2$ (R2)
$CH_3OCH_2O_2 + CH_3OCH_2O_2 \rightarrow CH_3OCH_2O + CH_3OCH_2O + O_2$ (R3)
$CH_3OCH_2O \rightarrow CH_3OCHO + H$ (R4) $H + O_2 + M \rightarrow HO_2 + M$ (R5)
$CH_3OCH_2O + O_2 \rightarrow CH_3OCHO + HO_2$ (R6)

To reproduce the OH profile, the direct forming pathway of OH is also assumed as in the case of 600 K; i.e.,

$CH_3OCH_2 + O_2 \rightarrow OH + 2\ HCHO$ (R7)

The above mechanism fairly reproduces the experimental observations. However, the adjustment to reproduce the HO_2 rapid rise tends to overestimate the OH formation while calculated HO_2 formation is still slower, as shown in Fig.1. Hence, a direct forming pathway of HCO is assumed as an additional channel; i.e.,

$CH_3OCH_2 + O_2 \rightarrow HCO + HCHO + H_2O$ (R8)

This channel is supported by our *ab initio* calculation using MRMP2 // CASSCF/cc-pVTZ level, in which the transition barrier of R8 is about 13 kJ/mol higher than that of R7. When the rate constants are assumed as $k_4 = 1.16\times10^{4}$ s^{-1}, $k_7 = 4.4\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, $k_8 = 4.05\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}, both profiles are well reproduced. For further analysis discriminating R2, R3 and R8 as the source of HO_2 production, tracing $CH_3OCH_2O_2$ is considered to be effective. For such a purpose, a single path UV absorption setup using D_2 lamp was established in the Herriott cell. Currently $CH_3OCH_2O_2$ is detected at 250 nm and the time resolved measurement is in progress.

Reference

1. M. E. Jenkin, G. D. Hayman, T. J. Wallington, M. D. Hurley, J. C. Ball, O. J. Nielsen, and T. Ellermann, *J. Phys. Chem* 97, 11712 – 11723 (1993)

L21. Trajectory Simulation of The Effect of Internal Excitation of Reagents on Dynamics of Long-Living Four-Atom Complex Formation in The System Cscl + RbJ

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Dynamics of four-atom complex formation via the process CsCl+RbJ→CsClRbJ is investigated by quasi-classical trajectories on potential energy surface, which ensure quantitative agreement between calculated data and experimental results in cross molecular beams in wide range of collision energies [1].

Maximum cross sections of this reaction correspond to close to zero values of collision energy and decrease practically to zero at their growth above 0,5 eV. Principal cause of stabilization of a complex at so low energies is the centrifugal barrier arising because of its rotation.
Internal energy of reagents was chosen by Monte-Carlo technique for preset values of temperatures of sources of molecular beams in the assumption of equilibrium distributions on their states. Trajectory calculations were fulfilled at relative energy of collision 0,1 eV for temperatures of sources of both beams equal 1000K, that corresponds to experimental conditions, and also lowered up to 500K and increased up to 1500K values of temperatures of each source of a beam of molecules-reagents separately.

It turns out that the cross section of formation of four-atom complex is rather sensitive to internal excitation of reagents. It increases at downturn of temperatures of sources of molecular beams and decreases at their growth. So, rise in temperature of any of sources up to 1500K leads to reduction of cross section twice. A little bit greater influence renders change of internal energy of molecules CsCl.

References:

1. V. M. Azriel, V. M. Akimov, L. Yu. Rusin, *Soviet J. Chem. Phys*. 21, 18 (2002).

L22. Investigating Internal Rotation in Molecules and Radicals

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Almost every chain molecule or molecule with a chain branch and a single bond can perform an internal rotation around this bond. When calculating the thermochemical properties of molecules or radicals that have internal rotations, this type of internal motion needs to be taken properly into account. This is becoming increasingly important as new approaches that have the potential to deliver high-accuracy values for enthalpies of formation by combining all the available experimental and theoretical determinations, such as Active Thermochemical Tables, are being developed. In particular, the current limiting step to extending the full benefit of the improved thermochemical accuracy to such areas as combustion modeling appears to be linked to the accuracy of the computed ideal gas thermochemical properties that depend on the partition function (heat capacity, entropy, enthalpy increment), particularly at elevated temperatures relevant in combustion and many kinetics experiments. One of the bottlenecks is in the proper treatment of various anharmonic effects, another in the proper treatment of hindered rotors. Though treating internal rotors as pseudo-vibrations is a favorite shortcut, exploited by many composite high-level ab initio calculations (such as the popular G*n* ab initio family), this simplification often produces unacceptably large errors at combustion temperatures. However, in many cases the results from such ab initio approaches that have now reached near-chemical accuracy can be satisfactorily expanded toward combustion temperatures by carrying out relatively inexpensive additional computations of the angular dependence of the torsional potential. These computations can produce the needed V_n terms in the popular periodic potential function representations, such as $V = \frac{1}{2}\sum_{n=1}^{6} V_n (1 - \cos n\phi)$. We have recently started a systematic exploration of simple cases of internal rotors, many of which have not been so far extensively examined. The present study involves testing the limitations of the cosine expansion for the computed one-dimensional potentials, as well as an exploration of the effects of various simplifications on the computed thermochemistry at combustion temperatures, such as expressing the potential through a single averaged term (e.g. V_3 for a methyl rotor) or using estimated hindered rotation barriers. While this study indicates that independent rotors can be properly treated with a relatively small additional computational effort, cases that have multiple rotors that are coupled, or where the internal rotation couples to some other internal motion, such as a wag, are a challenge that still awaits a simple general solution.

This research has been 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. This work has benefited in several ways from the support and effort of the numerous team members of the Collaboratory for Multi-Scale Chemical Science (CMCS), which is a project within the National Collaboratories Program sponsored by the U.S. Department of

Energy's Division of Mathematical, Information, and Computational Sciences of the Office of Advanced Scientific Computing Research. Portions of this research are related to the effort of a Task Group of the International Union of Pure and Applied Chemistry (2003-024-1-100), which focuses on the thermochemistry of chemical species implicated in combustion and atmospheric chemistry.