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Accurate Potential Energy Surfaces and Quantum Dynamics for Polyatomic Chemical Reactions

Dong Hui Zhang
State Key Laboratory of Molecular Reaction Dynamics
Dalian Institute of Chemical Physics, CAS, Dalian 116023
*E-mail: Zhangdh@dicp.ac.cn

Abstract

In this talk, I will present some of our recent works on quantum dynamics studies of some polyatomic reactions. Highly accurate potential energy surfaces have been constructed for these systems by using the Fundamental Invariant Neural Network (FI-NN) method based on extensive CCSD(T) *ab initio* calculations. Time-dependent wave packet method has been employed to study these reactions at the state-to-state level. Dynamics resonances and the effects of vibrational excitation on the reactions will be discussed.

A NICE APPROACH TO CONTROL THE EFFECTIVE KINETICS OF CATALYTIC PROCESSES

Marc-Olivier Coppens[1,*]
[1] University College London (UCL), Department of Chemical Engineering and Centre for Nature-Inspired Engineering (CNIE), Torrington Place, London WC1E 7JE, UK

Keywords

Diffusion, Nature-Inspired Chemical Engineering, Hierarchically Structured, Zeolites, Surface Barriers.

The product distribution and yields of a heterogeneously catalyzed process utilizing a porous catalyst depend on the intrinsic kinetics, as well as the pore network structure. The latter influences the molecular transport rates of the species involved in the reactions. Catalyst pellets or particles often consist of nanoporous grains, e.g., of a microporous zeolite or mesoporous alumina, which have very high surface areas. These lead to high intrinsic catalytic rates per unit mass, but diffusion limitations may ensue, lowering the effective rates and skewing selectivity. Broader meso- and macropores within the grains and between them can alleviate overall diffusion limitations. A lot of research has focused on hierarchically structured porous catalysts with optimized porosity, pore size and spatial distribution, to obtain higher effective activity, mitigate effects of catalysts deactivation and/or increased selectivity towards desired components. Multiscale computation can guide synthesis methods that have become increasingly sophisticated to fine-tune pore sizes and pore network architecture, although not all methods are amenable to scalable economic and sustainable production.

Recently, it has become apparent that this textbook picture of diffusion and reaction in porous catalysts might need to be updated, especially for microporous catalysts, such as zeolites, but possibly also for mesoporous catalyst supports, such as alumina. Thanks to advanced, single-particle experimental characterization methods and molecular simulations, there is mounting evidence for both internal and external surface barriers. Thus, the rate-limiting transport step may become the surface permeability across a crystal or grain surface, rather than intra-particle diffusion. This is especially so for hierarchically structured porous materials consisting of very small, nanograins, and which already include macropores to reduce diffusion limitations.

Nature-inspired chemical engineering (NICE) is a method to learn lessons from fundamental mechanisms underpinning desired properties in nature, such as efficiency and scalability, to guide the design of engineering processes and products by borrowing these mechanistic features for similarly improved or even optimized properties in applications. For transport and reaction problems, nature uses highly effective hierarchical transport networks, as seen in the lung, the vascular network, or trees. Nature also uses surfaces and interfaces as selective membranes, as in the skin or cells. The combination leads to process intensification.

Here, I will discuss how NICE can be used to optimize hierarchically structured catalysts in a holistic, multi-scale way, considering both the pore network architecture and the interfaces. Beyond optimizing the pore network structure, controlling surface barriers offers unprecedented opportunities to control the effective kinetics of porous catalysts, and intensify processes.

*Corresponding author: m.coppens@ucl.ac.uk

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*Corresponding author: m.coppens@ucl.ac.uk

Mechanistic Investigation of the Kinetic Resolution of α-methyl-Substituted Phenylacetaldehyde by Norcoclaurine Synthase

Shiqing Zhang, **Aijing Guo**, Hao Su, Xiang Sheng*
[1] Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Keywords

Biocatalysis, Reaction mechanism, Kinetic resolution, Quantum chemistry.

The norcoclaurine synthase from *Thalictrum flavum* (*Tf*NCS) can stereoselectively catalyze the Pictet-Spengler reaction between dopamine and 4-hydroxyphenylacetaldehyde to give (*S*)-norcoclaurine which acts as an important intermediate in benzylisoquinoline alkaloid biosynthesis [Minami et al., 2007]. Recently, the kinetic resolution of α-methyl-substituted phenylacetaldehyde (MPAA) was achieved by *Tf*NCS with high stereoselectivity and yields the (1*S*, 2*R*) chiral product [Roddan et al., 2019]. However, the reaction mechanisms and the origins of enantiopreference of *Tf*NCS towards MPAA are still unclear. Herein, a cluster model of the enzyme was designed on the basis of the crystal structure and quantum chemical calculations were then performed to obtain the detailed reaction mechanism and energy profiles. Our calculations reveal that the reaction of dopamine with MPAA by *Tf*NCS follows a similar mechanism as the natural substrate, in which the deprotonation of C-H of the cyclized intermediate is the rate-liming step for both *R*- and *S*-pathways, and the corresponding energy barriers are 20.1 and 21.6 kcal/mol, respectively. The results are thus able to reproduce the experimental results. Importantly, the calculations could also rationalize the observed enantioselectivity of *Tf*NCS towards the non-natural substrate. By analyzing the geometries of the intermediates and transition states, the M97 and L72 residues are indicated as the important residues in controlling the selectivity of *Tf*NCS on MPAA. The detailed information about the mechanism and the enantioselectivity is helpful to rationally design variants of *Tf*NCS with improved reactivity and selectivity properties for a wider scope of substrates.

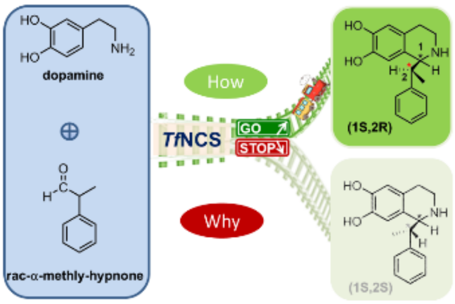

***Figure.** The kinetic resolution reaction of α-methyl-substituted phenylacetaldehyde catalyzed by TfNCS.*

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*Corresponding author: shengx@tib.cas.cn

ON THE MECHANISM OF SOOT NUCLEATION

Alexander M. Mebel[1,*], Alexander N. Morozov[1], and Michael Frenklach[2]
[1]Department of Chemistry and Biochemistry, Florida International University, Miami, Florida, 33199, USA
[2]Department of Mechanical Engineering, University of California at Berkeley, Berkeley, California, 94720, USA

Keywords

Polycyclic aromatic hydrocarbons (PAH), soot, nucleation, non-equilibrium dynamics, molecular dynamics

The mechanism of carbon particulate (soot) inception has been a subject of numerous studies and debates. We critically reviewed prior proposals, analyzed factors enabling the development of a meaningful nucleation flux, and then introduced new ideas that lead to the fulfillment of these requirements. In the new proposal, a rotationally-activated dimer is formed in the collision of an aromatic molecule and an aromatic radical; the two react during the lifetime of the dimer to form a stable, doubly-bonded bridge between them, with the reaction rooted in a five-member ring present on the molecule edge. Several such reactions were examined theoretically and the most promising one generated a measurable nucleation flux. The consistency of the proposed model with known aspects of soot particle nanostructure is discussed. The foundation of the new model is fundamentally the H-Abstraction-Carbon-Addition (HACA) mechanism with the reaction affinity enhanced by rovibrational excitation. In particular, by carrying out molecular dynamics simulations of dimerization of midsize polycyclic aromatic hydrocarbons (PAH), which is the presumed critical step in formation of carbonaceous particles in terrestrial and extraterrestrial environments, we have discovered non-equilibrium precursor mediated kinetics for reactions of gaseous molecules at high temperatures. The non-equilibrium precursor state originates from inelastic collisional dynamics of two PAH monomers, with low-frequency modes acting as a sink for translational energy in the reaction coordinate. Owing to the prolonged lifetime of the non-equilibrium physical dimer, the probability of chemical dimerization increases by an order of magnitude. This phenomenon brings us closer to a solution for the carbon-particle inception puzzle and should prove useful for the fundamental understanding of gas-phase chemical reactions involving large molecules.

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*Alexander M. Mebel: mebela@fiu.edu

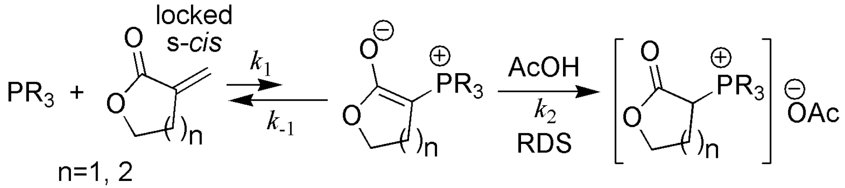
ANCHIMERIC ASSISTANCE IN REACTION OF TERTIARY PHOSPHINES WITH α-METHYLENE LACTONES AND ITS APPLICATION IN ORGANOCATALYSIS

Alexey V. Salin*, Andrey A. Shabanov and Ramil I. Nugmanov
Kazan Federal University, A. Butlerov Institute of Chemistry, 18 Kremlevskaya Street, Kazan, Russian Federation

Keywords

Stereoelectronic effects, Organocatalysis, Phosphonium enolates, Lactones.

α-Methylene lactones represent a wide family of naturally occurring products, many of which exhibit multiple biological activities: anticancer, anti-inflammatory, antiviral, antibacterial, antifungal, antimalarial (Kitson et al., 2009). During the kinetic studies, we found that the addition of tertiary phosphines to α-methylene lactones in acetic acid is strongly accelerated in comparison with reactions of open-chain α,β-unsaturated esters. Six-membered α-methylene-δ-valerolactone exhibited a more pronounced rate increase than five-membered α-methylene-γ-butyrolactone.



RDS=rate-determining step

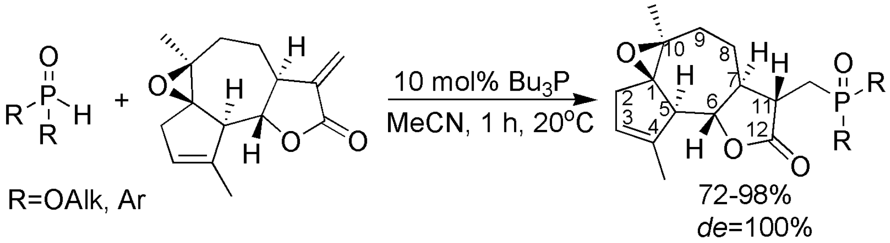
$$\text{Rate} = \frac{k_1}{k_{-1}} k_2[\text{PR}_3][\text{lactone}][\text{AcOH}] = k_{\text{III}}[\text{PR}_3][\text{lactone}][\text{AcOH}]$$

The observed reactivities were rationalized by DFT calculations at the RwB97XD/6-31+G(d,p) level of theory. The calculations showed that intramolecular electrostatic interaction between phosphonium and enolate oxygen centers provided by the locked s-*cis*-geometry of the heterocycles plays an important role in stabilization of intermediate zwitterions leading to the enhanced reaction rates.

Recalling that phosphonium enolates are key intermediates of phosphine-catalyzed reactions (Salin and Shabanov, 2023), we performed highly efficient Michael additions of phosphorus, nitrogen, and carbon pronucleophiles to α-methylene-γ-butyrolactones using *n*-Bu_3P as the organocatalyst (Salin and Islamov, 2019).

Sesquiterpene lactone arglabin bearing multiple functional groups also tolerated well the reaction conditions, providing corresponding Michael adducts in excellent yields and stereoselectivities. The increased reactivity of α-methylene-γ-butyrolactones allowed to perform phosphine-catalyzed double Michael addition of active methylene compounds, which is not typical to open-chain α,β-unsaturated esters. The absolute configuration at the created C11 stereocenter in the arglabin derivatives was determined to be *S* by single-crystal X-ray diffraction.

*Corresponding author: salin555@mail.ru



The cytotoxicity of the Michael adducts derived from arglabin was tested against normal and tumor human cell lines. The arglabin derivatives showing high cytotoxicity against M-Hela and HuTu 80 tumor cell lines and low cytotoxicity against Chang liver and WI38 normal cell lines were found.

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*Corresponding author: salin555@mail.ru

Kinetics of OH + Methylamine reaction

Anxo Lema-Saavedra,[1,*] Daniel González,[2] Sara Espinosa,[2] Emilio Martínez-Núñez,[3] Antonio Fernández-Ramos,[1,3] André Canosa,[4] Bernabé Ballesteros[2,5] and Elena Jiménez[2,5]

[1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS), University of Santiago de Compostela, 15782, Santiago de Compostela, Spain

[2]*Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avda. Camilo José Cela 1b, 13071, Ciudad Real, Spain.*

[3]*Departamento de Química Física, Facultade de Química, Campus Vida, Universidade de Santiago de Compostela, Avda das Ciencias s/n, 15782, Santiago de Compostela, Spain*

[4]*CNRS, IPR (Institut de Physique de Rennes)-URM 6251, Université de Rennes, F-35000 Rennes, France*

[5]*Instituto de Investigación en Combustión y Contaminación Atmosférica (ICCA), Universidad de Castilla-La Mancha,Camino de Moledores s/n, 13071, Ciudad Real, Spain*

Keywords

astrochemistry, glycine, tunnelling, Pilgrim, low pressure.

The presence of biologically interesting molecules (BIM) in the interstellar medium (ISM) has attracted scientists' attention for a long time. Among them, glycine, the simplest aminoacid, stands out. In this regard, methylamine (CH_3NH_2) has been proposed as a possible precursor of gly and has also been detected in the ISM.

Since one of the most abundant radicals in space is OH, we have explored the reaction between OH and methylamine and evaluated the kinetic constants of their reactions employing the Competitive Canonical Unified Statistical (CCUS) model at the low-pressure and high-pressure limits, with the Pilgrim program (Ferro-Costas et al., 2020), in the range of temperatures from 10 to 500 K. Additionally, quantum tunnelling was considered through the Small Curvature Tunneling (SCT) approximation. Also, to ensure the accuracy of our results, we calculated the anharmonic partitions functions (González et al., 2022).

We have compared our results with experiments - obtained using a pulsed CRESU reactor (Jiménez et al., 2015) that reproduces a large range of ultralow temperatures (11.7-177.5 K) – obtaining a good agreement between theory and experiments.

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*Corresponding author: anxo.lema.saavedra@usc.es

First-principles Surface Reaction Rates by Molecular Dynamics and Neural Network Potentials

Bin Jiang[1,*]
[1] Key Laboratory of Precision and Intelligent Chemistry, Department of Chemical Physics,
University of Science and Technology of China, Hefei, Anhui 230026, China P. R. China

Keywords

Rate constants, Surface reaction, Molecular dynamics, Neural network potential.

Elementary gas-surface processes are essential steps in heterogeneous catalysis. A predictive understanding of catalytic mechanisms remains challenging due largely to the difficulties of accurately characterizing of the kinetics of such steps. Experimentally, thermal rates for elementary surface reactions can be now measured using a novel velocity image technique, providing a stringent testing ground for ab initio rate theories. In this talk, I will introduce our recent progress in combining the ring polymer molecular dynamics (RPMD) rate theory with the state-of-the-art first-principles-determined neural network potential to calculate surface reaction rates. Taking NO desorption from Pd(111) as an example, we show that the harmonic approximation and the neglect of lattice motion in the commonly-used transition state theory overestimates and underestimates the entropy change during the desorption process, respectively, leading to opposite errors in rate coefficient predictions and artificial error cancellations. Including anharmonicity and lattice motion, our results reveal a generally neglected surface entropy change due to the significant local structure change during desorption and obtain the right answer for the right reasons. Recrossing effects are found relevant to the energy dissipation to the substrate. The proposed strategy is promising to predict more accurate rate constants for those surface reactions where the conventional harmonic transition state theory fails.

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*Corresponding author: bjiangch@ustc.edu.cn

Quantitative kinetics of Criegee intermediates by using theoretical methods

Bo Long[1,*]
[1]College of Materials Science and Engineering, Guizhou Minzu university, Guiyang 550025, China

Keywords

Criegee, Theoretical methods, Kinetics, dual-level strategy

Criegee intermediates are produced in the ozonolysis of unsaturated compounds in the atmosphere. Criegee intermediates play important roles in the atmosphere because they make main contribution to the production of OH during the nighttime and affects the formation of secondary organic aerosols. Additionally, they are also important oxidants that can initiate atmospheric oxidation reactions for the sink of atmospheric molecules. For example, Criegee intermediates are important oxidant for sulfur dioxide conversion to sulfur trioxide. The key parameters are kinetics of Criegee intermediates for atmospheric modeling and elucidating the atmospheric chemical transformation processes. However, the kinetics of Criegee intermediates are still limited because experimental methods can only be used to investigate the reactions of small-sized Criegee intermediates at the narrow temperature range; this does not cover atmospheric temperature. Although theoretical methods provide an alternative tool for obtaining quantitative kinetics of Criegee intermediates, Criegee intermediates have some multireference features; this leads to lager uncertainties at the CCSD(T) level. Herein, we have developed theoretical methods and designed computational strategies to obtain the quantitative kinetics of bimolecular reactions of Criegee intermediate with atmospheric molecules and their unimolecular reactions.

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*Corresponding author: wwwltcommon@sina.com

Mechanism reduction-assisted optimization for the ethylene chemistry of the AramcoMech 2.0 combustion mechanism

Boyang Su[1], Tibor Nagy[2], Máté Papp[1], Tamás Turányi[1,*]
[1] Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary
[2] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Budapest, Hungary

Keywords: *Ethylene, combustion mechanism, mechanism reduction, mechanism optimization*

As the smallest alkene, ethylene is a key intermediate in the combustion and pyrolysis of larger hydrocarbons, thus a better understanding the chemistry of ethylene combustion is important for the description of the chemistry of complex hydrocarbon fuels in combustion systems. A large set of experimental data covering wide ranges of condtions on ethylene combustion was collected: ignition delay times measured in shock tubes (1160 data points in 114 data series) and rapid compression machines (83/5); concentration profile measurements in flow reactors (649/59) and jet-stirred reactors (1586/157) and laminar burning velocities (882/59). Mechanism AramcoMech 2.0 [1] was chosen as the initial mechanism for the development based on its overall satisfying performance in simulating the experiments. Since the size of the AramcoMech 2.0 mechanism (493 species and 2716 reactions) makes it unfeasible for parameter optimization against such large amount of experimental data, we reduced it using the simulation error minimization (SEM) method [2]. The reduced mechanism with only 75 species and 612 reactions could reproduce the simulation results of the full mechanism accurately. A novel active parameter selection method [3] based on the principal component analysis of sensitivity matrices scaled by the uncertainties of parameters and the uncertainty of the experimental data was used to identify the important reaction groups on ethylene combustion. The Arrhenius parameters of the reaction groups were optimized using the Optima++ code [4–6]. We inserted the optimized parameters into the original AramcoMech 2.0 mechanism. The performance of the optimized mechanism was compared with those of 14 published mechanisms based on the collected experimental data. The optimized mechanism was found to exhibit improved accuracy compared to the others.

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*Corresponding author: tamas.turanyi@ttk.elte.hu

Comprehensive Kinetics on the C_7H_7 Potential Energy Surface

Carles Martí[1], Hope A. Michelsen[2], Habib N. Najm[1], and Judit Zádor[1*]
[1]Combustion Research Facility, Sandia National Laboratories, Livermore, California 94550, United States.
[2]Department of Mechanical Engineering, University of Colorado Boulder, Boulder, Colorado 80309, United States.

Keywords:
Benzyl, Vinylcyclopentadienyl, Tropyl, Resonance-stabilized radicals, Automation, KinBot, Potential Energy Surface, Master equation, Temperature and pressure dependent rate coefficient.

The study of the reactivity of hydrocarbon radicals has attracted significant interest in the history of gas-phase physical chemistry. Their kinetics, however, is very complex, and is not completely understood, even for relatively small systems, playing a role for instance during the first aromatic ring formation. This is caused by the enormous complexity of the underlying potential energy surfaces (PESs) that govern their reactivity, traditionally hindering our ability to deal with them in a comprehensive and systematic manner. Species with mass 91 (C_7H_7) have been observed in flames, pyrolysis systems, and the interstellar medium. However, their isomeric identities are still debated due to contradictory experimental findings. At the same time, the chemistry of C_7H_7, with several different resonantly stabilized radicals (RSRs), has been postulated to play a crucial role in particle-inception processes.

Thanks to the increase of the available computational power and the algorithmic developments in quantum chemistry codes, automated and systematic treatment of chemical kinetics is now possible. In this work, we used KinBot (https://github.com/zadorlab/KinBot) to explore and characterize the portion of the C_7H_7 PES that is relevant for combustion using an automated and systematic approach. The exploration was carried out by first performing a complete characterization of the lower-energy region (which includes key species, like vinylcyclopentadienyl, tropyl and benzyl or bimolecular products, such as fulvenallene + H and cyclopentadienyl + acetylene), which was then expanded to include two higher-energy entry points, vinylpropargyl + acetylene and vinylacetylene + propargyl. Notably, our automated search allowed to identify, in a single study, all literature reactions published in previous work. Additionally, three new important routes were discovered: a lower-energy pathway connecting benzyl with vinylcyclopentadienyl, a decomposition mechanism from benzyl that results in side-chain hydrogen atom loss to produce fulvenallene + H, and shorter and lower energy routes to the dimethylene-cyclopentenyl intermediates.

Moreover, a method to systematically trim the PES to a chemically relevant domain was developed, leading to a PES composed of 63 wells, 10 bimolecular products, 87 barriers, and 1 barrierless channel. A master equation of the C_7H_7 was constructed using the CCSD(T)-F12a/cc-pVTZ//ωB97X-D/6-311++G(d,p) level of theory to provide rate coefficients for chemical modeling. Our calculated rate coefficients show excellent agreement with measured ones. We also simulated concentration profiles and calculated branching fractions from the important entry points to provide an interpretation of this important chemical landscape.

*Corresponding author: jzador@sandia.gov

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*Corresponding author: jzador@sandia.gov

Automation of rate constant evaluation for barrierless reactions: status and challenges

Andrea Della Libera and Carlo Cavallotti*
Dept. Chemistry, Materials, and Chemical Engineering, Politecnico di Milano
Piazza Leonardo da Vinci, 32, Milano, Italy

Keywords:

Barrierless reactions, VRC-TST, variational transition state theory, ab initio

The theoretical determination of rate constants of gas phase chemical reactions from first principles has progressed greatly in the last years. In particular, the accuracy of the predictions performed using the ab initio transition state theory-based master equation (AITSTME) approach has become comparable to that of experiments, as long as calculations are performed at an adequate level of theory. In order to decrease the human time necessary to perform AITSTME calculations, considerable effort has been recently placed in the development of software that can automate the whole computational process, thus opening the way to the automatized exploration of potential energy surfaces (PES) and the automatic construction of chemical mechanisms [1].

Despite the significant progress in the field, the automation of rate constant estimation for the barrierless reaction class remains particularly complex. This is an important reaction class that includes bond scission reactions, as well barrierless abstraction and addition reactions. The reason is that the theoretical determination of reaction rates for this reaction class is complicated by two challenging aspects. The first is that the PESs over which barrierless reactions take place have a distinct multireference nature, which means that it is not possible to use black box quantum chemistry theoretical methods to determine energies and Hessians. Secondly, the Rigid Rotor Harmonic Oscillator approach is unsuitable to compute the density of states along the reaction coordinate, as the large amplitude motions that are active at the transition state are highly anharmonic.

Here, we describe the progress we recently made in the automation of rate constant calculation for barrierless reactions. The proposed methodology consists in the determination of the minimum energy path (MEP) for a chosen bond breaking process, followed by the evaluation of PES and Hessians. Rate constants are then computed using either Variational Transition State Theory (VTST) or, at a higher level, Variable Reaction Coordinate Transition State Theory (VRC-TST). Several strategies are developed and tested in order to automate efficiently the necessary multireference calculations along the MEP, as well as for determining correction terms for geometry relaxation and energy refinement required by VRC-TST. The developed algorithms have been implemented in EStokTP [2], am open source code whose purpose is the automatic evaluation of rate constants through the AITSTME approach, and used to estimate the recombination rate constants of a large set of test reactions. Several examples of the application of this approach will be given, highlighting both the remaining challenges as well as the perspectives for its further development.

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*Corresponding author: carlo.cavallotti@polimi.it

Catalyst Screening for Partial Oxidation of Methane with the Blowers-Masel Approximation

Chao Xu[1], Richard West[1,*]
[1] Department of Chemical Engineering, Northeastern University, Boston, U.S.

Keywords

catalyst screening, micro-kinetic modeling, catalytic partial oxidation of methane

Mean-field microkinetic modeling (MKM) is an effective tool for investigating reaction mechanisms in heterogeneous catalysis and can be used to screen for catalysts, account for coverage effects, or fit computational results to experimental data. To accurately represent thermo-chemistry and kinetics in the mentioned cases, it is essential to adjust the energy of species and modify the activation energy of reactions accordingly. One way to accomplish this is through the Blowers-Masel (BM) approximation, which scales the activation energy based on the enthalpy change of a reaction. Unlike the Bell-Evans-Polanyi (BEP) expression which requires 2 parameters, the BM approximation requires only one parameter, the intrinsic activation energy, to estimate the activation energy in three enthalpy ranges. We have incorporated this new rate expression into Cantera, an open-source software for simulating kinetic and thermodynamic processes.

This study focuses on utilizing the BM approximation to model the catalytic partial oxidation of methane (CPOM) over a series of hypothetical metal surfaces. We generated 81 CPOM mechanisms on various metal catalysts using the Reaction Mechanism Generator (RMG) based on linear scaling relations, which were then merged into a single mechanism to encompass all reaction pathways. Using BM rate parameters, the CPOM mechanism was simulated in 81 plug flow reactors (PFRs) with different hypothetical metallic catalysts in Cantera. We utilized Density Functional Theory (DFT) data from literature to discuss the validity of the BM approximation. The BM-adjusted reaction barrier was employed to analyze the energy diagram of the primary reaction path. Species concentration profiles and reaction kinetic sensitivity analysis results were minimally affected by the addition of the BM approximation. In contrast, the BM approximation had a significant impact on species thermo-sensitivity, and "volcano surface" plots of thermo-sensitivity with and without the BM approximation revealed differing active regions, resulting in different conclusions when screening for catalysts. Furthermore, another research group has made a recent advancement that enables Cantera to determine species enthalpy based on coverage. This has allowed for the coupling of the Blowers-Masel (BM) approximation with coverage-dependent thermodynamics to modify reaction barriers in reactor simulations. As a result, this work explores the feasibility of swiftly estimating coverage effects using MKM.

*Corresponding author: r.west@northeastern.edu

Advantage and Disadvantage of Hydrogen Transfer to the Stability of Energetic Compounds

Chaoyang Zhang*, Ying Xiong, Jing Huang
Institute of Chemical Materils, China Acadamy of Engineering Physics, Mianyang Sichuan, P. R. China 621999

Keywords

Hydrogen transfer, thermal stability, impact sensitivity, energetic compounds.

Hydrogen is the smallest and lightest atom, and facilitates to form hydrogen bond (HB) to influence micro-structures and be transferred to affect response degree against external stimuli. That is, HB and H transfer are intrinsic factors determining sensitivity of energetic compounds. This representation summaries the advantage and disadvantage of hydrogen transfer to the stability of energetic compounds as follows: (1) By hydrogen transfer, the ionization and separation of unstable molecules can significantly increase thermal stability thereof. (2) The protonation proceeds by a H^+ transfer from a NH_3OH^+ to its neighboring one, and subsequently decompose NH_3OH^+ to the final stable products of NH_3 and H_2O simultaneously to collapse the crystal lattice of dihydroxylammonium-5,5′-bistetrazole-1,1′-diolate (TKX-50), responsible the relatively low thermal stability of NH_3OH^+based salts to other ones. (3) In some cases, reversible hydrogen transfer can occur and serve as a chemical buffer against external stimuli. It implies a completely novel impact sensitivity mechanism for energetic materials, i.e., the external impact energy can partly be converted into the chemical energy stored firstly (when heating to approaching ignition) and dissipated by the chemical energy release subsequently (when cooling), which contributes to low impact sensitivity.

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*Corresponding author: chaoyangzhang@caep.cn

Theoretical rate coefficients for tert-butyl hydroperoxide decomposition

Cheng Xie[1], Yunrui He[3], Lili Xing[3] and Zhandong Wang[1,2,*]
[1] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China
[2] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
[3] Energy and Power Engineering Institute, Henan University of Science and Technology, Luoyang, Henan 471003, China

Abstract: In the low-temperature oxidation process, due to the fragile bond energy between the O-O bonds, the O-OH is easily decomposed into an oxygen-containing radical and a hydroxyl group, and the latter is a key initiator in the low-temperature oxidation process. Therefore, exploring the dissociation rate of O-OH bonds is a key step in refining the low-temperature oxidation kinetic model. In this work, the barrierless reaction of $IC_4H_9OOH \rightarrow IC_4H_9O + OH$ is studied theoretically. The complete active space self-consistent field theory with second order perturbation (CASPT2) method combined with cc-pVDZ basis set was adopt to optimize, and variable reaction coordinate transition state theory (V-TST) was used to compute the temperature- and pressure-dependence of the rate coefficients. Finally, this work proposed a reliable rate constant for t-butyl hydroperoxide decomposition, which could be used in further study in hydrocarbon oxidation.

Keywords: t-butyl hydroperoxide; rate constant; hydroperoxide, pyrolysis, ignition

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[*] Corresponding author: E-mail: zhdwang@ustc.edu.cn (Z. Wang)

Bayesian inference of combustion kinetics models via neural network accelerated Hamiltonian Monte Carlo

Chengcheng Liu[1,2], Yiru Wang[1,2], Keli Lin[1,2], Chenyue Tao[1,2], Bin Yang[1,2, *]
[1] Tsinghua University, Center for Combustion Energy and Department of Energy and Power Engineering, 30 Shuangqing Road, Beijing, P. R. China
[2] Tsinghua University, Key Laboratory for Thermal Science and Power Engineering of MOE, 30 Shuangqing Road, Beijing, P. R. China

Keywords

Uncertainty quantification, Bayesian inference, Hamiltonian Monte Carlo, Artificial neural networks, Ammonia.

The predictive ability of the combustion kinetics models needs to be improved by constraining the parameter uncertainty through inverse uncertainty quantification (UQ) (Yang, 2021). Bayesian inference provides a probabilistic perspective for implementing inverse UQ with informative experimental data. However, as the workhorse of Bayesian methods, the Markov Chain Monte Carlo (MCMC) method exploits the Metropolis-Hastings algorithm to explore the parameter space. The random walk property leads to a low acceptance rate of proposed parameters and consequent high computational cost. A Bayesian inference method with a high acceptance rate is necessary for high-dimensional tasks. This work proposes the artificial neural network-based Hamiltonian Monte Carlo (ANN-HMC) method. HMC is a dynamics-based MCMC method that utilizes Hamiltonian dynamics to avoid random walk behavior (Neal, 2011). The high acceptance probability allows more efficient exploration of the high posterior density region. But the increased efficiency comes at a price. HMC requires onerously computing the first-order log-posterior gradient to guide the exploration direction, which limits its application to optimizing combustion kinetics models. The ANN in the ANN-HMC method serves as surrogate models of the targets, such as ignition delay time, and provides first-order log-posterior gradient via backpropagation. The proposed ANN-HMC is demonstrated in an ammonia auto-ignition combustion system. A total of 118 screened experimental measurements were used to optimize all 275 pre-exponential factors in the ammonia kinetics model. The results show that ANN-HMC can effectively reduce the uncertainty of the parameters and constrain the model predictions within the uncertainty band of the experimental measurements. Compared with ANN-MCMC, the efficiency of generating samples in the Markov chain is increased by 184 times. ANN-HMC provides an option for complex combustion kinetics model optimization.

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*Corresponding author: byang@tsinghua.edu.cn

CHEMICAL KINETIC MODEL STUDY ON AMMONIA AND AMMONIA/HYDROGEN COMBUSTION

Chenyue Tao[1,2], Yiru Wang[1,2], Lanxiong Liao[1,2] and Bin Yang[1,*]
[1] Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China
[2] Key Laboratory for Thermal Science and Power Engineering of MOE, International Joint Laboratory on Low Carbon Clean Energy Innovation, Tsinghua University, Beijing 100084, China

Keywords

Ammonia, Combustion reaction, Sensitivity analysis, Model optimization, Sensitivity entropy

Ammonia, as a zero-carbon fuel, has broad application prospects. In order to make better use of ammonia and improve the shortcomings of ammonia itself, it is necessary to conduct in-depth research on the combustion characteristics of ammonia. The combustion reaction kinetics model can describe the whole process of combustion reaction in detail and make predictions. At present, the combustion reaction kinetics model of ammonia still has a lot of room for development, and the performance of existing models in terms of prediction accuracy and uncertainty needs to be improved. Therefore, it is crucial to develop the combustion reaction kinetics model of ammonia.

This research is devoted to the development of the combustion reaction kinetics model of ammonia. This study is based on the existing kinetics model of ammonia in the combustion system of ammonia and hydrogen (Zhang et al., 2021). Through sensitivity analysis and other means, this study reveals the essential reasons for the similarities and differences in the model prediction results under different experimental conditions. Further, this study adopts the method of surrogate model similarity analysis to explain the reasons for the variation of the similarity coefficient under different experimental conditions, and based on the results of the similarity analysis, an experimental dataset with a reduced number of groups and a wide range of experimental conditions for model optimization is selected. With experimental data, the MCMC algorithm (Wang et al., 2019) is used to carry out model optimization, and some input parameters in the model are adjusted to improve the model. The effect of the model optimization is verified under a wide range of experimental conditions. Finally, based on the results of sensitivity entropy analysis (Li et al., 2016), this study provides guidance for the selection of operating conditions when conducting experiments.

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*Corresponding author: byang@tsinghua.edu.cn

A comprehensive chemical kinetic modeling study of ammonia and ammonia/hydrogen combustion

Yuxiang Zhu[1], Henry J. Curran[2], Chong-Wen Zhou[*1,2]
[1]School of Energy and Power Engineering, Beihang University, Beijing 102206, China
[2]Combustion Chemistry Centre, School of Biological and Chemical Sciences, University of Galway, Galway H91TK33, Ireland

Keywords: Ammonia, hydrogen, ignition delay time, flame speed, speciation

In order to boost the practical applications of ammonia and ammonia/hydrogen as combustion fuels in generating cleaner power without CO_2 emissions, it is necessary to understand the combustion chemistry of ammonia and ammonia/hydrogen. A number of fundamental combustion experiments have been carried out under wide range of thermodynamic conditions, however, the current models cannot capture the combustion properties of the fuels under all these conditions. Discovering the chemistry in governing fuel reactivity and controlling the formations of NO_x, under different conditions, can be clearly elucidated. In this work, a sophisticated detailed ammonia combustion kinetic model has been developed and comprehensively validated by using the available experimental data under broad range of conditions in the literature. The model is able to capture the combustion properties of ammonia and ammonia/hydrogen under most conditions quite well. The key reactions in controlling fuel reactivity under high-temperature and low-to-intermediate temperature combustion regimes were highlighted through sensitivity analyses and reactive flux analyses. Furthermore, the effect of hydrogen in the fuel mixtures on the chemistry are discussed.

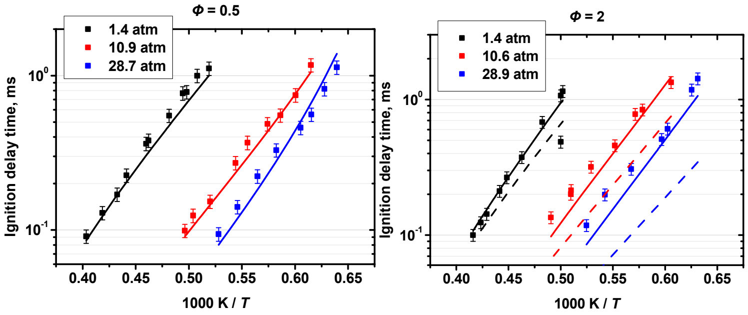

Figure 1. IDTs of $NH_3/O_2/Ar$ in a shock tube at P = 1.4, 11 and 29 atm, and Φ = 0.5, 1, 2. Symbols: experimental data from Mathieu and Petersen [1]; solid lines: this work, simulations; dashed lines: Zhang model [2], simulations. The definition of IDTs in simulations are consistent with the experiment.

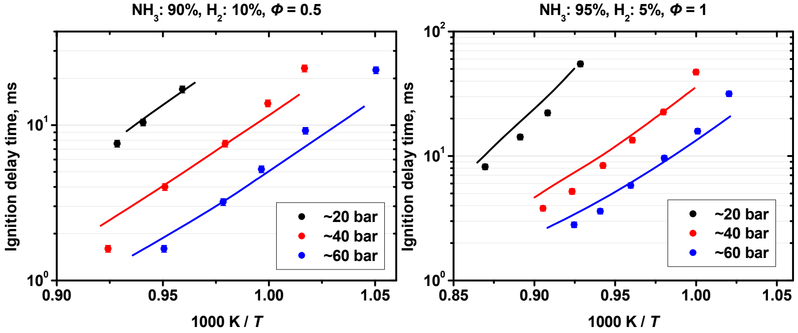

Figure 2. IDTs of $NH_3/H_2/O_2/N_2/Ar$ in a RCM with varying H_2 contents in the fuel (by mole fraction) at P = 20–70 bar and Φ = 0.5, 1, 2. Symbols: experimental data from Dai et al. [3]; lines: this work, simulations.

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*Corresponding author: e-mail address: cwzhou@buaa.edu.cn

THE REACTIVITY OF PEROXY RADICALS

Christa Fittschen*
University Lille, PhysicoChimie des Processus de Combustion et de l’Atmosphère – PC2A, UMR 8522 Université Lille – CNRS, Cité Scientifique, 59650 Villeneuve d’Ascq, France

Keywords

Peroxy radicals, atmospheric chemistry, remote environments, cw-CRDS

Peroxy radicals, RO_2, are key species in the atmosphere. They are formed from a reaction of OH radi-cals with hydrocarbons:

$$RH + OH + O_2 \rightarrow RO_2 + H_2O$$

In polluted environments, RO_2 radicals react predominantly with NO, leading to formation of NO_2, and eventually through photolysis of NO_2 to formation of O_3.

At low NOx concentrations such as in the marine boundary layer or the background troposphere, the life-time of RO_2 radicals increases and other reaction pathways such as self- and cross reaction with other RO_2 or with HO_2 radicals become competitive. To study these reactions, UV absorption spectroscopy has been employed in the past: this technique gives good sensitivity for peroxy radicals, but poor selectiv-ity as these radicals have broad absorption features in the UV. We have established a technique allowing to follow peroxy radicals with a better selectivity compared to UV, but with still good sensitivity by cou-pling laser photolysis to cw-Cavity Ring Down Spectroscopy in the near IR [1].

Here, we will present some recent results on measurements of rate constants and branching ratios of the self-reaction of selected peroxy radicals (Assali and Fittschen, 2022a and 2022b, Shamas et al., 2022 . Radicals are generated by laser photolysis, and the detection of the peroxy radicals is done be cw-Cavity Ring Down Spectroscopy in the near IR (Zhang et al., 2021), a rather selective method compared to UV absorption spectroscopy.

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*Corresponding author: christa.fittschen@univ-lille.fr

Kinetics measurements of $C_2H_5O_2$ with Cl and CH_3O_2 by Cavity Ring Down Spectroscopy

Cuihong Zhang[1, 2], Chuanliang Li[3], Weijun Zhang[2], Xiaofeng Tang[2*], Laure Pillier[1], Coralie Schoemaecker[1], and Christa Fittschen[1*]

[1] PC2A UMR CNRS 8522, Université de Lille, Villeneuve d'Ascq, France
[2] Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, Anhui, China
[3] Shanxi Engineering Research Center of Precision Measurement and Online Detection Equipment and School of Applied Science, Taiyuan University of Science and Technology, Taiyuan 030024

Keywords

$C_2H_5O_2$, CH_3O_2, Cl, CRDS, kinetics,

The cross-reaction of ethyl peroxy radicals ($C_2H_5O_2$) with methyl peroxy radicals (CH_3O_2) (R1) has been studied using laser photolysis coupled to a time resolved detection of the two different peroxy radicals by continuous wave Cavity Ring Down Spectroscopy (cw-CRDS) in their $\tilde{A}$-$\tilde{X}$ electronic transition in the near-infrared region, $C_2H_5O_2$ at 7602.25 cm^{-1}, and CH_3O_2 at 7488.13 cm^{-1}. This detection scheme is not completely selective for both radicals, but it is demonstrated that it has great advantages compared to UV absorption spectroscopy. Peroxy radicals were generated from the reaction of Cl-atoms with the appropriate hydrocarbon (CH_4 and C_2H_6) in the presence of O_2, whereby Cl-atoms were generated by 351nm photolysis of Cl_2. For different reasons, all experiments were carried out under excess of $C_2H_5O_2$ over CH_3O_2. The experimental results were best reproduced with a rate constant for the cross-reaction of $k = (3.8\pm0.5) \times 10^{-13}$ cm^3s^{-1} and a yield for the radical channel of ($\phi_{1a} = 0.55\pm0.20$).

It turned out that the rapid reaction of Cl-atoms with peroxy radicals could not completely be neglected and for this reason, the reaction of Cl-atoms with $C_2H_5O_2$ has also been studied. HO_2 radicals, a reactive intermediate from this reaction, was detected via the $2\nu_1$ vibrational overtone transition at 6638.21 cm^{-1}. The rate constant for the reaction of Cl-atoms with $C_2H_5O_2$ has been obtained from fitting to a complex mechanism to $k = (7.5\pm1.0) \times 10^{-11}$ cm^3s^{-1}, with the major reaction path being the formation of the Criegee intermediate, CH_3CHO_2 ($\phi = 0.53\pm0.05$).

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christa.fittschen@univ-lille.fr, tangxf@aiofm.ac.cn

DESTRUCTION OF CH_3CN AT INTERSTELLAR TEMPERATURES (11.7-177.5 K): GAS-PHASE RATE COEFFICIENTS WITH OH RADICALS

D. González[1,2], S. Espinosa [1,2], A. Canosa [3], B. Ballesteros [1,2], J. Albaladejo [1,2] and Elena Jiménez[1,2*]
[1] Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha (UCLM), Avda. Camilo José Cela 1B, 13071 Ciudad Real, Spain.

[2] Instituto de Investigación en Química y Contaminación Atmosférica, UCLM, Camino de Moledores s/n, 13071 Ciudad Real, Spain.

[3]Institut de Physique de Rennes-CNRS-UMR 6251, Université de Rennes, F-35000 Rennes, France

Keywords

Prebiotic chemistry, gas-phase kinetics, low-temperature kinetics, bimolecular reactions

Acetonitrile (CH_3CN) is a widespread molecule in the space, which has been detected in many sources of the interstellar medium (ISM), including ultra-cold environments where temperatures are extremely low ($T \sim 10$-100 K). Its first detection was toward the Galactic Center in the molecular clouds near Sgr B2 and Sgr A (Solomon et al., 1971). Some years later, cyanomethyl radical (CH_2CN) was also observed in Sgr B2 (Irvine et al. 1988). As hydroxyl (OH) radicals are ubiquitous in many interstellar sources, CH_2CN could be formed through the gas-phase OH+CH_3CN reaction:

$$OH + CH_3CN \rightarrow H_2O + CH_2CN \qquad \text{(Reaction 1)}$$

In addition, it is important to characterize the destruction routes of CH_3CN because it is believed to be a link in the chain of chemical processes leading to formation of amino acids (Danger et al., 2011). Regarding the kinetics of Reaction 1, there are experimental studies performed from 250 K and up to 424 K, which show an increase of the rate coefficient, $k_1(T)$, when temperature increases. According to these data, it is reasonable to think that the titled reaction should be slow and not significant at the ultra-low temperatures of the ISM. However, we have explored the 11.7-177.5 K temperature range thanks to a pulsed CRESU (French acronym for *Reaction Kinetics in a Uniform Supersonic Flow*) apparatus together with laser techniques (Jiménez et al., 2015), and we can confirm that below 200 K, $k_1(T)$ increases when decreasing temperature, radically breaking the Arrhenius tendency.

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*Corresponding author: elena.jimenez@uclm.es

Origin of PrebioTIc Molecules in the InterStellar Medium (OPTIMISM): Modeling Interstellar Chemistry in AI Era

Donghui Quan[1,*], Xia Zhang[2], Guoming Zhao[1], Yisheng Qiu[1], Yang Lu[1], Yan Zhou[1], Longfei Chen[1], Rong Ma[2], and Fangfang Li[2]
[1] Zhejiang Laboratory, Kechuang Avenue, Hangzhou, 311121, China
[2] Xinjiang Astronomical Observatory, 150 Science-1 Street, Urumqi, China

Keywords

Interstellar Chemistry, modeling, intelligent computing.

So far, approximately 300 molecules have been identified in the interstellar medium and circumstellar shells, which are commonly referred to as interstellar molecules (Müller et al., 2023). Interestingly, over one-third of these molecules are complex organic molecules (COMs), revealing rich chemistry in various astronomical sources. Moreover, certain interstellar molecules, particularly organic ones, serve as precursors for biological molecules such as amino acids and nucleosides, sparking the fascination of astrochemists. These molecules are known as prebiotic molecules in the interstellar medium, and are mostly detected in star-forming complexes, as well as in quiescent clouds with nearby shocks.

Our research project, entitled the Origin of Prebiotic Molecules in the Interstellar Medium (OPTIMISM), employs computer-assisted modeling using chemical kinetics rate equations. In this talk, we focus on hydroxylamine (NH_2OH), cyanamide (NH_2CN), and carbodiimide (HNCNH) isomers - all recognized as precursors of amino acids or nucleosides. Our models offer an insight into the physical environments and associated chemical/physical processes of these species and related molecules. We identify the primary formation and destruction reactions, as well as the optimal physical conditions for detecting these molecules and related ones. In light of the rapidly advancing field of intelligent computing, we also explore the potential for AI to aid in OPTIMISM studies.

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*Corresponding author: donghui.quan@zhejianglab.com

Developing the new-generation forcefield for solid propellants

Qingzhao Chu[1], Xiaoya Chang[1], Mingjie Wen[1] and Dongping Chen[1,*]
[1] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology,
Beijing, 100081, China.

Abstract :
Atomistic simulation provides a deep understanding of microscopic physical and chemical mechanisms and serves as an important tool for studying complex combustion processes. The core of atomistic simulation lies in the development of reactive forcefield. However, the existing force fields can only describe partial components of practical systems, i.e. propellants, and are not suitable for simulating the combustion process of real propellant formulations. To address this issue, we have developed a set of new forcefield based on the scheme of Deep Potential. The key components of propellants such as metal fuel (aluminum), AP, binders (HTPB, PVDF), and high-energy explosives (RDX, HMX, CL-20) are considered in the development of the forcefield. This forcefield is trained against a dataset obtained from first-principles calculations, providing a basis for its good accuarcy. Extensive tests and validations have been conducted for the energy, forces, equations of state, mechanical properties, and thermal decomposition of several key components. The results show that the forcefield not only maintains the accuracy of first-principles calculations but also exhibits high computational efficiency, offering a promising theoretical basis for the development of real propellant formulations. The preliminary applications of the new forcefield in the gaseous reaction kinetics are illustrated in the examples of soot inception and the decomposition of flurinated species. A nanoreactor scheme is designed to enhance the sampling in the potential reaction kientics.

Keywords

Molecular modeling, forcefield development, soot inception, gaseous decomposition

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*Corresponding author: dc516@bit.edu.cn

AUTOMATED REACTION MECHANISM DISCOVERY AND (SEMI) AUTOMATED KINETICS

Emilio Martínez-Núñez[1,*]
[1]Department of Physical Chemistry, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

Keywords

AutoMeKin, Chemical Reaction Networks, Molecular Dynamics, Graph Theory, Kinetic Monte Carlo.

A computational protocol is proposed in this talk for use in discovering reaction mechanisms. The method does not rely on either chemical intuition or assumed a priori mechanisms, working in a fully automated fashion.

The pipeline consists of three steps:
1. Exploration of reaction mechanisms through Molecular Dynamics simulations or chemical knowledge-based algorithms.
2. Use of Graph Theory to build the reaction network.
3. Kinetics simulations.

The method has been successfully employed to study combustion chemistry, cycloaddition reactions, photodissociations, organometallic catalysis, radiation damage of biological systems, simulation of mass spectrometry experiments, and astrochemistry, and a few examples will be given in this talk.

This methodology has been implemented in the open-source program AutoMeKin (Martínez-Núñez et al., 2021).

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*Corresponding author: emilio.nunez@usc.es

Reaction Mechanism, Regioselectivity and Substrate Specificity of Achmatowicz Rearrangement Catalyzed by Chloroperoxidase

Fuqiang Chen[1], Xiang Sheng[1]*
[1] Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Keywords

Achmatowicz rearrangement, Chloroperoxidase, Reaction mechanism, Quantum chemistry.

Achmatowicz rearrangement [Achmatowicz et al., 1971] is a type of reaction that converts renewable biomass resources such as furfural into pyrans and pyridines. The products are important chemical intermediates and have a wide range of applications in the field of organic synthesis. Chloroperoxidase (CPO) is a heme-dependent enzyme that can completely retain the stereoconfiguration of the substrate. Interestingly, the enzyme can catalyze the achmatowicz rearrangement of *rac*-1-(2-furyl)ethanol, but is inactive on some structurally similar compounds, such as 5-substituted furylketones and 1-(2-Furyl)-2-propyn-1-ol [Thiel et al., 2014]. In addition, the reaction mechanism of CPO-catalyzed achmatowicz rearrangement is unclear, which hinders the further application of CPO. In the present study, we use quantum chemical calculations and molecular dynamics simulations to investigate the mechanism, regioselectivity, and substrate specificity of CPO reaction. The results of quantum chemical calculations show that the reaction starts with the formation of an epoxide intermediate, which is followed by the ring-opening rearrangement of the epoxide to form the product. The process of generating epoxide intermediate is the selectivity-determining step, and the regioselectivity is rationalized by the steric hindrance between the active site residues and the substrate, and also the stability of the forming radical on the substrate. In addition, molecular dynamics results show that the reason for the inability of CPO in catalyzing 5-substituted furylketones and 1-(2-Furyl)-2-propyn-1-ol is that the residues located in the binding channel prevent the substrate entering the active site. This study lays a theoretical foundation for the rational design of CPO.

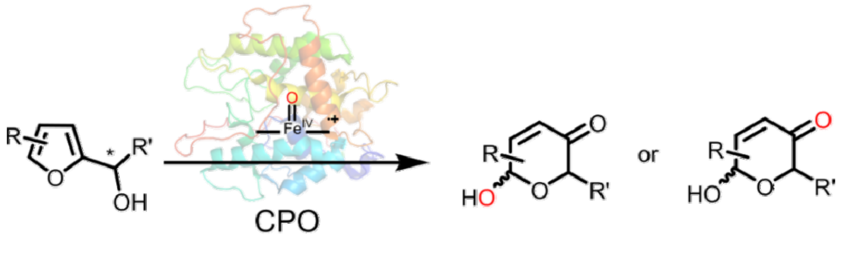

Figure. *The CPO-catalyzed biological Achmatowicz rearrangement.*

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*Corresponding author: shengx@tib.cas.cn

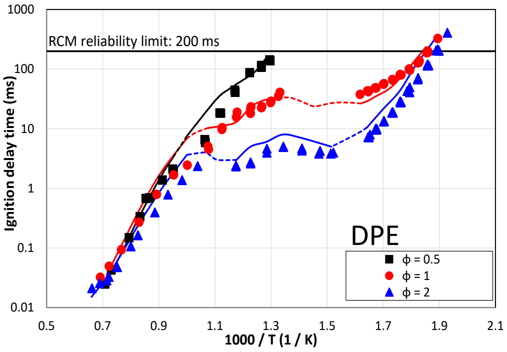
EXPERIMENTAL AND MODELING STUDY ON THE IGNITION DELAY TIMES OF DI-*N*-PROPYL AND DI-*ISO*-PROPYL ETHERS IN DILUTED MIXTURES

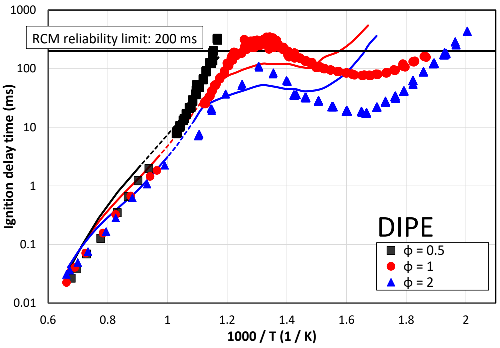
Giorgia Cenedese[1], Ahmed Mohamed[3], Zeynep Serinyel [1,*], Fabrice Foucher[2], Guillaume Dayma[1], Henry Curran[3]
[1] Université d'Orléans, CNRS–ICARE, 1C av. de la Recherche Scientifique, 45071 Orléans, France
[2] Université d'Orléans, PRISME, 8 rue Léonard de Vinci, 45072 Orléans, France
[3] Combustion Chemistry Centre, School of Biological and Chemical Sciences, Ryan Institute, MaREI, University of Galway, Galway, Ireland

Keywords

di-n-propyl ether, di-iso-propyl ether, ignition delay times, rapid compression machine, shock tube, kinetic modeling

Oxygenated compounds, like ethers, have been considered very interesting for different applications. This study aims to study the auto-ignition behavior of two propyl ether isomers, di-*n*-propyl (DPE) and di-*iso*-propyl (DIPE) ether, through the measurements of ignition delay times (IDTs). Besides the interest given by the possible application as biofuels, this study on the global reactivities of these two molecules allows for a deeper insight on the combustion behavior of these two ethers from a fundamental point of view. These two fuels have already been studied in a jet-stirred reactor by our team (Serinyel et al. 2020; 2021; 2022) reporting detailed speciation and the present study targets the global reactivity. The kinetic mechanism previously developed is tested against the present data. Three set-ups have been used: two rapid compression machines (at Orléans and Galway) and a high-pressure shock tube (Galway). These allowed to cover a wide temperature range (500–1510 K) at 15 bar. Three equivalence ratios (0.5, 1.0 and 2.0) were tested for both fuels, but with different dilution due to the different reactivities. A fuel-rich mixture with the same dilution for the two isomers was also tested, in order to have a direct comparison. At intermediate temperatures (600–770 K) DIPE shows a marked negative temperature coefficient regime at $\varphi = 1$ and 2, while this is also true for DPE at $\varphi = 2$. At high temperatures (> 1100 K), a typical trend is observed where the IDTs measured at all equivalence ratios overlap for both fuels. The previously developed model was tested against the experimental data, showing a reasonable agreement for DPE, while there is still room for improvement for DIPE, especially at low and intermediate temperatures.





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*Corresponding author: zeynep.serinyel@cnrs-orleans.fr

ON THE IMPACT OF THE O-ATOM ON THE IGNITION OF A 5-MEMBERED RING: A COMPARATIVE STUDY BETWEEN CYCLOPENTANE AND TETRAHYDROFURAN

H.- Q. Do[1, 2], B. Lefort[2], L. LeMoyne[2], Z. Serinyel[1, 3], G. Dayma[1, 3, *]

[1] Université d'Orléans, 6 avenue du Parc Floral, 45100 Orléans, France
[2] DRIVE, EA1859, Université de Bourgogne-Franche Comté, 49 rue Mademoiselle Bourgeois, 58000 Nevers, France
[3] CNRS, Institut de Combustion, Aérothermique, Réactivité et Environnement, 1C avenue de la recherche scientifique, 45071 Orléans cedex 2, France

Keywords

cyclopentane, tetrahydrofuran, shock tube, ignition delay times, kinetic mechanism

Cyclopentane (CPT) is one of the simplest cycloalkanes with five membered carbon ring, which has high-octane and knock-resistant characteristics, and it is commonly found in commercial gasoline. Tetrahydrofuran (THF) is a saturated cyclic ether compound, and has been shown to be as a promising bio-fuel for internal combustion engines. The molecular structure of CPT and THF is similar excluding the oxygen heteroatom in THF ring which induces lower bond dissociation energies of the C-H bonds on the α-sites, but higher BEDs on the β-sites. This work aims at comparing the auto-ignition delay times of CPT and THF measured in shock tube, and explain the differences and similarities observed with the help of a unique detailed kinetic mechanism. The ignition delay times have been measured in a high-pressure shock tube over a wide temperature range for various mixture compositions. The kinetic model used in the simulations was developed by introducing a sub-mechanism for CPT from Lokhachari et al. (2021) into the THF mechanism from Fenard et al. (2018). The present mechanism contains 1322 species and 6709 reactions. It was observed that despite differences in terms of bond dissociation energies, CPT and THF have very similar ignition delay times at the same equivalence ratio. However, when X_{Fuel}/X_{O2} is kept constant, it turns out that a discrepancy appears between CPT and THF when the mole fraction of O_2 decreases, CPT becoming longer than THF to ignite. This observation indicates that CPT is more sensitive to the O_2 content than THF.

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*Corresponding author: guillaume.dayma@univ-orleans.fr

Homogeneous Catalytic Effect of Water on Formic Acid Decomposition:

Implication for Kinetic Modeling in Supercritical Water

Guoxing Li[1,*], Hao Chen[1] and Peter Glarborg[2]
[1] School of Energy and Electrical Engineering, Chang'an University, Shangyuan Road, Xi'an, 710018, P. R. China
[2] Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark

Keywords

Water catalysis; Formic acid; Decomposition; Kinetic modeling; Supercritical water

Formic acid is attracting increasing attention as a promising liquid material for chemical storage of hydrogen. This work presents a kinetic modeling study of formic acid decomposition in both gas phase and supercritical water (SCW), with emphasis on the catalytic effect of water. For gas-phase conditions, the Machado model was proved to show satisfactory performance for the experimental data from literature. Possible uncertainties of gas-phase experiments were carefully assessed to reconcile the discrepancies between modeling results and data. With consideration of water catalysis, a kinetic model that could reproduce well the limited data at SCW conditions was further developed. Based on the models, the differences of characteristics of formic acid decomposition under the two conditions were comparatively explored. The dehydration reaction was predominant for formic acid decomposition in gas phase, but the decarboxylation reaction became the preferred reaction path in SCW. Water catalysis lowered the onset temperature for formic acid decomposition and accelerated the reaction rate. Finally, the catalytic mechanism of water was elucidated in detail. The findings of present study provide an in-depth insight into the catalytic effect of water on chemical reactions and facilitate the use of formic acid for hydrogen storage.

(I prefer to make an Oral Presentation in the conference)

*Guoxing Li: liguoxing@chd.edu.cn

Neural-network-based molecular dynamics study on the initial pyrolysis mechanism of Spiro-Norbornanes

Hang Xiao[1], and Bin Yang[1,*]
[1] Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, P R China

Keywords

Molecular dynamics, Neural network potential energy surface, Pyrolysis, Spiro-Norbornanes, Aviation fuel

This work investigates the initial pyrolysis process of two Spiro-Norbornanes compound fuel molecules Spiro[bicyclo[2.2.1]heptane-2,1'-cyclopropane] (**1**) and Spiro[cyclopropane-1,6'-tricyclo[3.2.1.0^{2,4}]octane] (**2**) which are reported to be the potential aviation fuel of the future (have better or comparable fuel characteristics to JP-10). Molecular dynamics (MD) based on the neural network potential energy surface (NNPES) is applied to this work. The pyrolysis process can be roughly divided into two stages. The first stage is the decomposition process of fuel molecules, and the second stage is the intermolecular radical reactions which play an important role in the growth of the molecular weight. For the complex molecular structures of two fuel molecules, we first investigate the initial bond-breaking reactions, the reaction sites of which affect the subsequent reaction types and product distribution. For each initial reaction site, representative cleavage reaction pathways are studied to explore the principles of these reactions. Small species formed by decomposition of fuel molecules are classified. Due to the complex ring structures of fuel molecules, the content of olefins and alkynes in the pyrolysis product is relatively high. Besides, a large number of resonantly stable radical structures is observed during pyrolysis, which may contribute to the formation of the monoaromatic hydrocarbons (MAH) and polyaromatic hydrocarbons (PAH). This work reveals the decomposition pathways and the pool of pyrolysis products unique to polycyclic hydrocarbons and provides a promising direction for future research on the pyrolysis and combustion process of complex polycyclic fuels.

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*Corresponding author: anopaul@qq.com

Understanding of Real-Fluid Behavior in Supercritical Combustion Theory

Hao Zhao*
Peking University, College of Engineering, No. 5 Yiheyuan Road, Beijing, P. R. China

Keywords: Supercritical combustion, Jet stirred reactor, Virial equation of state, Real-fluid behavior

Supercritical combustion gains an increasing potential in advanced air-breathing engines and rockets due to its high combustion efficiency, ultra-lean flammability, and low emissions. However, it owns very different combustion characteristics and chemistry kinetics from subcritical combustion. Especially, its combustion chemistry study has key challenges, such as very few ultra-pressure experimental data, low simulation predictabilities, and complicated kinetic mechanisms. This talk brings some insights of supercritical combustion kinetics in ultra-high pressure experiments at 100 bar by employing a supercritical-pressure jet stirred reactor and in statistics computations by employing Virial equation of state. It assists to understand distinct low and intermediate temperature chemistry of alkanes, non-equilibrium collisional behaviors, and the pressure-dependent negative temperature coefficient in supercritical combustion kinetics. The real-fluid impact on the high-pressure thermodynamics and transport process is also discussed.

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*Corresponding author: h.zhao@pku.edu.cn

Synchrotron photoionization mass spectrometry study of plasma-assisted low-temperature oxidation of *n*-alkanes

Haodong Chen[1], Zhongkai Liu[1], Zhaoying Li[1], Feng Zhang[2], Jiuzhong Yang[3], and Bin Yang[1,*]
[1] Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing, 100084, P. R. China
[2] Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, 230029, P.R. China
[3] National Synchrotron Radiation Laboratory of China, University of Science and Technology of China, Hefei, 230029, P.R. China

Keywords

Plasma-assisted combustion, synchrotron photoionization mass spectrometry, low-temperature oxidation, n-alkanes, kinetic modeling.

Plasma-assisted combustion and reforming are seen as promising technologies for the efficient and clean energy conversion, and the study of their kinetics is essential for the application. The present work explores the chemical kinetics of plasma-assisted low-temperature oxidation (340 K, 30 Torr) of *n*-alkanes: methane (Zhang et al., 2019), propane (Chen et al., 2022), and *n*-butane (Chen et al., 2023), using synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) and kinetic modeling. Species measurements are conducted in a flow reactor activated by a nanosecond discharge. Using SVUV-PIMS, detailed species identification and quantification are achieved in the present work, in particular, the detection of ions and oxygenated intermediate species such as cyclic ethers and alkyl hydroperoxides are reported for the first time in these reaction systems. These experimental data can be helpful for the mechanism development and pathway analysis. Kinetic mechanisms for the plasma-assisted low-temperature oxidation of methane, propane, and *n*-butane are developed, and their prediction performance is evaluated against the experimental data. Reaction pathways are analyzed based on the experimental and numerical results, and important channels are highlighted. Electron-impact dissociations are important pathways for fuel consumption and species pool formation. Reactions involving alkyl peroxy (RO_2), especially the self- and cross-reactions of RO_2, are essential for RO_2 depletion and the formation of alcohols, ketones, and aldehydes. Further theoretical and experimental research on these reaction pathways is recommended for the kinetics study.

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*Corresponding author: byang@tsinghua.edu.cn

Hierarchical Palladium Catalyst for Highly Active and Stable Water Oxidation in Acidic Media

Jing Peng,†1 Haofeng Sun,†1 Kun Ni,†1 Jiajing Wu,[1] Xinyu Sun,[1] Yueqi Su,[1] Han Cheng,[1] Yuhua Liu,[1] Yuqiao Guo,[1] Wentuan Bi,[12] Yanwu Zhu,[1] Changzheng Wu,[12]* and Yi Xie[12]

[1] Hefei National Laboratory for Physical Science at the Microscale, CAS Center for Excellence in Nanoscience, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), and CAS Key Laboratory of Mechanical Behavior and Design of Materials, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China

[2] Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui, 230026, P. R. China.

Keywords

palladium; oxygen evolution reaction; acidic condition; strain; electrolysis.

Acidic water electrolysis is of great importance for boosting the advances in renewable energy, while it suffers from sluggish oxygen evolution reaction on the anode because of the challenge to achieve electrocatalysts with both high activity and stability. Here we demonstrate a new oxygen evolution model catalyst, hierarchical palladium (Pd) that can replace and even surpass the benchmark Ir- and Ru-based materials. The Pd catalyst delivers ultralow overpotential (196 mV) and excellent durability with mitigated degradation (66 μV h^{-1}) at 10 mA cm^{-2} in 1 M $HClO_4$. Tensile strain in Pd (111) facets is ascribed to enable the inactive bulk Pd into highly active in hierarchical structure with two orders of magnitudes enhancement for intrinsic mass activity. Furthermore, the Pd catalyst with bifunctional properties renders low cell voltage of 1.771 V to achieve 2 A cm^{-2} when fabricated into polymer electrolyte membrane electrolyzer.

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*Corresponding author: e-mail address

Theoretical study of the reaction kinetics of methyl formate + NO_2

Yiran Zhang[1], Sihao Wang[2], Zhenpeng Zhang[2], Li Fu[1] and Hongbo Ning[2,*]

[1]*School of Physical Science and Technology, Southwest Jiaotong University, Chengdu, Sichuan 610031, PR China*

[2]*Key Laboratory of Advanced Technologies of Materials, Ministry of Education, Southwest Jiaotong University, Chengdu 610031, P. R. China*

Abstract: In the exhaust gas recirculation (EGR), the primary kinetic effect of nitrogen dioxide (NO_2) on low temperature auto-ignition is not only through the radical-radical reactions but also the fuel + NO_2 reactions. Therefore, it is worth studying on the fuel/NO_2 combustion chemistry for both kinetic model construction and EGR application. In this work, the potential energy curves are predicted for H-abstraction, NO_2-addition and subsequent dissociation of methyl formate (MF) + NO_2 at the CCSD(T)/CBS(T-Q)//M062X/6-311+G(2df,2p) level of theory. The corresponding pressure-dependent rate coefficients are then calculated by RRKM/ME simulations with one-dimensional hindered rotor approximation and asymmetric Eckart tunneling correction. The results reveal the dominant channels are to form *cis*-HONO + $HCOOCH_2$/$COOCH_3$ for NO_2 abstractions and the formation of *cis*-$OCH(ONO)OCH_3$ is also 10.2 kcal mol^{-1} lower than *trans*-$OCH(ONO)OCH_3$ for NO_2 additions. Moreover, the lowest energy barrier of addition channel (add-*cis*) is 14.0 kcal mol^{-1} larger than the abstraction one (abs-*cis*). It indicates that the additions cannot compete with abstractions due to their higher barrier heights. The reported reaction kinetics for MF + NO_2 in this work are useful for building the rate rules for similar methyl esters with NO_2 interaction reactions.

Keywords: Methyl formate; NO_2; Rate coefficients

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*Corresponding author: hbning@swjtu.edu.cn

Effect of Nano-curved Electric Field on Nanoelectrocatalysis

Huijun Jiang
Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, 96 Jinzhai Road, Hefei, P. R. China

Keywords

Nano-curved electric field, Nanoelectrocatalysis, Mass transfer.

As the size of nanocatalysts is comparable to the thickness of electrical double layer, electric field is actually nano-curved near the electrode surface. As a result, the nano-curved electric field (NEF) would induce mass transfer along directions paralleling to the electrode surface, leading to catalytic performance differs from that predicted by conventional theories for catalysts at the macroscale. In this talk, I will introduce briefly our recent progresses on the effect of NEF on nano-electrocatalysis. We found that, the NEF induced extra mass transfer is critical for experimentally observed sharp-tip-enhanced carbon dioxide electrocatalytic reduction (Jiang et al. 2017) and roughness-enhanced high selectivity of carbon monoxide electrocatalytic reduction (Liu et al. 2021). The importance of NEF on nano-electrocatalytic reactions further inspired us to design nanocatalysts optimizing the kinetic to achieve high reaction performance (Chen et al. 2019, Chen et al. 2021). These findings highlight the importance of NEF in nano-eletrocatalysis and provide a new concept for design of nanocatalysts in future.

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*Corresponding author: e-mail address

Recent advancements in the Reaction kinetics branch of the ReSpecTh Information System

M. Kovács[1], A. Gy. Szanthoffer[1], É. Valkó[1], P. Zhang[1],
M. Papp[1], T. Nagy[2], I. Gy. Zsély*[1], T. Turányi[1]

[1] Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

[2] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Budapest, Hungary

Keywords:ReSpecTh Information System, RKD format, experimental data collection, detailed combustion kinetic mechanisms, program collection, searchable database

The ReSpecTh Information System [1] was launched in 2014 by the Institute of Chemistry, ELTE Eötvös Loránd University and the MTA-ELTE Research Group on Complex Chemical Systems. The system has three branches: REaction kinetics, SPECtroscopy, and THermodynamics [2]. These data are frequently used for simulation of complex gas-phase chemical systems and at the interpretation of gas-phase kinetic experiments.

The Reaction kinetics branch was continuously developed since 2014. The number of indirect experimental data (ignition delay times, laminar burning velocities, and concentration profiles measured in various facilities and conditions) increased from 2430 datapoints in 262 data series to 152000 datapoints in 4600 data series. Now it includes data collections for the combustion of hydrogen, carbon monoxide, methanol, ethanol, methane, ammonia, butanol and measurements in the $H_2/O_2/NOx$ and methanol/NOx systems. Between 2014 and 2022, the number of stored direct experimental measurements and theoretical rate determinations also increased from 2091 datapoints in 61 data series to 6884 datapoints in 354 data series. The collected data points were checked and encoded in ReSpecTh Kinetic Data (RKD) format [3] files. These data files are standalone xml files, thus they can also be used outside this information system.

The reaction kinetics branch offers 15 freely available computer codes (e.g. Optima++, FluxViewer++, KINALC, SEM) which can facilitate the analysis, testing, development, optimization or reduction of detailed reaction mechanisms. The mechanism collection section provides 149 published detailed combustion kinetic mechanisms.

For beginners and less advanced users, the ‘How to?’ section provides descriptions of the various tasks that can be carried out using the computer programs and experimental data published in this website. Several video tutorials were recorded which discuss e.g. the encoding of combustion experimental data and the application of computer clusters for testing combustion kinetic mechanisms.

But not only did the experimental data, mechanism and program collection evolve dynamically in the past 9 years, but the site also received a completely new user interface with modernized design and a very powerful search engine. The interconnection of the direct kinetics database with the *k-evaluation* website [4] is planned in the near future.

All information, data and computer codes are freely available for researchers and developers. The mission of our research group is to continue the development and extension of this information system in cooperation and collaboration with other researchers for the benefit of the whole research community.

*Corresponding author: istvan.zsely@ttk.elte.hu

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*Corresponding author: istvan.zsely@ttk.elte.hu

Kinetic modelling of chloroethane pyrolysis: a computational case study for chlorinated hydrocarbons

Jeroen Aerssens[1], Lander Nelis[1], Ruben Van de Vijver[1] and Kevin M. Van Geem[1,*]
[1] Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, B-9052
Ghent, Belgium

Keywords: chlorinated hydrocarbon pyrolysis, automatic kinetic modelling, computational chemistry

Recycling of polyolefinic plastic waste is a key future challenge and it is 100% clear that recycling must be improved to ensure the continued, sustainable use of thermoplastics. Several methods will contribute to plastic waste recycling, one of these will be thermochemical recycling, which involves pyrolysis of plastic waste to a liquid pyrolysis oil and subsequent steam cracking to produce virgin monomers. The main feedstock for thermochemical recycling will be mixed plastic waste, which contains a wide range of impurities. One of these is chlorinated halocarbons (Kusenberg et al., 2022), originating from trace amounts of PVC or various additives. Pyrolysis of these chlorinated components results in HCl formation and thus a corrosive reagent that will jeopardize the process equipment. A better understanding of the pyrolysis of halocarbon components in steam cracking conditions is required to accurately predict the extent of corrosive products that are formed. The present study employs an in-house automatic kinetic model generator, Genesys (Vandewiele et al., 2012), to predict the decomposition of chloroethane in a tubular reactor at temperatures ranging from 606-630 °C validated with literature data (Yildirim and Senkan, 1992).

Accurate thermodynamic and kinetic parameters are obtained via ab initio calculations on the CBS-QB3 level of theory. The use of this method has been validated for kinetic modelling for hydrocarbons with oxygen and sulfur containing functional groups and proves to be adequate for chlorinated hydrocarbons as well. However, for key kinetic parameters involving low reaction barriers or that do not possess a clear transition state structure on the CBS-QB3 level of theory, alternative methods were used to obtain accurate kinetic parameters. This includes the use of computational methods at a higher level of theory as well as VTST calculations, when classical transition state theory cannot be applied. Figure 1 shows that the generated kinetic model accurately predicts the decomposition of chloroethane, prediction of minor products such as vinylchloride and ethane is currently a work in progress.

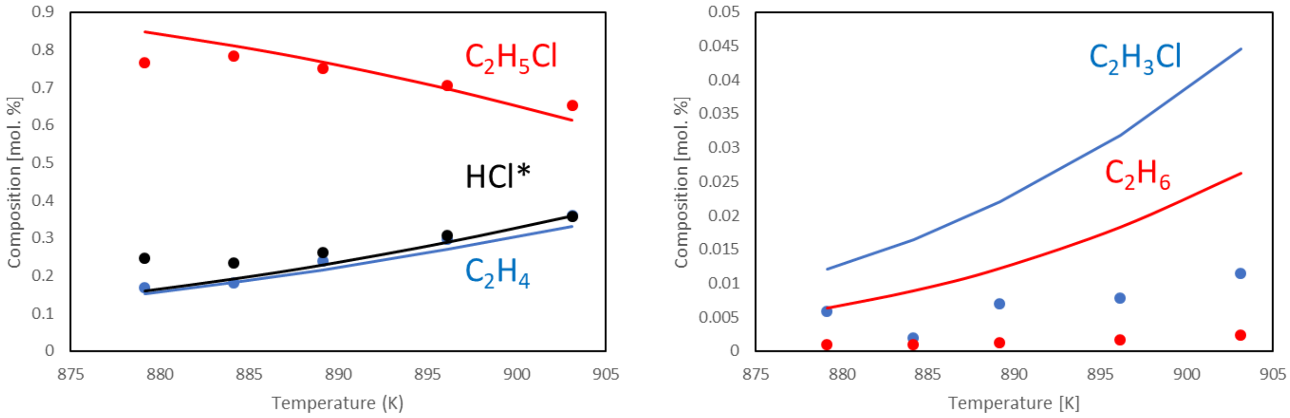

Figure 1: Experimental mole percentages (dots) and model results (lines) for the decomposition of chloroethane.

*Corresponding author: Kevin.VanGeem@UGent.be

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*Corresponding author: Kevin.VanGeem@UGent.be

A Joint Photoelectron Spectroscopic and Theoretical Study on $[HFIP_{-H} \bullet H_2O_2]^-$ and $[HFIP_{-H} \bullet HO_2]^-$ Anion Complexes

Jia Han[1], Lei Wang[1], Xiaoguo Zhou[1,*], Shilin Liu[1], Xue-Bin Wang[2,*]
[1] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China
[2] Pacific Northwest National Laboratory, Physical Sciences Division, Richland, Washington, the Unite State

Keywords

Negative ion photoelectron spectroscopy, Ion-molecule complex, Hexafluoroisopropanol, hydrogen peroxide.

The catalytic oxidation system involving hexafluoroisopropanol (HFIP) as both solvent and catalyst in conjunction with hydrogen peroxide (H_2O_2) as oxidant has garnered considerable attention in organic synthesis owing to its remarkable rate- and yield-enhancing effects on epoxidation reactions of alkenes. This study aims to present the cryogenic negative ion photoelectron spectroscopy study on model systems for the catalytic oxidation reaction medium comprising of HFIP and H_2O_2. Using an electrospray ion source, we generated the $[HFIP_{-H} \bullet H_2O_2]^-$ anion complex composed of deprotonated HFIP anion and H_2O_2 molecule. The combination of low-temperature negative ion photoelectron spectroscopy and theoretical calculations unveils a surprising prevalent existence of an energetically high-lying isomer, and reveals an influential direction-specific effect in the course of complexation, providing critical insights into the relevant catalytic reaction mechanisms and important clues for designing novel synthetic routes. Additionally, we measured and analyzed the photoelectron spectrum of $[HFIP_{-H} \bullet HO_2]^-$ anion complex formed by deprotonated HFIP anion complexed with perhydroxyl radical (HO_2). Our findings demonstrated the capability of $[HFIP_{-H} \bullet HO_2]^-$ anion complex to effectively generate an oxidant with high selectivity and reactivity, *i.e.*, singlet oxygen ($^1O_2$), upon photodetachment. Inspired by this spectroscopic study, we proposed an ideal strategy for the generation of $^1O_2$ using electron attachment and UV radiation, which shows potential applications in wastewater treatment with possibilities of achieving varying degrees of dye pollutant degradation.

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*Corresponding author: xzhou@ustc.edu.cn; xuebin.wang@pnnl.gov

Photodetachment cross sections calculation for negative ions

Jiabin Huang[1], Sai Duan[2,*] and Feng Zhang[1,*]

[1] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China
[2] Collaborative Innovation Center of Chemistry for Energy Materials, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, MOE Key Laboratory of Computational Physical Sciences, Department of Chemistry, Fudan University, Shanghai, P. R. China

Keywords: photodetachment cross sections, Dyson orbitals, negative ions

Photodetachment is a process that is widely observed and plays a critical role in astrophysical and atmospheric environments. The photodetachment cross section, which quantifies the probability of photodetachment, is a fundamental parameter for characterizing this process. Accurate determination of the photodetachment cross section is vital for interpreting spectroscopic observations, modeling astrophysical environments, and understanding chemical reactivity in the gas phase. Precise computation of transition matrix elements is necessary for an accurate determination of the photodetachment cross section, which describes electronic transitions from the initial bound state to the final continuum state of the system. In this study, we propose a computational method that utilizes plane waves to describe the outgoing electron and Dyson orbitals obtained by density functional theory methods to analytically calculate transition matrix elements. Our method is an effective approach for computing the photodetachment cross section and anisotropy parameter β of anionic species. We demonstrate the effectiveness of our method through test calculations on H^-, Li^-, C^-, O^-, F^-, H_2^-, and offers significant potential for applications in large systems.

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*Corresponding author: hjbnsrl@mail.ustc.edu.cn

AMMONIA COMBUSTION VIA THE PARTIALLY PRE-DISSOCIATION STRATEGY: A REVIEW

Jian Gao*, Hongnan Wang and Heyan Li
College of Urban Transportation and Logistics, Shenzhen Technology University,
3002 Lantian Road, Pingshan District, Shenzhen Guangdong, China, 518118

Keywords

Ammonia combustion, Ammonia dissociation, oxidation kinetics, engine combustion, NO$_x$ emission.

Ammonia is considered as a promising zero-carbon fuel in the future energy system. Low oxidation reaction activity is the bottleneck problem of combustion application of ammonia. An effective strategy to combust ammonia in spark ignition engines is to partially dissociate ammonia into ammonia/hydrogen/nitrogen mixtures before the fuel injected into the engine cylinder.

In recent years, combustion characteristics of partially dissociated ammonia gas, namely, the ammonia/hydrogen/nitrogen gas mixtures, have been extensively studied. This report shall first talk about why the partially pre-dissociation strategy is necessary, effective, and affordable. Then, recent studies on fundamental and engine combustion properties of ammonia via the pre-dissociation strategy will be comprehensively reviewed, including the oxidation kinetics studies (e.g., Zhang et al., 2021), experimental measurement and kinetic modeling studies of the key combustion property parameters such as the laminar burning velocity (e.g., Mei et al. 2021), flammability (Lesmana et al. 2021), and the minimum ignition energy (Lesmana et al. 2022), and the power and emission properties of ammonia engines. Finally, unsolved scientific and technical problems and challenges of ammonia combustion via the partially pre-dissociation strategy will be addressed.

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*Corresponding author: gaojian@sztu.edu.cn

STEERING FROM ELECTROCHEMICAL DENITRIFICATION TO AMMONIA SYNTHESIS

Jianping Xiao[1,*]
[1] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China

Keywords

electrocatalytic denitrification, potential/pH effects, reaction phase diagram

The removal of nitric oxide is an important environmental issue, as well as a necessary prerequisite for achieving high efficiency of CO_2 electroreduction. To this end, the electrocatalytic denitrification is a sustainable route. Herein, we employ reaction phase diagram to analyze the evolution of reaction mechanisms over varying catalysts and study the potential/pH effects over Pd and Cu. We find the low N_2 selectivity compared to N_2O production, consistent with a set of experiments, is limited fundamentally by two factors. The N_2OH^* binding is relatively weak over transition metals, resulting in the low rate of asproduced N_2O^* protonation. The strong correlation of OH* and O* binding energies limits the route of N_2O^* dissociation. Although the experimental conditions of varying potential, pH and NO pressures can tune the selectivity slightly, which are insufficient to promote N_2 selectivity beyond N_2O and NH_3. A possible solution is to design catalysts with exceptions to break the scaling characters of energies. Alternatively, we propose a reverse route with the target of decentralized ammonia synthesis.

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*Corresponding author: xiao@dicp.ac.cn

Kinetic studies of the isomerization reaction of nitroethane and ethyl nitrite: The role of recrossing, tunneling and multistructural anharmonicity effects

Jibiao Xie[1], Jinou Song[1,*], Bangxin Jin[2], Yongdi He[1]

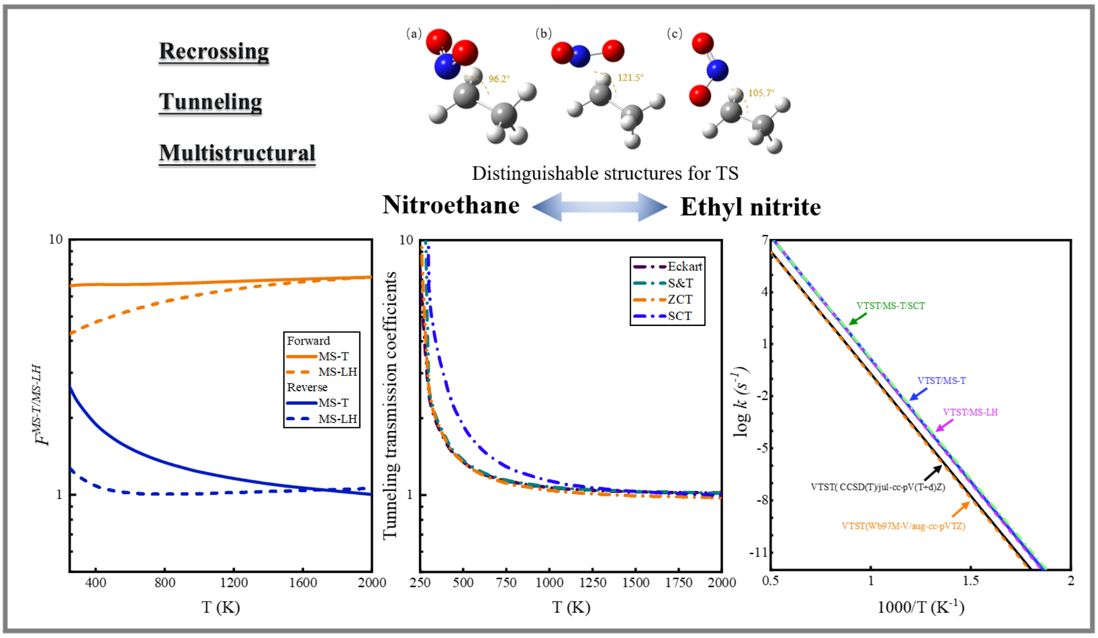
[1]Tianjin University, State Key Laboratory of Engines, Tianjin, P. R. China

[2]University of Science and Technology of China, State Key Laboratory of Fire Science, Hefei, P. R. China

Keywords

Nitroethane, Ethyl nitrite, isomerization, Multistructural anharmonicity, Tunneling.

Graphical abstract



Nitroethane (NE) can rapidly decompose with large energy release. This important energetic material it is often used as a fuel additive, high explosive and propellant (Wang et al., 2009). The isomerization of nitroalkanes and alkyl nitrite plays a non-negligible role on the pyrolysis of nitroalkanes (He et al., 2022, 2023; Jia et al., 2019; Wang et al., 2017; Zhu et al., 2013). Determining the accurate rate constants of the isomerization reaction is difficult. For this purpose, we carried out a detailed kinetic study including multistructural anharmonicity, tunneling and variational effects. A benchmark calculation for barrier height of isomerization was performed. The small-curvature tunneling (SCT) (Liu et al., 1993), zero-curvature tunneling (ZCT) (Kuppermann and Truhlar, 1971), Eckart tunneling and Skodje-Truhlar tunneling (S&T) (Skodje and Truhlar, 1981) were used to describe and compare the tunneling effect. The multistructural local harmonic approximation (MS-LH) and multistructural torsional anharmonicity (MS-T) effects were investigated and the rate constants were calculated by using multistructural variational transition state theory (MS-VTST) (Zheng et al., 2013; Zheng and

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*Corresponding author: xjb_skle@tju.edu.cn

Truhlar, 2013).The results show that the tunneling effect of the title reaction at low temperatures is not negligible. The results of ZCT, Eckart and S&T are almost identical, while the rigorous method of SCT with the consideration of corner-cutting tunneling gives a larger tunneling transmission coefficient. At high temperatures, the multistructural factors of MS-LH for the isomerization reaction are close to those of MS-T, whereas at low temperatures a more accurate contribution is derived from the MS-T method due to the inclusion of torsional anharmonicity in addition to the multistructural anharmonicity. The analysis and proposed rate constants in the present work are expected to be provide new insights into the decomposition chemistry and kinetic modeling of nitroethane.

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Dissociation dynamics of anionic carbon monoxide in dark states

Jingchen Xie[1], Mengyuan Fan[1], Xiao-Fei Gao[1], Bin Wu[1],
Kedong Wang[2,*] and Shan Xi Tian[1,3,*]
[1] Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China
[2] Henan Normal University, College of Physics, Xinxiang 453007, China
[3]University of Science and Technology of China, Hefei National Laboratory, Hefei 230088, China

Keywords

Dissociation electron attachment, Carbon monoxide, Dark quartet resonant states.

A resonant system consisting of an excess electron and a closed-shell atom or molecule, as a temporary negative ion, is usually in doublet-spin states that are analogous to bright states of photoexcitation of the neutral. However, anionic higher-spin states, noted as dark states, are nearly invisible in usual spectroscopic detections. Metastable CO ($a^3\Pi$) has a lifetime of milliseconds and been found in atmosphere of Mars (J.-C. Gérard et al., 2017) and in comets (H. A. Weaver et al., 1994). Its DEA process $e^- + CO \rightarrow C + O^-$ could happen with the atmospheric free electrons and consequentially influences the substance evolution therein. There are no experimental studies on this issue so far, although it has become routine to prepare the gas-sample CO ($a^3\Pi$) in laboratories. Here we report the dissociation dynamics of CO^- in dark quartet resonant states that are formed by electron attachments to electronically excited CO ($a^3\Pi$). Among the dissociations to $O^-(^2P) + C(^3P)$, $O^-(^2P) + C(^1D)$, and $O^-(^2P) + C(^1S)$, the latter two are spin-forbidden in the quartet-spin resonant states of CO^- while the first process is preferred in $^4\Sigma^-$ and $^4\Pi$ states. The present finding sheds new light on anionic dark states.

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*Corresponding author: wangkd@htu.cn; sxtian@ustc.edu.cn

Benchmarking kinetics calculations for combustion elementary steps on full-dimensional accurate potential energy surfaces

Yang Liu[1], Kaisheng Song[1], Jia Li[1], Xiaoshan Huang[1], Jun Li[1,*]
[1]School of Chemistry and Chemical Engineering & Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, 401331

Keywords: Potential energy surface, Molecular dynamics, Ring-polymer molecular dynamics, Master equation, KIEs

Combustion is complicated and consisted of a series of elementary steps, which can be reactive or non-reactive. For elementary reactions, statistical rate theories, like transition state theory (TST), Rice−Ramsperger−Kassel−Marcus (RRKM) theory, master equation, and their variants, have been widely employed in predicting the temperature- and pressure-dependent kinetics successfully. Only information along the minimum energy path is required. For elementary nonreactive collisions, simple interactions, like the Lennard-Jones (L-J) form, are often adopted to simulate the collision energy transfer.

We recently constructed several full-dimensional accurate potential energy surfaces (PESs) for elementary steps that are important in combustion. These elementary reactions include $O + H_2O$, $H + HO_2$, $OH + CO$, $OH + SO$, $OH + HO_2$, $OH + CH_4$, $OH + CH_3OH$, $HO_2 + HO_2$, $H + CH_4$, etc. The non-reactive elementary steps include $CO + CO$, $CO + H_2O$, $CO_2 + CO_2$, $C_2H_2 + Ne$, etc. For each system, ample configurations ($10^4 \sim 2\times10^5$) are sampled and computed at as-accurate-as-possible quantum chemical levels, often coupling clusters or multiple reference configuration interaction. Then the permutation invariant polynomials (PIP), neural networks (NN), PIP-NN is used to fit full dimensional accurate PESs. Our group has devoted to developing and applying the PIP-NN method to make the construction of accurate PESs efficiently.

In the talk, we will present our benchmark theoretical kinetics studies on reactions $OH + HO_2 \rightarrow H_2O + O_2$, $OH + SO \rightarrow H + SO_2$, $OH + CO \rightarrow H + CO_2$, $OH + CH_3OH \rightarrow H_2O + CH_3O$ / CH_2OH, $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$, etc. They are important in combustion. The quasi-classical trajectory (QCT), ring-polymer molecular dynamics (RPMD), reduced-dimensional quantum dynamics (QD), as well as TST or RRKM-based master equation (ME) calculations are carried out, and the results are compared and analyzed.

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*Corresponding author: jli15@cqu.edu.cn

Towards Accurate and Efficient Determination of Thermodynamics and Kinetics of Large Complex Reaction System

Junjun Wu[1,2*], Wei Ren[1,2], Xun Zhu[1] and Qiang Liao[1]
[1] Key Laboratory of Low-grade Energy Utilization Technologies and Systems, and School of Energy and Power Engineering, Chongqing University, Shapingba District, Chongqing, China
[2] Department of Mechanical and Automation Engineering, The Chinese University of Hong Kong, New Territories, Hong Kong SAR, China.

Keywords

thermodynamics, kinetics, large complex system, first-principle calculation

It remains a long-standing challenge to predict accurate thermodynamics and kinetics of large hydrocarbons by the first-principle calculations[1]. This is mainly caused by the very high computational cost for high-accuracy electronic structure calculations and the overwhelming complexity of anharmonicity treatment in large reaction systems. Developing or validating accurate and efficient quantum chemistry methods is the prerequisite to removing the hurdles towards large hydrocarbon reaction models.

Herein, several newly-developed methods are introduced to approach accurate thermodynamics and kinetics of large reaction systems at affordable cost. First, the cascaded-group-additivity ONIOM (CGA-ONIOM) method is adopted to obtain the enthalpy of formation (EOF) of various hydrocarbons at CCSD(T)/CBS level of theory.[2] It is found that the CGA-ONIOM is able to provide a very accurate determination of the EOFs with the computational efficiency improved by up to five orders of magnitude. Second, the multi-structural two-dimension torsion (MS-2DT) is developed to reduce the computational cost in treating the torsional anharmonicity of large flexible reaction systems[3]. Third, new efforts in calculating the rate coefficients of JP-10 and n-dodecane reaction with hydroxyl were presented. Finally, we highlighted the figure of merit of CGA-ONIOM and MS-2DT combination and suggested the possible future reaction direction for high-efficiency and high-accuracy thermodynamics and kinetics of large reaction systems.

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*Corresponding author: jjwu@cqu.edu.cn

ChemTraYzer – A Tool Supporting the Construction of Chemical Models

Kai Leonhard[1*], Wassja Kopp[2], Lukas Krep, Felix Schmalz, and Enia Mudimu[1,]
[1] RWTH Aachen University, Institute of Technical Thermodynamics, Schinkelstr. 8, Aachen, Germany

Keywords

Reaction network exploration, Ab initio calculation, molecular dynamics, Acceleration, Transition state

Chemical models are used widely in combustion, atmospheric chemistry, and chemical engineering applications. Their construction is usually very tedious, requiring many experiments and quantum mechanical calculations as well as substantial experience. An alternative is the use of many analogies, which reduces the reliability of the resulting chemical models, especially for unconventional systems. Therefore, many projects have been started to aid in the construction of such models or to fully automate it. The Chemical Trajectory analYzer, ChemTraYzer, is such a tool that is based on molecular dynamics (MD) simulations using a reactive force field or DFTB ab initio MD simulations (Döntgen et al 2015). We demonstrate how tailored acceleration techniques extend the accessible time scale beyond the second scale by using CTY-TAD (ChemTraYzer-Temperature Accelerated Dynamics) and Metadynamics. We also show our recent progress on finding challenging transition states from MD trajectories in order to refine rate constants via high-level ab initio methods.

We illustrate our progress on two case studies: (1) is the formation and oxidation of chlorinated dibenzofurans, which can occur in wildfires and waste incineration but are challenging to study experimentally due to their extremely high toxicity (Krep et al. 2023). In case study (2) we show how ChemTraYzer can automatically identify reaction pathways and rate constants in ethyl formate oxidation.

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*Corresponding author: Kai.Leonhard@LTT.rwth-aachen.de

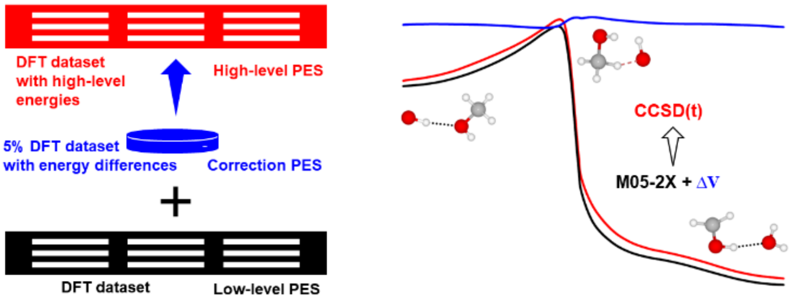
The neural network based Δ-machine learning approach efficiently brings the DFT potential energy surface to the CCSD(T) quality: a case for the OH + CH_3OH reaction

Kaisheng Song[1], Jun Li[1,*]
[1] School of Chemistry and Chemical Engineering & Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chonqing University, Chongqing 401331, P. R. China

Keywords

Δ-Machine learning, PIP-NN, Potential Energy Surface, Reaction Kinetics

The recently proposed permutationally invariant polynomial-neural network (PIP-NN) based Δ-machine learning (Δ-ML) approach (PIP-NN Δ-ML) is a flexible, general, and highly cost-efficient method to develop a full dimensional accurate potential energy surface (PES). Only a small portion of points, which can be actively selected from the low-level (often DFT) dataset, with high-level energies are needed to bring a low-level PES to a high-level of quality. The hydrogen abstraction reaction between the methanol and hydroxyl radical, OH + CH_3OH, has been studied using theories and experiments for a long time due to its great importance in combustion, atmospheric and interstellar chemistry. However, it is not trivial to develop the full dimensional accurate PES for it. In this work, the PIP-NN Δ-ML method is successfully applied to the title reaction. The DFT PES was fitted by using 140 192 points. Only 5% of the DFT dataset was needed to be calculated at the level of UCCSD(T)-F12a/AVTZ, aiming to improve the DFT PES to the target high-level, UCCSD(T)-F12a/AVTZ. More than 92% of the original unaffordable calculation costs were saved. The kinetics, including rate coefficients and branching ratios, were then studied by performing quasi-classical trajectory calculations on this newly fitted PES for the title reaction.



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*Corresponding author: jli15@cqu.edu.cn

Mechanistic insight of methane combustion over MOF-derived Ni-CeO2 catalysts

Kangwei Xu[1, 2], Xiaohan Wang[1, 2,*] and Lidong Zhang[3,*]
[1] University of Science and Technology of China, School of Energy Science and Engineering, 96 Jinzhai Road, Hefei, P. R. China
[2] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, 2 Nengyuan Road, P. R. China
[3] University of Science and Technology of China, National Synchrotron Radiation Laboratory, 42 Hezuohuana Road, Hefei, P. R. China

Keywords

methane combustion, flame pyrolysis, MvK mechanism, kinetic study, DFT.

Methane catalytic combustion is a significant technique in the fields of enhanced combustion, methane removal, and methane detection with the development of the natural gas industry and the demand for low-carbon combustion. Here, using a facile flame pyrolysis technique, two different types of Ni-CeO_2 catalysts for methane combustion were synthesized from metal-organic framework (MOF) and metal salt (MS). Kinetic study, combined systematically characterization with density functional theory (DFT) calculation, was conducted to elucidate the reaction mechanism of methane heterogeneous combustion based on the Mars–van Krevelen (MvK) mechanism. The performance shows that Ni-CeO_2(BTC) catalysts give high activity owing to the large surface area, abundant Ni cations, and adsorbed oxygen. Additionally, abundant oxygen vacancies on the catalyst surface not only promote its intrinsic activity, but also contributes to the implementation of the MvK mechanism. In terms of kinetic analysis, methane heterogeneous combustion is dependent on the chemisorbed CH_4 and requires gaseous oxygen to participate by refilling oxygen vacancy to be surface lattice oxygen. The experimental data is well fitted by the MvK mathematical model, demonstrating that catalytic methane combustion agrees with a two-step reduction-oxidation mechanism. DFT calculations further clarify that, according to the MvK mechanism, the reduction of the active site is via dissociative adsorption of C-H of CH_4 on the catalytic site Ni-O-Ce, resulting in the formation of an oxygen vacancy, followed by dissociation of gas-phase oxygen on the oxygen vacancy to reoxidize the active site. Furthermore, the oxidation pathway of CH_3 is more thermodynamically stable than its continuous dehydrogenation. Summarily, the MvK mechanism dominates the methane heterogeneous combustion over Ni-CeO_2 and provides insight into the catalyst design for strengthening combustion.

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*Corresponding author: wangxh@ms.giec.ac.cn, zld@ustc.edu.cn

TOWARD FAST ESTIMATION OF KINETICS FOR UNIMOLECULAR DECOMPOSITION OF 1,3-DIOXETANE DERIVATIVES

Kevin De Ras[1], Gilles Dossche[1], Joris W. Thybaut[1], Kevin M. Van Geem[1,*]
[1]Laboratory for Chemical Technology (LCT), Ghent University,
Technologiepark-Zwijnaarde 125, B-9052 Ghent, Belgium.

Keywords

Unimolecular decomposition, 1,3-dioxetane, Gas-phase kinetics, Quantum chemistry.

Polyoxymethylene dimethyl ethers, or so-called oxymethylene ethers (OMEs), have received much attention in recent years as a sustainable alternative for fossil-based fuels. OMEs are categorized as an e-fuel as they can be synthesized starting from CO_2 and renewable electricity. During the low-temperature combustion of OMEs, several cyclic ethers are formed with consecutive carbon and oxygen bonds, for example 1,3-dioxetane and 1,3,5-trioxane (De Ras et al., 2022). These cyclic ethers decompose in the gas phase at elevated temperatures via unimolecular pathways in which consecutive carbon-oxygen bonds are broken and transformed into double bonds. For example, 1,3-dioxetane decomposes into two formaldehyde molecules, see *Fig. 1*. Due to the unstable nature of these cyclic ethers, it is difficult to obtain experimental data for the rate coefficients. Moreover, quantum chemical calculations cannot be performed for all reactions occurring in an oxidation network, as this would be too computationally intensive. However, accurate kinetic parameters are a prerequisite to develop a reliable kinetic model. Therefore, in this study, a multitude of fast estimation techniques, i.e., reaction rate rules, kinetic group additivity values and Evans-Polanyi relations, are investigated to determine the rate coefficients for unimolecular decomposition of 1,3-dioxetane derivatives. A large data set with quantum chemical parameters at the CBS-QB3 level of theory is constructed with several different substituents positioned on the four-membered ring, which is used to assess and compare the accuracy of the different techniques.

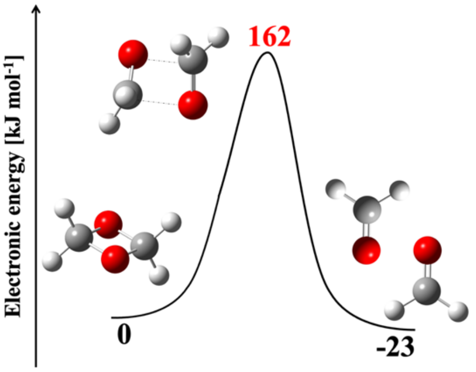

Fig. 1. Energy diagram (at 0 K) for the unimolecular decomposition of 1,3-dioxetane.

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*Corresponding author: Kevin.VanGeem@UGent.be

SCALING UP PLASTIC PYROLYSIS USING KINETIC MONTE CARLO

Laura Pires da M. Costa[1], Oğuzhan Akin[1], Robin J. Varghese[1], Florence H. Vermeire[2], Istvan Lengyel[1] and Kevin M. van Geem[1,*]

[1] Laboratory for Chemical Technology, Department of Materials, Textiles and Chemical Engineering, Faculty of Engineering and Architecture, Ghent University, Technologiepark 121, 9052, Zwijnaarde, Belgium

[2] Chemical and Biochemical Reactor Engineering and Safety (CREaS), Department of Chemical Engineering, KU Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

Keywords

Polystyrene, polyethylene, pyrolysis, chemical recycling, kinetic Monte Carlo, mathematical modeling

Chemically recycling plastics, specifically via pyrolysis, constitutes an appropriate route for disposal of post-consumption material as high amounts of naphtha can be obtained and used for the production of recycled plastic materials, reducing the use of virgin fossil feedstocks. Although kinetic models for steam cracking and polyolefins synthesis have been studied extensively, modeling plastic pyrolysis is an area that has been overlooked. Additionally, even though experimental data have been gathered at different operation conditions and reactors, the data is frequently not reproducible, and investigations aiming to understand the possible reasons are also scarce. In a scenario of urgency to solve post-consumer waste, global warming and depletion of natural resources, filling up these gaps is mandatory. Therefore, in order to understand and describe the kinetic degradation dynamics of plastics, specifically polystyrene and polyethylene, through pyrolytic processes, a detailed mechanistic model was developed and implemented using a kinetic Monte Carlo approach. Besides the kinetic package, the models also take into consideration thermodynamic equilibriums to simulate the multi-phase system. Reaction temperatures in the range of 500 – 700 °C were used to validate the proposed model based on experimental data obtained through micropyrolysis experiments. How the reactor configuration (batch, semi-batch, fluidized bed, etc.) affects the product distribution will also be discussed. The good agreement between simulated and the experimentally measured data and the short computational time of our code proved the methodology to be an adequate alternative for the implementation of first principles based kinetic plastic pyrolysis models.

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*Corresponding author: Kevin.VanGeem@UGent.be

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*Corresponding author: Kevin.VanGeem@UGent.be

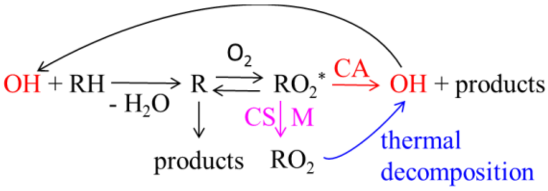
THE REACTIONS OF OH WITH A NUMBER OF FORMATES; KINETICS AND BRANCHING RATIOS

L. Onel[1,*], R. Shannon[1], N. Robertson[1], O. Dudman[1], M. A. Blitz[1, 2] and P. W. Seakins[1]
[1]University of Leeds, School of Chemistry, Leeds, LS2 9JT, UK
[2]University of Leeds, NCAS, Leeds, LS2 9JT, UK

Keywords

formate, OH radical , kinetics , chemical activation , site specific branching ratios.

Esters are volatile organic compounds emitted into the atmosphere from biogenic and anthropogenic sources and also formed by atmospheric oxidation. The tropospheric photochemistry of esters is mainly controlled by the reaction with OH radicals. In addition, esters such as methyl ester ($CH_3OC(O)H$, MF) and ethyl ester ($CH_3CH_2OC(O)H$, EF) have been studied as surrogates to give insight into biodiesel combustion chemistry. Fuel consumption in low temperature combustion is typically initiated through reaction with OH, resulting in the generation of radicals, R, which then associate with O_2 to produce peroxy radicals (RO_2; Scheme 1). The conditions of the experiments can be arranged such that chemical activation (CA), leading to OH regeneration, is occurring (Potter et al., 2019).



Scheme 1

Typically, CA is promoted at low pressures, where the collisional stabilisation (CS) of the highly energetic RO_2 (RO_2*) is less important. The competition between CA and CS and between the R + O_2 reaction and the unimolecular decomposition of R is controlled by the potential energy surface of the R + O_2 reaction, which can be explored by theory.

Here the kinetics of the OH reactions with MF, EF and TBF (*tert*-butyl formate, $(CH_3)_3OC(O)H$) are studied using the laser pulsed photolysis–laser induced fluorescence technique. CA in the presence of O_2 is explored in a range of temperatures (294–600 K) and pressures (typically 5–50 Torr). The decomposition of R formed by the OH abstraction from the C(O)H site, R'OCO $\rightarrow$ R' + CO_2, has a lower energy barrier than the decomposition(s) of R(s) produced by the abstraction(s) from the alkyl site(s). Above ~500 K R'OCO decomposes before reacting with O_2 and the OH yield generated by CA and the thermal decomposition of RO_2 gives the branching ratio for the alkyl abstraction(s). Analysis using the Master Equation Solver for Multi-Energy well Reactions (MESMER; Onel et al., 2015) is in progress to enable the determination of the branching ratios in the OH + formate reactions under a wide range of conditions, relevant for atmospheric and combustion chemistry.

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*Corresponding author: l.onel@leeds.ac.uk

Fuels of the future: AI-based fuel design screening millions of candidates and their highly-automated chemical model development

Liming Cai[1,*]
[1] Tongji University, School of Automotive Studies, 4800 Cao'an Road, Shanghai, P. R. China

Keywords

Fuels of the future, Chemical model development, Uncertainty analysis, Artificial intelligence (AI).

The growing demand for energy security and sustainability motivates the systematic design of petroleum replacements and blending components from renewable resources. Carbon-neutral synthetic fuels, which are produced from renewable electricity by the hydrogenation of carbon dioxide captured from air or exhaust gas, are attracting growing interest due to their positive impact on the overall CO_2 balance. The catalytic conversion of carbon dioxide can produce fuel species with complex molecular structures and tailored physical and chemical properties. This opens the unprecedented possibility to enhance combustion performance with co-optimization of fuels and engines. For this, a novel fuel design process is highly desired, as fuel candidates are conventionally selected from existing fuel databases of molecules, which is limited by the extent of the databases and the accuracy of the property values. In addition, a deep knowledge about fuel combustion behaviors and underlying reaction kinetics in form of chemical mechanisms is also important prerequisite.

This work presents a highly-automated chemical model development procedure for AI-designed advanced fuels. First, a novel artificial intelligence-based fuel design approach is developed, which identifies molecules tailor-made for a particular application by screening millions of possible candidates. This approach is demonstrated by designing fuel blending components for spark-ignition engines. A virtual molecule pool consisting of 26.2 million fuel components is developed by taking all possible combinations of defined structural groups into account. The application potential of these fuel molecules is evaluated based on joint consideration of various properties estimated by quantitative structure-property relationship models using artificial neural network approaches. A three-stage fuel design process is performed. In particular, a number of species with novel and complex structures are identified, which are expected to allow for high engine efficiency and low emissions simultaneously but have not attracted investigation yet. Following this, a highly automated and rapid chemical mechanism development process is presented by combing advanced automatic model generation, optimization, uncertainty analysis, and reduction methods. The methodology is demonstrated by generating a chemical mechanism for the promising class of synthetic e-fuels oxymethylene ethers (OMEs). It is shown that this highly automated model development process is able to provide accurate chemical mechanisms with compact model size in a very efficient manner for e-fuel components of interest.

*Corresponding author: lcai@tongji.edu.cn

*Corresponding author: lcai@tongji.edu.cn

Coarse-grained transition path mechanisms analysis in methane combustion system

Meng Li, Mengze Ai, Lin Ji *
Department of Chemistry, Capital Normal University, No.105 Xisanhuan Beilu, Haidian District Beijing China, 100048

The mechanisms of combustion reactions are characterized by a network of fundamental elementary reaction steps, whose structure and properties depend on the fuel properties and external factors such as temperature and pressure. To model the reaction processes at mesoscopic and macroscopic scales in computational fluid dynamics (CFD) simulations, it is only viable to isolate a limited number of key reactions and intermediates to represent the overall kinetics. But the size of the combustion mechanism models increases with the size of the fuel molecule, roughly in an exponential trend (Lu et al., 2009). Therefore, mechanism reduction is a critical bridge connecting microscopic elementary reaction mechanisms with a phenomenological representation suitable for simulation of combustion processes in fuel chemistry. This talk introduced the coarse graining idea into the analysis of detailed combustion models to determine the key reaction steps that drive macroscopic combustion characteristics such as ignition and extinction as well as the overall reactivity of the chemical system (Ji et. Al 2022; Du et al 2023). Based on an unsupervised machine learning technique and big data analytics, a novel method that combines network community detection and parametric bifurcation techniques is proposed. The effectiveness of the method is demonstrated in a methane fueled combustion system, in which the coarse-grained states and transition paths are identified during the oxidation processes under wide temperature and pressure conditions at different resolution.

Keywords: coarse grain, unsupervised machine learning, transition path theory

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*Corresponding author: jilin@mail.cnu.edu.cn

Mixed quantum-classical dynamical simulation with long short-term memory networks

The mixed quantum-classical dynamical simulation is essential for studying nonadiabatic phenomena in chemistry. Many machine learning models have been developed to accelerate the time evolution of the nuclear subsystem. Recently, we have implemented long short-term memory networks to accelerate the time evolution of the electronic subsystem during the most widely-used dynamical method in photochemistry, i.e., fewest-switches surface hopping. It demonstrates that machine learning-based propagators can be applied to the most popular surface hopping simulations.

Kinetic modeling and mechanistic analysis of hydrogenolysis of bisphenol A based polycarbonate over NiO supported on Mg(Al)O

Lingfeng Li, Ruben Van de Vijver, Hari Sekhar Mitta, Yonggang Cheng, Kevin M. Van Geem*
Ghent University, Laboratory for Chemical Technology (LCT), Technologiepark 121, 9052 Gent, Belgium

Keywords

Oxygenated plastic waste; catalytic hydrogenolysis; intrinsic kinetics; Mg(Al)O based catalyst; NiO

The growing issue of plastic waste has become a major concern in recent years, with oxygenated plastic waste being a significant contributor to this problem. Despite their advantageous properties such as high impact-resistance and heat-resistance, oxygenated plastics such as bisphenol A based polycarbonate (BPA-PC) are difficult to recycle through traditional methods like mechanical and thermo-chemical recycling, making their disposal a significant challenge for the industry. Recent research has shown that hydrogenolysis using a Mg (Al)O support NiO catalyst is a promising approach to reduce these polymers into monomers, thereby significantly improving efficiency in recycling. To better understand the intrinsic kinetics of this process, advanced tools such as Cantera and KASTER are utilized to investigate the mechanism based on product distribution. The Langmuir-Hinshelwood mechanism has shown good potential in fitting and describing the experimental results. Two rate determining kinetic steps have been identified: the cleavage of the C-O bond between units, and the diffusion of polymer chains from metallic sites to basic sites, which go through an ether intermediate facilitated by an electron donator. The experimental dataset is then regressed to identify corresponding kinetic parameters, including activation energy, pre-exponential factors and reaction orders. In avoid of potential convergence issues and ensure the accurate exploration in the search space, a hybrid optimization method of Genetic algorithm (GA) and Levenberg Marquardt (LM) has been applied to fulfill the task, with the GA being responsible for exploring the entire search space and the LM for further fine-tuning of the global optimum returned by GA. These findings provide a comprehensive understanding of the hydrogenolysis of BPA-PC and offer practical guidance for designing the catalyst, ultimately improving the recycling efficiency of oxygenated polymers. This research has the potential to make a significant impact in addressing the pressing issue of plastic waste and pave the way for a more sustainable future.

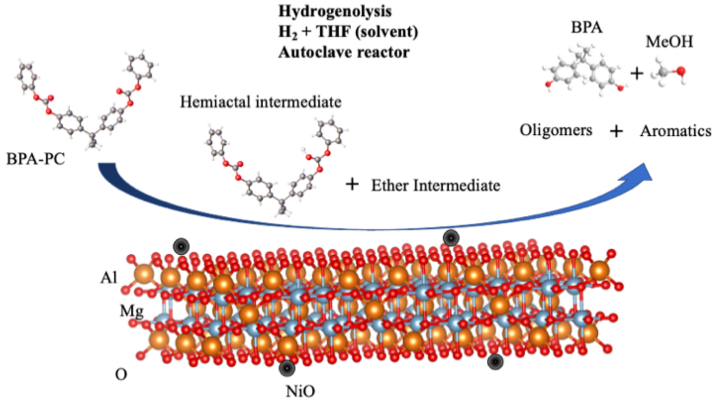

Figure 1 Schematic of Hydroigenolysis happened on the surface of NiO/Mg(Al)O

*Corresponding author: Kevin.VanGeem@Ugent.be

THEORETICAL STUDIES ON PHOTOHOTOCATALYTIC REDUCTION OF CO_2 BY AN IRIDIUM CATALYST: MECHANISM AND SELECTIVITY

Ling-Ya Peng and Ganglong Cui*
Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, Beijing Normal University, No. 19, Xinjiekouwai Street, Haidian District, Beijing, P. R. China

Keywords

Carbon dioxide reduction, Photocatalysis, Excited-state electronic structures, Reaction mechanisms, CASPT2.

Photocatalytic reduction of CO_2 to beneficial organic compounds is one of the viable options to alleviate energy crisis and complement carbon cycle. Recently, an experimental study reported an efficient catalyst, tetradentate phosphine-bipyridine (bpy) -phosphine (PNNP) -type Ir photocatalyst, Mes-IrPCY2, was developed for the reduction CO_2 with 87% HCOOH selectivity compared to CO. However, the underlying mechanism at atomic level remains elusive. Herein, we combine the complete active space second-order perturbation (CASPT2) theory with density functional theory (DFT) to investigate the photophysical process, the single electron transfer process, and the reaction mechanism. It was found that the initial photophysical process of $[Ir(III)H]^+$ can be well explained by the four-state model (S_0, ^{1}MLCT, ^{3}LE, and ^{3}MLCT). After reaching the ^{3}MLCT state, there are two competing reaction pathways: the efficient electron transfer process with sacrificial electron donor BIH leading to the formation of one-electron-reduced species (OERS) and $BIH^{\bullet+}$, or the deprotonation reaction with DMA, H_2O, or BIH leading to the formation of CO formation precursors, Ir(I) species. Subsequently, with the assistance of the $BIH^{\bullet+}$, OERS reacts with CO_2 to form HCOOH, and Ir(I) reacts with CO_2 to form CO. The efficient generation of OERS and the lower energy barrier of the rate-limiting step during HCOOH generation lead to the high HCOOH selectivity. This study provides theoretical guidance for further design of efficient photocatalytic CO_2 reduction systems.

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*Corresponding author: ganglong.cui@bnu.edu.cn

VUV photoionization study on the five-carbon-ring involved aromatic propagation

Keywords

gas-phase reactions, reaction mechanism, reactive intermediates, ab initio calculations.

The presented formation models based on C6-closures still underestimate the PAH content, both in the combustive conditions and the cosmic environments. Recent investigations illustrated that the formation of first aromatic-like 5-membered (C5-) ring, e.g. cyclopentadiene structure, plays vital roles in the growth of polycyclic aromatic hydrocarbons (PAHs). Exploiting a chemical microreactor in combination with an isomer-selective product identification through fragment-free photoionization utilizing tunable vacuum ultraviolet (VUV) light in tandem with the detection of the ionized molecules by a high resolution reflection time-of-flight mass spectrometer (Re-TOF-MS),[1] along with quantum theoretical calculations, we are focusing on the formation of C5 ring and further propagation to PAHs, in which the first ring is emphasized as the rate-determining step. The investigations provides compelling experimental and theoretical evidences on formations of the first C5-cyclic molecules and subsquent PAHs, including cyclopentadiene, fulvenallene, indene, naphthalene, etc., broadening our knowledge on the formation reactions in PAH formation processes in combustion conditions, extraterrestrial atmospheres and the interstellar medium.

* Long Zhao <zhaolong@ustc.edu.cn

Understanding the transcriptional dynamics and inhibitors' acting mechanisms in viral RNA polymerase

Lu Zhang[1,*]
[1] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of
Matter, Chinese Academy of Sciences, Fuzhou, Fujian 35000, China

Keywords

RNA polymerase, Molecular dynamics simulation, Markov State Model, Transcriptional dynamics.

RNA polymerase is the essential enzyme for viral transcription and replication, and thus become one important target for antiviral therapeutics. Although the high-resolution X-ray and cryo-EM structures have laid a valuable structural basis for understanding the transcriptional mechanism, they are insufficient to provide dynamic information, hampering the comprehensive understanding of viral transcription and the further inhibitor design.

Herein the dynamics of SARS-CoV-2 RNA-dependent RNA polymerase (RdRp) were investigated by molecular dynamics (MD) simulations and kinetic model. First, the translocation dynamics of double-stranded RNA (dsRNA) were examined by Markov State Model based on extensive MD simulations. Translocation is one key step in the nucleotide addition cycle for viral transcription. Our kinetic model identified two previously uncharacterized intermediates which pinpoint an asynchronous and rate-limiting translocation of the dsRNA. The millisecond translocation trajectory was generated and our investigations suggest that the translocation of SARS-CoV-2 RdRp follows a coupled Brownian-ratchet model. Second, the molecular mechanisms of the "delayed chain termination" and "template-dependent inhibition" exerted by Remdesivir were elucidated and the potential inhibitors were further proposed. Overall, our investigations have facilitated the understanding of the transcriptional dynamics of SARS-CoV-2, and also shed light on the rational design of RdRp inhibitors.

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*Corresponding author: luzhang@fjirsm.ac.cn

Detailed theoretical investigation of the ring-insertion pathway determining the product distribution of the $C_6H_5 + O_2$ reaction

L. Pratali Maffei[1*], C. Cavallotti[1], T. Faravelli[1], and S. J. Klippenstein[2]
[1]Dipartimento di Chimica, Materiali e Ingegneria Chimica «Giulio Natta », Politecnico di Milano, 20133, Milano, Italy
[2] Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

Keywords: phenyl oxidation, aromatic hydrocarbons, system interconversion, master equation

O_2 recombination with phenyl radical is one of the most relevant reactions in the mechanism of benzene oxidation at intermediate and high temperatures, hence its product distribution largely determines the subsequent reactivity of the system. While the rate constant for the entrance channel is relatively well determined (Zhang et al. 2017), literature studies are more controversial as regards the formation of products. The two main competing channels for the decomposition of the adduct C_6H_5OO are the O-O bond-fission and the insertion of the oxygen atom into the ring, eventually leading to the formation of O and H atoms, respectively (Fig. 1a). In their recent theoretical investigation, Morozov et al. found that the ring insertion channel prevails over almost the full range of temperature, contradicting some previous experimental and theoretical evidences (Kumaran and Michael 1997; Morozov et al. 2021; Tanaka et al. 2011).

In this work, the full potential energy surface of C_6H_5 + O_2 is re-investigated at CCSD(T)/CBS//ωB97X-D/6-311+G(d,p) level of theory using EStokTP automated routines (Cavallotti et al. 2019). The minimum energy paths for barrier-less channels and for reaction pathways with relevant multi-reference effects were instead determined at CASPT2/aug-cc-pVTZ level. The main result of this work is the careful analysis conducted for the ring insertion channel. The ring insertion proceeds through the breaking of the O-O bond, followed by C_{2v} and C_s symmetry breaking. The maximum found upon increasing the OCO angle (Fig. 1b) corresponds to a conical intersection between the A' and A" states and shows a complex electronic configuration with 8 quasi-degenerate states. Further refinement of the energy at MRCI level suggests a barrier of 21 – 22 kcal/mol, as opposed to the 8.1 kcal/mol found in (Morozov et al. 2021). We were also able to locate the transition state as the conical intersection between the first A' and A" states in C_s symmetry (as well as between the first two states in C_1 symmetry). The assessment of the interconversion rate is ongoing.

Preliminary rate constants obtained using the maximum energy configuration of Fig. 1b as ring insertion TS reveal that the formation of C_6H_5O + O prevails in the full range of temperature. This result is in better agreement with literature ST data measuring O and H fractions (Kumaran and Michael 1997), which instead seem incompatible with previous literature works (Fig. 1c).

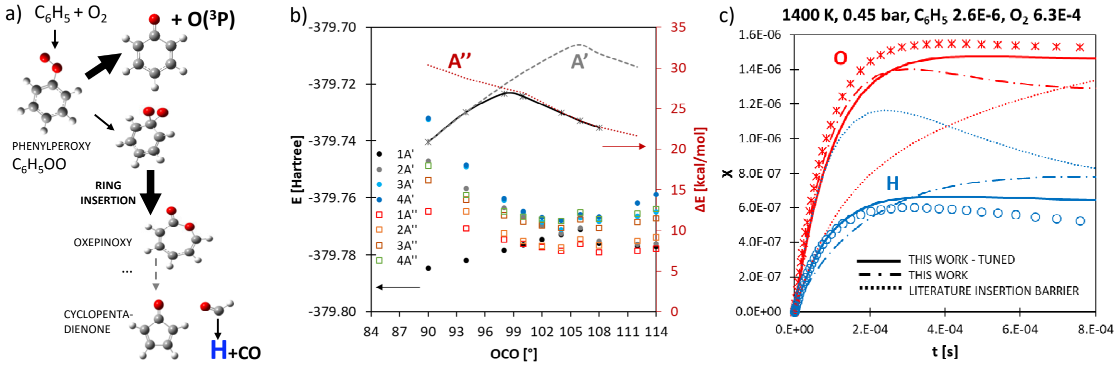

Figure 1: a) main reaction pathways for the $C_6H_5 + O_2$ reaction; b) energies of A' and A" states for the ring insertion pathway at CASPT2(11e,9o)/cc-pVDZ level of theory; c) O and H profiles from diluted shock tube reactor data (Kumaran and Michael 1997) simulated with the rate constants obtained in this work and with those from the literature.

*Corresponding author: luna.pratali@polimi.it

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*Corresponding author: luna.pratali@polimi.it

Mechanism reduction-assisted kinetic parameter optimization for the n-pentanol chemistry of the NUIGMech multifuel combustion mechanism

László Horváth[1,4], Shijun Dong[2], Chiara Saggese[3], Máté Papp[4], William J. Pitz[3], Henry J. Curran[2],
Tamás Turányi[4], Tibor Nagy[1*]

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Budapest, Hungary
horvath.laszlo@ttk.hu, nagy.tibor@ttk.hu
[2]Combustion Chemistry Centre, National University of Ireland Galway, Galway, Ireland
shijun.dong@nuigalway.ie, henry.curran@nuigalway.ie
[3]Materials Science Division, Lawrence Livermore National Laboratory, Livermore, USA
saggese1@llnl.gov, pitz1@llnl.gov
[4]Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary
mate.papp@ttk.elte.hu, tamas.turanyi@ttk.elte.hu

Abstract

Regarding the combustion of the long chain bioalcohols, biobutanol have already been researched for more than a decade, whereas on n-pentanol combustion still little is known. Recently, the NUIGMech 1.1 multifuel combustion mechanism has been extended with detailed pentanol chemistry (Chatterjee, 2022). The aim of the present work is to improve the accuracy of the n-pentanol submechanism of this updated NUIGMech mechanism by optimizing its rate parameters. We collected 2185 experimental data in 133 datasets covering wide range of conditions from the literature: ignition delay times from rapid compression machine and shock tube measurements, concentrations from jet-stirred reactor measurements and laminar flame speeds. The size of the NUIGmech mechanism (2831 species and 11680 reactions) makes it unfeasible for parameter tuning against such large amount of experimental data, therefore, we reduced it using a simple flux-based mechanism reduction method. This method ranks and selects reactions according to their rates normalized to the fastest reaction at each state of the system (p, T, c) sampled from simulations of the experiments. The reduced mechanism could reproduce the simulation results of the full mechanism very accurately, while it had only 322 species and 2096 reactions and could be simulated 30 times faster. We identified 44 important reactions of the remaining pentanol submechanism using a novel active parameter selection method (Kovács, 2022) which is based on the principal component analysis of a scaled local sensitivity matrix, which via the scaling can take into account the prior uncertainty of parameters, the uncertainty and the simulation error of each data and sizes of the data sets. The Arrhenius parameters of the reaction groups defined by the principal components were optimized using the Optima++ code (Goitom, 2022, Papp, 2021, Turányi, 2012), which halved the mean square error function. The optimized parameters were inserted back into the detailed NUIGMech mechanism and thereby its accuracy could be improved by the same degree. In summary, beyond developing an optimized reduced mechanism for n-pentanol combustion, we have significantly improved the accuracy of the pentanol submechanism of the updated NUIGMech 1.1 multifuel combustion mechanism by using our novel idea of mechanism reduction-assisted parameter optimization, which made this seemingly impossible task feasible.

Keywords: n-pentanol, biofuel, combustion mechanism, mechanism reduction, parameter optimization

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An investigation of the gas phase and surface chemical kinetics active during the plasma assisted chemical vapor deposition of diamond

Maristella Di Teodoro* and Carlo Cavallotti
Dept. Chemistry, Materials, and Chemical Engineering, Politecnico di Milano
Piazza Leonardo da Vinci, 32, Milano, Italy

Keywords:

Plasma, surface chemistry, diamond, chemical kinetic

Plasma technologies have the potential to become a technological pillar for the electrification of the chemical industry [1]. One of the advantages are the fast switch on/off response times, compatible with the use of renewable energies [2]. In this respect microwave enhanced plasma (MP) reactors are particularly interesting as they allow both the production of high value and functionalized materials and the efficient transformation of the feed gas. The implementation of these technologies however requires the development of predictive models of the plasma processes, able to describe both their magnetohydrodynamics as well as the chemical kinetics.

In this context, we present a conjunct fluid dynamics and kinetic investigation of the epitaxial MP chemical vapor deposition (CVD) of (100) diamond from methane. The model is composed of a 3D fluid dynamic part, used to study the temperature distribution within the reactor and to provide information for a 0 D model, applied to describe the gas phase and the surface reactivity. The model is able to explicitly account for plasma electroneutrality by including electrons and ions among the reactive species. The gas phase kinetics includes electrons impact process and reactions among neutral and radical species. Much care was placed in developing a new surface kinetic model, composed of a set of about 200 elementary reactions that describe the interaction between gas phase radicals and ions with the (100) reactive surface. It consists of: ion wall reactions; adsorption and desorption of atomic hydrogen and CH_x radicals, isomerization of the surface pseudo-species, and incorporation of adsorbed carbon in the crystal bulk. Some examples of the model predictions are shown in Figure 1.

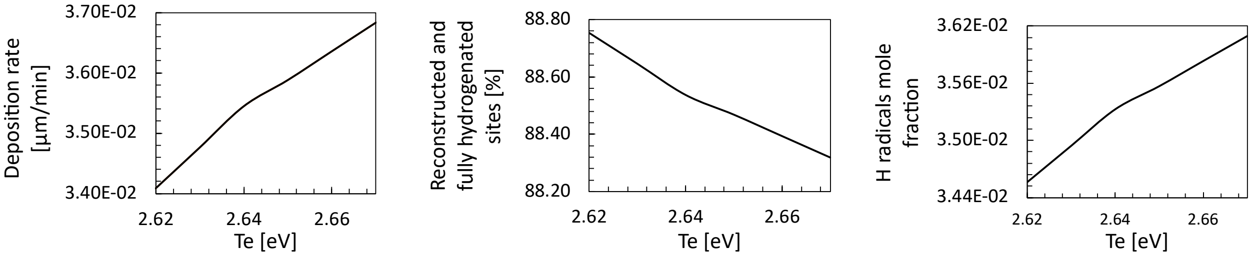

Figure 1. Behavior of three key system parameters as a function of the electron temperature.

Rate constants for gas phase and surface reactions are either taken from the literature or evaluated through the ab initio transition state theory (TST) based master equation approach, as implemented in EstokTP [3]. In particular, desorption and H abstraction rates of surface H atoms were evaluated assuming a representative crystal sample cluster of 5 layers and 17 heavy atoms. Structures, electronic energies and Hessians were calculated at the ωB97X-D/jun-cc-pVTZ level and rate constants with conventional TST. The model proved to properly describe the investigated system, as the diamond growth rate and the power absorbed are in good agreement with measured experimental values, without the need of using adaptive parameters.

*Corresponding author: maristella.diteodoro@polimi.it

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*Corresponding author: maristella.diteodoro@polimi.it

GAS-PHASE KINETICS OF 2-METHYL-2-PENTENAL WITH Cl ATOMS AND SUNLIGHT

María Asensio[1,2], María Antiñolo[1,2], José Albaladejo[1,2] and Elena Jiménez[1,2*]
[1] Universidad de Castilla-La Mancha, Facultad de Ciencias y Tecnologías Químicas, Departamento de Química Física, Avd. Camilo José Cela 1B, 13071 Ciudad Real, Spain.
[2] Universidad de Castilla-La Mancha, Instituto de Investigación en Combustión y Contaminación Atmosférica, Camino de Moledores s/n, 13071 Ciudad Real, Spain.

Keywords

Gas-phase reactivity, Photolysis, Pollutants, atmosphere.

The biogenic oxygenated volatile compound 2-methyl-2-pentenal (2M2P) is emitted into the low atmosphere from several sources such as wildland fires, vegetation and from some foods. During daytime, the oxidation of 2M2P can be initiated by sunlight, hydroxyl radicals (OH), or chlorine atoms (Cl) in marine atmospheres. Only one theoretical study has been found on the gas-phase kinetics of 2M2P with OH radicals by Grosjean and Williams (1991). However, neither kinetic measurements of the Cl-reaction nor 2M2P photolysis in the actinic solar region ($\lambda \geq 290$ nm) were reported in the literature.

The aim of this work is, therefore, to determine the rate coefficients at 298 K and 1 atm for the photolysis (J) of 2M2P in the troposphere and for its reaction with Cl atoms (k_{Cl}) to evaluate the contribution of these homogeneous degradation routes to the total loss of 2M2P in the troposphere. J has been measured in a Pyrex cell irradiated by a solar simulator and coupled to a Fourier Transforms Infrared (FTIR) spectrometer to monitor the loss of 2M2P (Asensio et al., 2022). The Cl + 2M2P kinetics has been investigated by the relative method in a smog chamber coupled to a FTIR spectrometer to monitor de loss of 2M2P and the reference compounds (Ballesteros et al., 2017).

Finally, the atmospheric implications of the 2M2P reactivity will be discussed in terms of its lifetime due to the homogeneous reaction with Cl, OH and photolysis by sunlight. And, as the photochemical degradation of 2M2P may contribute to the formation of secondary pollutants, the formation of products gaseous and secondary organic aerosols will be evaluated.

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*Corresponding author: Elena.Jimenez@uclm.es

REACTIVITY STUDY OF 2-ISOPROPOXYETHANOL WITH THE ATMOSPHERIC OXIDANTS

Inmaculada Aranda[1], Sagrario Salgado[1,2], Pilar Martin[1,2], Florentina Villanueva [2,3], María Teresa Pinés [1,2,*] and Beatriz Cabañas[1,2].
[1]Universidad de Castilla-La Mancha, Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Avda. Camilo José Cela s/n 13071, Ciudad Real, Spain.
[2]Universidad de Castilla-La Mancha, Instituto de Combustión y Contaminación Atmosférica (ICCA), Camino de los Moledores s/n, 13071, Ciudad Real, Spain.
[3]Parque Científico y Tecnológico de Castilla-La Mancha, Paseo de la Innovación 1, 02006 Albacete, Spain.

Keywords

Hydroxy ethers, atmospheric chemistry, relative rate coefficients, reaction products, FTIR, Gas Chromatography/Mass Spectrometry

Abstract

The use of glycol esters as solvents and chemical intermediates has increased markedly in recent years (Cheremisinoff, 2003). Once released into the atmosphere, they can undergo degradation processes mainly by reactions with the atmospheric oxidants that can have significant effects on the environment. In this work, the kinetic and products study of reactions of 2-isopropoxyethanol (2iPE, $(CH_3)_2CHOCH_2CH_2OH$) with OH and NO_3 radicals and Cl atoms have been performed using a relative method. No previous data are available on its reactivity with NO_3 or Cl atoms. The rate coefficients obtained were (units cm^3 $molecule^{-1}$ s^{-1}): $(2.18 \pm 0.15) \times 10^{-10}$, $(1.88 \pm 0.10) \times 10^{-11}$ and $(3.28 \pm 0.46) \times 10^{-15}$ for Cl, OH and NO_3 reactions, respectively. The kinetic results obtained have been compared to the general reactivity of hydroxy ethers to extract conclusion of the relationship between structure-reactivity of this type of compounds. The main products obtained have been isopropyl formate, 2-hydroxyethyl acetate and nitrated compounds and a reaction mechanism can be proposed in which the main initial attack of the $\cdot OH$ and $\cdot NO_3$ is in the O-CH<. For Cl reactions, different initial attacks have similar percentages. The calculated lifetimes as well as the Global Warming Potential (GWP) and the Photochemical Ozone Creation Potential ($POCP_E$) have been estimated concluding first that the reaction with OH radicals is the main pathway of degradation of these and others glycol ethers in the atmosphere, second that these compounds have GWP negligible and third, that they have influence on global ozone generation.

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*MTeresa.Pines@uclm.es

A COMPREHENSIVE CHEMICAL KINETICS FRAMEWORK FOR CARBON MATERIALS AND TURQUOISE HYDROGEN PRODUCTION FROM HYDROCARBONS PYROLYSIS.

Clarissa Giudici[1], Francesco Serse[1], Andrea Nobili[1], Mauro Bracconi[2], Alberto Cuoci[1], Alessio Frassoldati[1], Matteo Maestri[2], Matteo Pelucchi[1*]

[1]CRECK Modeling Lab, Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy
[2] Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Via La Masa 34, 20156 Milano, Italy

Keywords: Turquoise hydrogen, hydrocarbons cracking, carbon materials, carbon nanotubes, CVD/CVI, soot

Hydrogen (H_2) is a key energy vector in the context of sustainable development and circular economy (Diab et al. 2022, Hermessmann and Muller, 2022). The CO_2 emissions that accompany the most widely used process for its production today (i.e., steam methane reforming) highlights the need for efficient CO_2 capture technologies that are presently struggling for large scale implementation. Pyrolysis of fossil or biogenic hydrocarbons (e.g. methane, biomethane, natural gas) is one of the most promising solutions in a short- to mid-term perspective (Diab et al. 2022). Indeed, thanks to the concomitant carbon fixation in value-added carbon materials (VACs), the produced “turquoise” H_2 can be sold at a price comparable to that from SMR (Pasquali and Mesters, 2020). The key points to scale-up pyrolysis processes to produce H_2 and VACs are to accelerate deposition efficiency, minimize the formation of amorphous carbon (i.e., particulate matter) and improve the quality of carbon material by-products (Pasquali and Mesters, 2020). Therefore, it is of primary importance to control both homogeneous reactions in the gas phase, including particulate matter formation, and heterogeneous reactions occurring at the gas-solid interface. Detailed and semi-detailed chemistry models coupled with computational fluid dynamics models support the design of innovative reactor technologies by providing tools for process conditions optimization (Serse et al., 2023).

This work showcases recent research efforts in the development of a comprehensive chemical kinetic framework capable to contextually describe amorphous carbon formation in the gas phase (i.e. particulate matter) (Nobili et al., 2022), structured pyrocarbon production in CVD/CVI processes (Serse et al., 2023), carbon nanotubes synthesis in floating catalyst CVD reactors and turquoise hydrogen production. Starting from a consolidated gas-phase model, including PAHs and soot formation (Bagheri et al., 2020, Nobili et al., 2022) the CRECK kinetic framework has been extended to describe the heterogeneous formation of pyrocarbon over a carbon preform. The CVD model from Lacroix et al. (2010) has been firstly updated defining a theoretical workflow for the determination of gas/solid rate constants. Missing pathways involving both armchair and zigzag edges have been implemented, also accounting for the formation of defects (e.g., 5 and 7 member rings) coming from the deposition of aromatics and PAHs in competition with growth pathways mostly involving small fuel fragments (e.g. HACA). The updated model generally improves the results compared to Lacroix et al. (2010), in particular in terms of deposited mass and deposition rates as a function of temperature, residence time, preform surface to volume ratio and hydrogen content.

*Corresponding author: matteo.pelucchi@polimi.it

In parallel, a discrete section model has been developed to describe the catalytic formation of single walled carbon nanotubes (CNT) in floating catalyst CVD reactors (Hoecker et al., 2017) using ferrocene as a precursor and CH_4 as feedstock. Despite the scarcity of well characterized experimental data (e.g. contextual gas-phase and growth rates measurements, catalyst size distribution) the model provides insights on the dynamic evolution of surface and gas-phase species and reproduces with reasonable accuracy the produced mass of carbon nanotubes (Figure 2).

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*Corresponding author: matteo.pelucchi@polimi.it

KINETICS OF SOLID PLASTIC WASTE PYROLYSIS: DEVELOPMENTS AND PERSPECTIVES FOR THEORETICAL RATE CONSTANTS AND POLYMER-POLYMER INTERACTIONS INVESTIGATION

Andrea Locaspi[1], Francesco Serse[1], Luna Pratali Maffei[1],
Marco Mehl[1], Alessio Frassoldati[1], Tiziano Faravelli[1], Matteo Pelucchi[1*]

[1]CRECK Modeling Lab, Department of Chemistry, Materials and Chemical Engineering,
Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy

Keywords: Solid Plastic Waste; Pyrolysis; Chemical Recycling; Lumped kinetics; Quantum metadynamics; Tight binding

In a circular economy perspective, solid plastic wastes (SPW) are a valuable source of chemicals, energy vectors and fuels, providing more efficient and environmentally sound options compared to landfill disposal (Dogu et al, 2021). In addition, thermochemical recycling allows to process multilayer materials for which mechanical recycling is hardly applicable.
Modelling the pyrolysis and gasification both at the particle and reactor scale requires first the definition of a suitable condensed phase pyrolysis mechanisms. A semi-detailed kinetic modelling framework has been developed to describe the thermal degradation of key components of SPW such as polyethylene (PE), polypropylene (PP), polystyrene (PS) (Locaspi et al., 2022, 2023), polyvinyl chloride (PVC) (Marongiu et al., 2023), poly(methyl methacrylate) (PMMA) and polyethylene terephthalate (PET). Based on the functional group approach employed also for biomass pyrolysis (Ranzi et al., 2017), the kinetic model proposed adopts a simplified description of polymeric chains while preserving a detailed description of products of interest. Beyond widely diffused single or few steps kinetics this approach offers the opportunity to investigate the impact of feedstock composition and operating conditions on product distribution and to unravel the occurrence of polymer-polymer interactions (e.g. PET/PVC (Coralli et al., 2022)).
Aiming to overcome the semi-empirical approach currently used for determining condensed phase rate constants a theoretical quantum metadynamics protocol has been developed for rate constants (e.g. beta-scission) determination in explicit solvent which combines rare events sampling techniques and generalized transition state theory. The protocol is validated by comparison with previous state-of-the-art calculations (Cuccato et al., 2010) as well as with PLP rate constants measurements (Li et al., 2006, Vir et al., 2019).
Moreover, moving from clear evidences of relevant interactions between heteroatoms containing polymers (e.g. PET/PVC), the aforementioned methodology has been applied to explore with extreme level of detail the effect of the liquid environment on reactivity that could strongly impact quality and value of pyrolysis products.

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Reaction kinetics of CN + toluene and its implication on the productions of aromatic nitriles in the Taurus molecular cloud and Titan's atmosphere

Mengqi Wu[1], Xiaoqing Wu[1,2], Qifeng Hou[1], Jiangbin Huang[1], Dongfeng Zhao[1,*] and Feng Zhang[1,*]
[1] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China
[2] China Jiliang University, College of Information Engineering, 258 Xueyuan Street, Hangzhou, P. R. China

Keywords

Astrochemistry; Interstellar medium; Titan; Interstellar clouds; Reaction rates.

Reactions between cyano radical and aromatic hydrocarbons are believed to be important pathways for the formation of aromatic nitriles in the interstellar medium (ISM) including those identified in the Taurus molecular cloud (TMC-1). Aromatic nitriles might participate in the formation of polycyclic aromatic nitrogen containing hydrocarbons (PANHs) in Titan's atmosphere. Here, ab initio kinetics simulations reveal a high efficiency of 10^{-10} cm^3 s^{-1} and the competition of the different products of 30–1800 K and 10^{-7}–100 atm of the CN + toluene reaction. In the star-forming region of TMC-1 environment, the product yields of benzonitrile and tolunitriles for CN reacting with toluene may be approximately 17% and 83%, respectively. The detection of main products, tolunitriles, can serve as proxies for the undetected toluene in the ISM due to their much larger dipole moments. The competition between bimolecular and unimolecular products is extremely intense under the warmer and denser PANH forming region of Titan's stratosphere. The computational results show that the fractions of tolunitriles, adducts, and benzonitrile are 19%–68%, 15%–64% and 17%, respectively, at 150–200 K and 0.0001–0.001 atm (Titan's stratosphere). Then, benzonitrile and tolunitriles may contribute to the formation of PANHs by consecutive C_2H additions. Kinetic information of aromatic nitriles for the CN + toluene reaction calculated here helps to explain the formation mechanism of polycyclic aromatic hydrocarbons (PAHs) or PANHs under different interstellar environments and constrains corresponding astrochemical models.

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*Dongfeng Zhao: dzhao@ustc.edu.cn
*Feng Zhang: feng2011@ustc.edu.cn

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*Dongfeng Zhao: dzhao@ustc.edu.cn
*Feng Zhang: feng2011@ustc.edu.cn

The dynamics of the dissociation electron attachment to CO_2 clusters

Mengyuan Fan[1], Jingchen Xie[1] and Shan Xi Tian[1,*]
[1] Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

Keywords

Dissociative electron attachment, Clusters, Velocity map imaging

Dissociative electron attachment (DEA) to single CO_2 molecule yields O^- as the only fragment ion arising from the well-known $^2\Pi_u$ shape resonance (ion yield centered at 4.4 eV). On proceeding to CO_2 clusters, non-dissociated complexes of $(CO_2)_n^-$ form and solvated fragment ions of $(CO_2)_nO^-$ form are generated. Although the process of attaching electrons to CO_2 clusters has long been of interest and has been investigated in a number of experiments (Klots and Compton, 1978; Stamatovic et al., 1985; Knapp et al., 1986), many unanswered questions remain about the attachment mechanism as well as the nature of the produced anions. Using our high resolution velocity map imaging apparatus, we experimentally study the dissociation electron attachment of CO_2 clusters from supersonic nozzle in the electron energy range of 2.5 to 6eV, record the ion velocity images of CO_3^- for the first time, and attempt to reveal the dynamics mechanism of the DEA to CO_2 clusters.

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*Corresponding author: sxtian@ustc.edu.cn

UV PHOTOLYSIS OF OXALYL CHLORIDE: DECOMPOSITION OF THE CLCO RADICAL AND QUANTUM YIELD OF THE CL_2 ELIMINATION CHANNEL

Michael Stuhr[1,*], Sebastian Hesse[1], Nancy Faßheber[1], Marcel Wohler[1], Mithun Pal[1],
Yasuyuki Sakai[2], Patrick Hemberger[3], and Gernot Friedrichs[1]
[1] Kiel University, Institute of Physical Chemistry, Max-Eyth-Str. 1, 24118 Kiel, Germany
[2] Ibaraki University, Carbon Recycle Energy Research Center, Nakanarusawa-cho 4-12-1, Hitachi 316-8511 Ibaraki, Japan
[3] Paul Scherrer Institute, Laboratory for Synchrotron Radiation and Femtochemistry, Forschungsstr. 111, 5232 Villigen PSI, Switzerland

Keywords

Oxalyl chloride, UV photolysis, Cl atom source, Frequency modulation spectroscopy, Mass spectrometry.

UV photolysis of oxalyl chloride, $(ClCO)_2$, is widely used as “a clean source for chlorine atoms” (Baklanov and Krasnoperov, 2001) in gas phase reaction kinetics, primarily for the generation of radicals via H-abstraction reactions such as alkane + Cl $\rightarrow$ alkyl radical + HCl. Early studies on $(ClCO)_2$ photolysis suggested that photofragmentation exclusively proceeds via a three-body dissociation process yielding ClCO* + Cl + CO. The chloroformyl radical ClCO* is generated with high excess energy and undergoes fast dissociation to Cl and CO. At higher pressures, ClCO* can at least be partially stabilized by collisions. Due to a very low bond energy of only 27.7 kJ/mol, the subsequent thermal unimolecular decomposition ClCO + M $\rightarrow$ Cl + CO + M often takes place on a time scale that is short compared to the target kinetics under consideration. Therefore, it is generally assumed that UV photolysis yields two Cl atoms per photolyzed $(ClCO)_2$ molecule and that secondary chemistry of ClCO is negligible.

However, a recent study by Huang et al. suggested that direct molecular elimination of Cl_2 can play a significant role in the UV photolysis of $(ClCO)_2$ (Huang et al. 2017). Based on cavity ring-down spectroscopic measurements of Cl_2 concentrations and supported by RRKM calculations, they derived a photolysis quantum yield for the Cl_2 elimination channel of $\phi(Cl_2) > 0.14$ at a photolysis wavelength of 248 nm. In view of this significant non-Cl product pathway and the widespread use of $(ClCO)_2$, this study aims to provide further insight into the kinetics of the ClCO radical and to quantify the wavelength-dependent quantum yield of the Cl_2 elimination channel.

In this work, on the one hand, the decomposition of ClCO radicals has been studied in a low-pressure slow-flow reactor using mixtures of $(ClCO)_2$, ethane, and argon at 295 K with photolysis wavelengths of 266 nm and 355 nm. Taking advantage of our recent progress on the implementation of mid-infrared frequency modulation spectroscopy (Stuhr et al., 2019), we were able to monitor concentration-time profiles of HCl with microsecond time resolution (Fig. 1). HCl is formed by the H-abstraction reaction of Cl atoms with ethane and was subsequently monitored by probing its P(7) rovibrational transition at 2727.78 cm^{-1}. Numerical simulations of the experimental HCl profiles provided the low-pressure limit rate constant of the decomposition reaction ClCO + M in argon buffer gas, $k = (1.08 \pm 0.20) \times 10^{10}$ $cm^3 mol^{-1} s^{-1}$.

On the other hand, the photolysis quantum yield of the Cl_2 elimination channel has been studied at photolysis wavelengths of 213 nm, 266 nm, and 355 nm. To this end, we recorded concentration-time profiles of Cl_2 following $(ClCO)_2$ photolysis using time-of-flight mass spectra measured with the photoelectron photoion coincidence spectroscopy (PEPICO) setup at the

*Corresponding author: stuhr@phc.uni-kiel.de

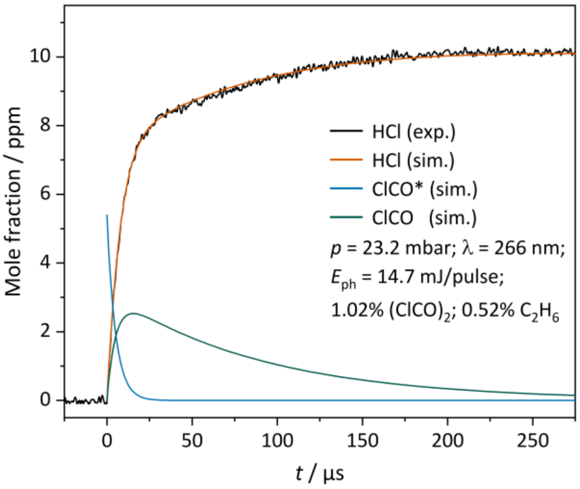

Figure 1: Typical experimental HCl profile (black) and simulated kinetic profiles (colored) for a low-pressure slow-flow measurement following UV photolysis of $(COCl)_2$ at a wavelength of 266 nm. The two different time scales of HCl formation (< 25 µs and > 25 µs) can be attributed to either Cl formation from ClCO* dissociation or thermal unimolecular decomposition of ClCO.

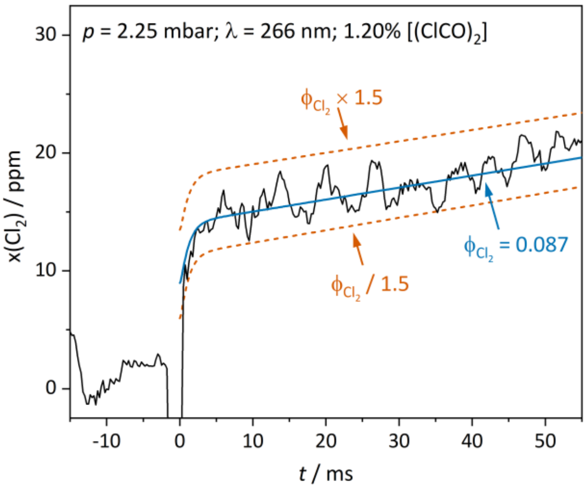

Figure 2: Typical experimental Cl_2 profile (black) and corresponding simulated kinetic profile (blue) for a time-of-flight mass spectrometric measurement after UV photolysis of $(COCl)_2$ at 266 nm. Alternative simulations with higher and lower assumed quantum yields of Cl_2 elimination are shown as well (orange).

vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS). The experimental Cl_2 profiles were obtained with millisecond time resolution and were analyzed based on a reaction mechanism accounting for direct Cl_2 elimination and additional contributions to the Cl_2 concentration from reactions involving Cl atoms, ClCO, and $(ClCO)_2$ (see Fig. 2). Relying on a careful calibration of the Cl_2 signal, the resulting pressure-independent photolysis quantum yields of molecular Cl_2 elimination were determined as $\phi(Cl_2) = (0.033 \pm 0.018)$, (0.088 ± 0.030), and (0.054 ± 0.025) at 213 nm, 266 nm, and 355 nm, respectively. This interesting wavelength dependence (with Cl_2 peaking at 266 nm) will be further discussed in terms of an updated potential energy diagram for $(ClCO)_2$ decomposition.

Although the Cl_2 yields are lower than originally reported by Huang et al. in 2017, our results clearly confirm that the direct molecular elimination channel is active at typical UV photolysis wavelengths. This has important implications for the practical use of $(ClCO)_2$ as a "quantitative" source of Cl atoms. Previous reaction kinetic studies relying on accurate Cl atom yields from $(ClCO)_2$ photolysis may therefore be biased by assuming too high Cl atom concentrations.

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*Corresponding author: stuhr@phc.uni-kiel.de

Low-temperature chemistry in plasma-driven ammonia oxidative pyrolysis

Mingming Zhang[1], Qi Chen[1*], Guangzhao Zhou[2], Jintao Sun[1], He Lin[2]
[1] *School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing 100044, P.R. China*

[2] *School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China*

Keywords

non-equilibrium plasma; ammonia fuel; oxidative pyrolysis; pathway flux analysis; sensitivity analysis

Ammonia is gaining increasing attention as a green alternative fuel for achieving large-scale carbon emission reduction. Despite its potential technical prospects, the harsh ignition conditions and slow flame propagation speed of ammonia pose significant challenges to its application in engines. Non-equilibrium plasma has been identified as a promising method, but current research on plasma-enhanced ammonia combustion is limited and primarily focuses on ignition characteristics revealed by kinetic models. In this study, low-temperature and low-pressure chemistry in plasma-assisted ammonia oxidative pyrolysis is investigated by integrated studies of steady-state GC measurements and mathematical simulation. The detailed kinetic mechanism of NH3 decomposition in plasma-driven Ar/NH_3 and $Ar/NH_3/O_2$ mixtures has been developed. The numerical model has good agreements with the experimental measurements in NH_3/O_2 consumption and N_2/H_2 generation, which demonstrates the rationality of modelling. Based on the modelling results, species density profiles, path flux and sensitivity analysis for the key plasma-produced species such as NH_2, NH, H_2, OH, H, O, $O(^1D)$, $O_2(a^1\Delta_g)$, $O_2(b^1\Sigma_g^+)$, Ar^*, H^-, Ar^+, NH_3^+, O_2^- in the discharge and afterglow are analyzed in detail to illustrate the effectiveness of the active species on NH_3 excitation and decomposition at low temperature and relatively higher E/N values. The results revealed that NH_2, NH, H as well as H_2 are primarily generated through the electron collision reactions $e + NH_3 \rightarrow e + NH_2 + H$, $e + NH_3 \rightarrow e + NH + H_2$ and the excited-argon collision reaction $Ar^* + NH_3 + H \rightarrow Ar + NH_2 + 2H$, which will then react with highly reactive oxidative species such as O_2^*, O^*, O, OH, and O_2 to produce stable products of NO_x and H_2O. $NH_3 \rightarrow NH$ is found a specific pathway for NH_3 consumption with plasma assistance, which further highlights the enhanced kinetic effects.

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*Corresponding author: qchen@bjtu.edu.cn

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*Corresponding author: qchen@bjtu.edu.cn

Linear and non-linear mechanism of catalytic hydrogenation of propene

Mirosław Szukiewicz[1], Adrian Szałek[1], Elżbieta Chmiel-Szukiewicz[2]

[1] Department of Chemical and Process Engineering, Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland, ichms@prz.edu.pl

[2] Department of Department of Organic Chemistry, Rzeszów University of Technology, al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland, ichms@prz.edu.pl

Abstract: The kinetics of heterogeneous catalytic reactions is a topic of theoretical and practical importance that combines theoretical and experimental efforts to improve the knowledge of the process. Theoretical aspects are concerned with determination of the process mechanism, whereas in practical applications kinetic experiments were applied to assist reactor design and scaling up of various processes. These approaches overlap and often are discussed simultaneously: the assumed mechanism that covers many elementary steps helps to derive the precise kinetic equation and vice versa; experimental data can confirm or deny the mechanism idea. The method most often applied is to find a single step having the strongest influence on the process rate. However, this 'classical approach' takes into account interactions between reagents and species only for the single rate-determining step. More complex interactions are neglected. For this reason, in the literature, a lot of works present successful applications of the concept, however, in many instances failed attempts are presented: the kinetic equations are of not sufficient precision. This phenomenon was observed, among others, for the gas-phase hydrogenation of the propene process. It suggests that not only interactions for the single step influence the process run. In this work, we present a procedure that is based on a catalytic cycle idea for linear and non-linear types of mechanisms assumed. Theoretical investigations completed with appropriate mathematical treatment and statistical analysis help to obtain a high-precision kinetic equation for the mentioned process. Both, linear and non-linear, approaches substantially differ from the rate determining step approach. The general form of the kinetic equation is feasible to obtain without any additional assumptions. It allows consideration of all possible interactions between the reagents and the species. The kinetic equations that resulted from the linear and nonlinear approaches and were developed and tested. Statistical analysis allowed simplifying the equation to obtain a form that includes only statistically significant variables. For the process under consideration, the kinetic equation that was obtained using the linear approach characterises the high precision confirmed by the values of statistical indicators and the criterion. The residual sum of squares is more than 15% lower than for the best equation established in the literature. The form of kinetic equation has not previously been reported in articles, where 'classical' applications of the rate determination step method dominate.

What will audience learn from your presentation?

- The most often reported in literature works are based on a choice of the step that has the strongest influence on the process rate, which is potential source of errors. Here, kinetic investigations are based on the idea of a catalytic cycle, and it allows the consideration of all possible interactions between reagents and species in a kinetic equation. For this reason, the kinetic equation can achieve better precision and can help determine the true mechanism of the process.
- The results of the work help to develop a high-precision kinetic equation concerning gas-phase heterogeneous processes.
- The precise kinetics gives a deeper insight into a process.

Unraveling the impacts of anharmonicity, recrossing and tunneling on hydrogen abstraction kinetics of cyclopentanol and cyclopentane by hydroperoxyl radical

Mo Yang and Juan Wang*
National Key Laboratory of Science and Technology on Aero-Engine Aero-Thermodynamics,
School of Energy and Power Engineering, Beihang University, Beijing 100191, P. R. China

Keywords

Cyclopentanol and cyclopentane, Combustion chemistry, Hydrogen abstraction, Multi-structural variational kinetics.

To date, it is still a challenge to accurately predict the reaction kinetics of H-atom abstractions by the HO_2 radical in cycloalkanes and cyclic alcohols, which play a fundamental role in combustion chemistry. Cyclopentanol is a novel alternative fuel derived from lignocellulosic biomass, while cyclopentane is a representative component in conventional fossil fuels. Both are promising gasoline additives due to their high-octane and knock-resistant features, and therefore selected as our target molecules. To implement the procedure of direct dynamics calculations, the suitable Kohn-Sham model chemistry was selected according to the minimum mean unsigned deviations (MUDs) as compared with the CCSD(T)-F12/jun-cc-pVTZ results. Then, the rate constants over 200–2000 K were calculated employing the canonical variational transition state theory (CVT) combined with multiple-structural and torsional anharmonicity (MS-T), as well the small curvature tunneling approximation (SCT). The site-specific features of considering the anharmonicity, recrossing and multi-dimensional tunneling effects were stressed by analyzing the MS-T and MS-LH factors and transmission coefficients for each studied reaction. The comparison of rate constants and branching ratios derived from different theoretical kinetic corrections or empirically estimated methods showed pronounced discrepancies.

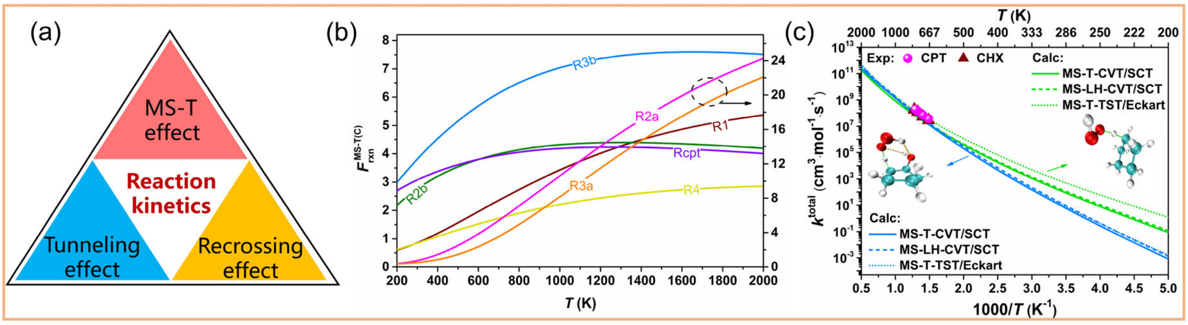

Fig. 1 (a) kinetic correction approaches; (b) Site-specific MS-T factors; (c) total rate constants.

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*Corresponding author: juanwang@buaa.edu.cn

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*Corresponding author: juanwang@buaa.edu.cn

LASER-BASED DIAGNOSIS OF FLAMES WITH MACHINE LEARNING

Muhammad Bilal[1, 2] and Zhen-Yu Tian[1, 2,*]
[1] Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China.
[2] University of Chinese Academy of Sciences, Beijing 100049, China.

Keywords

LIBS, Machine learning, PIV, Classification, Flame structure.

Laser-based diagnosis of flames has become an important tool for understanding combustion processes and optimizing combustion systems. Two of the most widely used techniques for laser-based diagnosis of flames are Laser-Induced Breakdown Spectroscopy (LIBS) and Particle Image Velocimetry (PIV) (Brend et al., 2020)(Wu et al., 2022). These techniques provide valuable insights into flame dynamics, species concentrations, temperature profiles, and other important parameters. However, the interpretation and analysis of the vast amount of data generated by these techniques can be challenging. This is where machine learning comes in. Machine learning algorithms can help to extract meaningful information from the data and provide insights into the underlying processes (Zheng et al., 2020). In this work, we discuss the importance of laser-based diagnosis of flames, including the use of LIBS and PIV, and the integration of machine learning for data analysis. We highlight the potential benefits of using machine learning to analyze flame data, including improved accuracy and speed of analysis, and the ability to extract more detailed information from the data. We also discuss the challenges and limitations of using machine learning for flame analysis, including the need for large datasets and the potential for overfitting. Overall, the integration of machine learning with laser-based diagnosis of flames has the potential to revolutionize our understanding of combustion processes and lead to more efficient and environmentally friendly combustion systems.

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*Corresponding author: tianzhenyu@iet.cn

THERMODYNAMIC PROPERTIES CALCULATIONS OF CU-BASED SPECIES

Muhammad Yousuf[1, 2], and Zhen-Yu Tian[1, 2,*]
[1]Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China.
[2]University of Chinese Academy of Sciences, Beijing 100049, China.

Keywords

Thermodynamics properties, Copper-based species, Dmol3 module, Density Functional Theory, DFT calculations, NASA's seven-term polynomial.

The present work focuses on the thermodynamic properties of five different copper-based species, namely copper, copper oxide, copper hydroxide, copper nitrate, and copper hydroxide nitrate. The study involved optimizing the structures of these species to achieve stable geometry and then using the density functional theory (DFT) calculations via the DMol3 package to compute various thermodynamic properties such as enthalpy, entropy, heat capacity at constant pressure, and Gibbs free energy (Zeck and Wolf 1993). The research aimed to analyze the relationship between these properties and temperature, and to compare the thermodynamic behavior of different species. The study found that species with a higher number of atoms tend to exhibit higher thermodynamic values, and that copper and copper hydroxide nitrate had higher thermodynamic values than their oxide and other counterparts. In addition, the DFT method was used to calculate the thermodynamic properties of copper hydroxide nitrate, and the results showed that the thermodynamic values of the compound structures were higher than their crystalline counterparts (Skiborowski, Temmann, and Brandenbusch 2018). The research findings can be useful for a range of future applications, including thermodynamic computations and kinetic modeling. The newly calculated thermodynamic data and polynomials can provide valuable insights into the thermodynamic behavior of copper-based species and help improve the understanding of their different crystalline structures and surface sites (Arshad et al. 2021). Further research in this area could lead to the development of new materials and technologies in industries such as metallurgy, electronics, and energy production.

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*Corresponding author: tianzhenyu@iet.cn

COMPARISON OF RECENT ACETONE COMBUSTION MECHANISMS BASED ON LARGE AMOUNT OF EXPERIMENTAL DATA

Márton Kovács[1], Henrik Schuszter[1], Máté Papp[1], István Gy. Zsély[1,*], Tamás Turányi[1]
[1]Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

Keywords

Acetone combustion, biofuel, experimental database, mechanism comparison, sensitivity analysis

The importance of acetone has become more and more certain in the past few decades. It may play a significant role in the chemistry of the atmosphere, because it is one of the most abundant oxygenated organic compounds. Acetone is also an important reaction intermediate in the oxidation of hydrocarbons and oxygenates in flames as well as in the atmosphere. It is a biofuel, as it can be produced through biological processes, and its mixtures with different hydrocarbon fuels are frequently used. The main source of bioacetone is the ABE mixture, which is a fermentation product. As fermentation engineering develops, ABE could become an economically feasible potential alternative to fossil fuels. Understanding the combustion properties and the chemical kinetics of the oxidation of acetone is essential for further development of kinetic models of hydrocarbon combustion.

In this work, the performance of 18 detailed chemical kinetic reaction mechanisms was compared based on how well they can reproduce the results of published experimental data. (Turányi et. al., 2012) Ignition delay times measured in shock tubes (281 data points, 25 data series) and rapid compression machines (28, 2), concentration measurements carried out in jet stirred reactors (1000, 56), flow reactors (2636, 189), shock tubes (13519, 29) and burner stabilized flames (5493, 174), and laminar burning velocity measurements (351, 32) were collected from the literature. The overall data collection consists of 23308 experimental data points collected from 25 publications. The simulations were performed using the *OpenSMOKE++* (Cuoci et al., 2015) and *Cantera* (Goodwin et al., 2022) simulation packages.

There are significant differences between the performances of the different models, and the performance of a mechanism may also vary significantly with the type of experiments. An example of this inconsistent behavior between the mechanisms is shown in Fig. 1. The best-performing models were further investigated by local sensitivity analysis to identify the key model parameters. Even

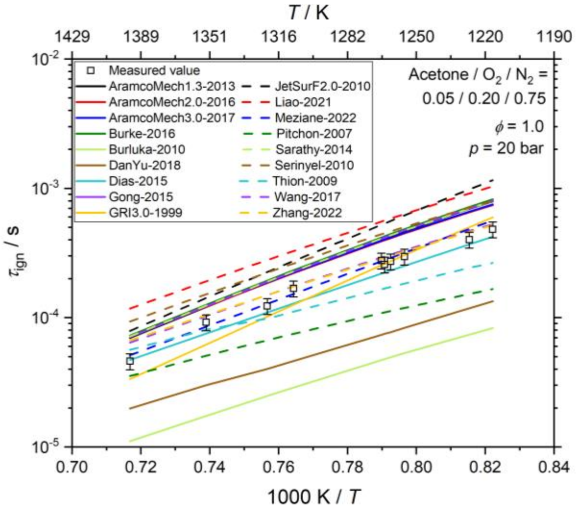

Fig. 1. Simulation results of an ignition delay time data series measured in shock tube (Minwegen et. al., 2017)

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*Corresponding author: istvan.zsely@ttk.elte.hu

though the investigated models have different parameter sets, the local sensitivity analysis revealed that the most important reactions and thermodynamic properties are similar. For zero dimensional and burner stabilized flame measurements, these reactions include acetone H-abstraction and acetone - methyl radical reactions. However, for the laminar burning velocity measurements, the highly sensitive reactions are those of the acetone thermal decomposition products and none of the reactions of the acetone molecule appeared in the list.
Results of this work can help in the selection of the best performing reaction mechanism and may serve as a good basis of the development of a better acetone combustion mechanism.

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*Corresponding author: istvan.zsely@ttk.elte.hu

Kinetic roles of electronically excited states species of plasma assisted n-pentane oxidation in a nanosecond-pulsed discharge

Nan. Liu[1], Qi. Chen[1,*], Xianwu. Jiang[2], Jie. Chen[1] and Lidong. Zhang[3]
[1] School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing, P. R. China
[2] Department of Physics, Wuhan University of Technology, Wuhan, P. R. China
[3] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, P. R. China

Keywords

Plasma assisted oxidation, electron-impact cross sections, R-matrix, excited state species, path flux analysis.

n-pentane is a typical component of gasoline and is the smallest linear alkane of liquid phase at atmospheric pressure and ambient temperature. Low temperature nanosecond discharge plasma assisted n-pentane oxidation has been studied at 60 Torr and 373 K experimentally and numerically. Electron-impact cross sections of n-C_5H_{12} were calculated by R-matrix and included in the detailed plasma kinetics mechanism. The numerical model has a good agreement with the experimental measurements. Excited state of n-pentane promoted the production of C_5H_{11} radical by RH (plasma) + X → R+XH. Further chain propagation and branching reactions of n-pentane oxidation were enhanced.

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*Corresponding author: qchen@bjtu.edu.cn

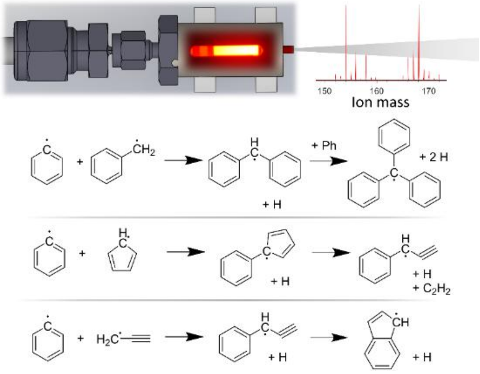
Hydrocarbon Radical-Radical Reactions: Well-Skipping, Ring-Opening, and Ring Closing

David E. Couch[1], Angie J. Zhang[1], Myrsini San Marchi[1], Ahren W. Jasper[2],
Goutham Kukkadapu[3], Craig A. Taatjes[1], Nils Hansen[1,*]
[1] Combustion Research Facility, Sandia National Laboratories, Livermore, CA, 94550, USA
[2] Chemical Sciences Engineering Division, Argonne National Laboratory, Lemont, Illinois 60439, USA
[3] Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA (present address: Intel Corporation, Hillsboro, OR, USA)

Keywords

radical radical reactions, polycyclic aromatic hydrocarbons, well-skipping, mass spectrometry

In this talk, we will summarize our work on radical-radical recombination reactions that are relevant for molecular-weight growth in soot formation. Through a combination of experiments employing dilute flash pyrolysis interfaced with molecular-beam mass spectrometry, theory, and simulations, we studied several radical-radical reactions, *i.e.,* phenyl (C_6H_5) + benzyl (C_7H_7), phenyl + propargyl (C_3H_3), and phenyl + cyclopentadienyl (C_5H_5).



For the C_6H_5 + C_7H_7 reaction, we observed that the initial adduct loses an H atom in a well-skipping reaction to form diphenyl methyl radicals that are best described as fully conjugated resonantly stabilized radicals. We also tested the importance of these well-skipping reactions in the phenyl + propargyl radical-radical reaction. Comparison with a simulation employing recent theoretical calculations involving all likely isomers revealed that the well-skipping pathways, especially to form indenyl radical, are prominent at temperatures of 1200 K and higher. The temperature and concentration dependence of the closed-shell (C_9H_8) and radical (C_9H_7) products agreed well with the simulation employing a chemical mechanism derived from a larger molecular-weight growth mechanism with updated coefficients from theoretical calculations. Eliminating the well-skipping reactions from the chemistry mechanism caused a substantial discrepancy in the temperature dependence of the radical concentration. For C_6H_5 + C_5H_5, substantial C_6H_5-C_5H_4 + H is formed, dominantly by a well-skipping pathway, at conditions around 30 Torr and 1400 K. This radical is thermally stable at moderate temperatures but decomposes at higher temperatures following ring opening of the 5-member ring. Products corresponding to the loss of H, C_2H_2, and C_3H_3 are observed experimentally. Calculation of the $C_{11}H_9$ potential energy surface reveals many decomposition channels with similar energetics consistent with the experimental results. These experimental and theoretical results will inform mechanisms and future studies involving reactions of larger polycyclics which are much more difficult to probe experimentally or theoretically.

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*Corresponding author: nhansen@sandia.gov

QuantumPioneer: Self-evolving AI machine for high-throughput automated potential energy surface exploration and closed-loop chemical reactivity discovery

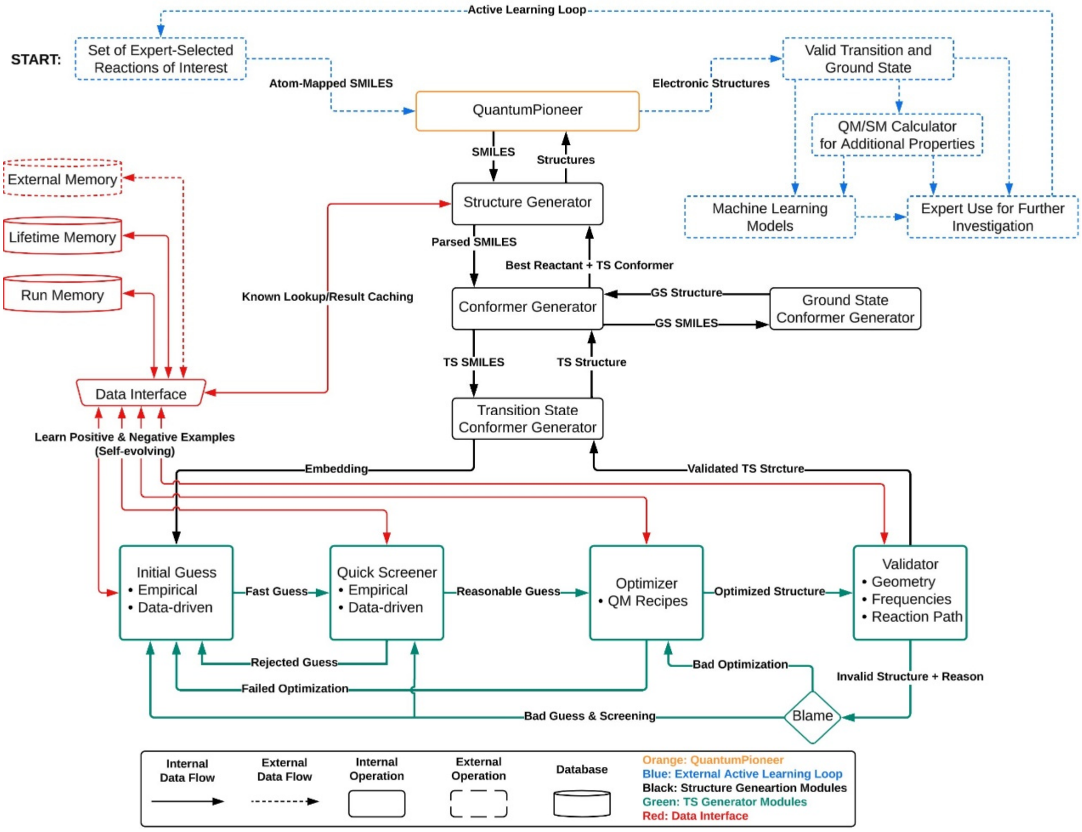
Haoyang Wu[1], Hao-Wei Pang[1], Xiaorui Dong[1], Jackson W. Burns[1], Kevin Spiekermann[1], Angiras Menon[1], Jonathan Zheng[1], Sayandeep Biswas[1], Shih-Cheng Li[2] and William Green[1]

(1) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA
(2) Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan

Keywords: Machine Learning, Computational Chemistry, High-throughput Virtual Screening, Autonomous Reactivity Discovery and Molecular Design

Acquiring accurate 3D geometries of reactive chemical species and transition states (TS) along reaction pathways over the potential energy surface is a critical prerequisite for computing high-quality thermodynamic and kinetic parameters via quantum chemistry and statistical mechanics. These calculated thermo-kinetic parameters are essential for creating impactful predictive models that can assist pharmaceutical design, high-performance material development, and renewable energy research. However, the search for transition states has historically been a trial-and-error process that demands considerable manual input. Although automated TS search has a rich history of algorithmic development, existing methods like single-ended and double-ended approaches are often computationally demanding, have high failure rates, and are highly localized to specific reaction systems, making it challenging to learn from previous examples and enhance performance. Therefore, efficiently automating the TS search is essential for enabling high-throughput chemical reactivity discovery and streamlining the generation of extensive theoretical reaction datasets that are valuable for developing machine-learning-based chemistry surrogate models. In this presentation, we introduce QuantumPioneer, a self-evolving artificial intelligence (AI) machine capable of automatically generating validated 3D electronic structures for a given reaction using atom-mapped SMILES as input. QuantumPioneer can enhance its performance over time by learning from past experiences and can be seamlessly integrated into an active learning loop for closed-loop chemical discovery. Moreover, QuantumPioneer can be tailored to specific chemical-exploration tasks and generate extensive theoretical reaction datasets that lay the foundation for future studies with wide-ranging applications. To showcase its capabilities, we employed QuantumPioneer to generate TS at wB97XD/def2svp level of theory for over 100,000 hydrogen atom abstraction (HAbs) reactions between peroxyl radicals and a diverse set of organic molecules chosen based on their functional groups. This dataset represents one of the largest DFT TS collections for radical-based reactions to date, laying the foundation for future studies with wide-ranging applications. We further refined the dataset with COSMO-RS and DLPNO-CCSD(T1)-F12D single-point calculations and trained D-MPNN models to predict HAbs reaction barriers. We will demonstrate how the machine learning model for HAbs barrier height prediction can potentially be applied to conduct high-throughput virtual screening of oxidative stability of organic molecules and aid better design of high-value chemicals such as active pharmaceutical ingredients

and carbon capture amines.



Modeling the kinetics of spatiotemporal precipitation

Paszkál Papp[1*], Ágota Tóth[1], Dezső Horváth[2]
[1] University of Szeged, Department of Physical Chemistry and Materials Science, 1 Rerrich Béla sq., Szeged, Hungary
[2] University of Szeged, Department of Applied and Environmental Chemistry, 1 Rerrich Béla sq., Szeged, Hungary

Precipitation kinetics, modeling, well-stirred systems, flow-driven systems

Precipitation reactions are essential in industry and nature. For example they not only play a major role in the syntheses of catalysts, nanoparticles and biomaterials in human activity, but also are vital in kidney stone formation and metal ion excretion by plants. These heterogeneous reactions can be coupled to transport processes, such as diffusion and convection, making each system unique. Although, there are many theoretical works on the kinetics of precipitation, the role of nucleation and growth, no general model exists that can be applied for every scenario. Therefore, the different precipitation processes require special methods to be treated with.

In case of a flow reactor the growth and displacement of the produced particles can be monitored with limited nucleation. However, in a well-stirred batch reactor, due to the large number of particles, individual tracking is generally not possible, therefore a different treatment is needed. With an appropriate computational model, experimental findings can be supported, and, in addition, the governing equations behind the various precipitation processes can be identified.

In this work numerical models are presented for precipitation reactions in flow-driven and well-stirred systems using the appropriate methodology. A reaction-diffusion-convection model is developed where the nucleation and growth of particles depends on the concentration fields. In order to describe the sedimentation of solid precipitate, Lagrangian particle tracking method is utilized. Nucleation, growth, and size distributions are characterized in a microfluidic reactor (Rakotozandriny et al., 2020), and in a Hele-Shaw cell where the simultaneous precipitation of copper(II)- and cobalt(II)-oxalate is studied (Papp et al., 2022). Furthermore, nucleation is modeled in a reactive mixture for a well-stirred system, in which turbidity is monitored to detect precipitate formation (Emmanuel et al., 2022).

With the theoretical description of these systems, the determination of kinetic parameters, rate coefficients and activation energy, can become feasible. Moreover, experimentally often inaccessible data, such as nucleation sites or particle size distributions, can also be computed, providing theoretical support for the experimental observations.

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*Corresponding author: papp.paszkal@szte.hu

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*Corresponding author: papp.paszkal@szte.hu

THE OH + METHYFORMATE REACTION – SITE SELECTIVE CHEMISTRY AND THE FATE OF THE RADICAL PRODUCTS

Lavinia Onel[1], Niamh Robertson[1], Robin Shannon[1] Mark Blitz[1] Daniel Stone[1] and Paul Seakins[1,*]
[1] University of Leeds, School of Chemistry, Woodhouse Lane, Leeds, LS2 9JT, UK.

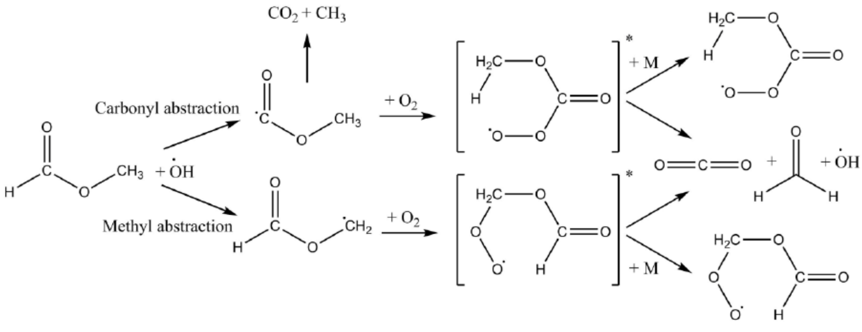
Keywords

OH + methylformate, Site specific kinetics, OH recycling, Transition State Theory, Chemical activation.

Methylformate, CH_3OCHO, is an important primary and secondary atmospheric pollutant and a model compound for biodiesel. Kinetic modelling of such complex systems requires absolute rate coefficients as a function of temperature, but equally importantly, site specific information as the products formed following reactions at alternative sits can be very different. For example, abstraction by OH from the methyl site eventually leads to a key atmospheric compound, formic acid, whereas abstraction at the methyl site leads to the ubiquitous HCHO product.

In this work we present laser flash photolysis/laser induced fluorescence data on the overall kinetics, bridging the temperature gap between previous low temperature (250 – 350 K) flash photolysis and higher temperature shock tube studies (>900 K). Marked curvature of the resultant Arrhenius plot links the previous literature data.

The figure below shows how OH can be recycled. The overall degree of OH recycling gives no site specific information. However, selective deuteration to give CD_3OCHO or CH_3OCDO which will recycle either OH or OD depending on the abstraction site.



Site specific rate coefficients have been determined, along with information on R + O_2 kinetics (see also poster by Onel et al.), and CH_3OCO decomposition. In contrast to the data from the Master Chemical Mechanism, we see limited evidence for chemically activated decomposition of CH_3OCO.

Experimental work is supported by theory ranging from transition state theory to dynamical calculations. Both experiment and theory paints a consistent picture of site selective chemistry and the resultant chemistry of the CH_3OCO and CH_2OCHO radicals and their peroxy radical counterparts. The implications of this work in atmospheric and low temperature combustion chemistry will be discussed.

*Corresponding author: e-mail address

Torsional PES Reconstruction and Metric-Based Assessment for Calculating Partition Functions by the MS-T Methods

Peng ZHANG[1,*]

[1] Department of Mechanical Engineering, City University of Hong Kong, Kowloon Tong, Kowloon, Hong Kong

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Keywords

Partition function, MS-T method, Torsional anharmonicity, Voronoi tessellation, dihedral metric, energy metric

The multi-structural approximation with the torsional anharmonicity (MS-T) method and its variants have been widely used for calculating conformational−rovibrational partition functions of large molecules. This talk will address two problems arising from applying the MS-T method, with one being about the accuracy of the method and the other about the efficiency of the method.

The first problem is about approximating the torsional potential energy surface (PES) as a sum of local periodic functions around the non-uniformly distributed local minima. We proposed an improved method to reconstruct an approximate PES by using the information of the local minima and their Voronoi tessellation. Two key innovations are that first, we established asymmetric barrier heights by introducing two periodicity parameters and assuming that the exact barrier positions are at the boundaries of Voronoi cells, and second, we used multiplicatively weighted Voronoi tessellation to refine the barrier heights and positions by defining a structure-related distance metric.

The second problem is about finding an appropriately chosen small subset of distinguishable torsional conformers, which can significantly reduce the computational cost of the MS-T method while retaining acceptable accuracy. First, we proposed the simplest variant MS-T(2NN) (two nearest neighborhood torsions are coupled) and systematically validated it for large alkanes n-C_nH_{2n+2} (n = 6−10) and their transition states of hydrogen abstraction reactions. Second, we proposed a metric-based method to explain the underlying reason for the good performance of MS-T(2NN)— it includes the torsional conformers that have dominant contributions to the partition function calculations. These conformers are closer to the lowest-energy conformer in the space of dihedral and energy metrics. Third, the same observation and explanation apply to the other two variants, MS-2DT (any two torsions are coupled) and MS-3DT (any three torsional are coupled), which contain increasingly more torsional conformers than MS-T(2NN) but are subsets of the complete set of torsional conformers considered by the MS-T method.

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*Corresponding author: penzhang@cityu.edu.hk

Infrared Photodissociation Spectroscopic Study of $Sc_2O_2(CO_2)_n^+$ (n = 1 – 4) Cluster Cations

Pengcheng Liu[1,2,3], Jia Han[3], Xiaoguo Zhou[3,*], Shilin Liu[3], Weijun Zhang[1,*]
[1]Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031, P. R. China
[2]Science Island Branch, Graduate School, University of Science and Technology of China, Hefei, 230026, P. R. China
[3]Department of Chemical Physics, University of Science and Technology of China, Anhui, Hefei, 230026, P. R. China

Keywords

CO_2, Scandium oxides, Cluster cations, Infrared photodissociation spectra.

Carbon dioxide (CO_2) has the potential to serve as one of the most plentiful and promising carbon feedstocks for chemical industry. Transition metal oxides have continuously been of great interest in the catalytic conversion of CO_2 given its capability to effectively activate highly thermodynamically stable CO_2. The investigation on gas-phase cluster ions consisting of transition metal oxides and CO_2 molecules with specific size and composition provides mechanistic insights into the catalytic reactivity of transition metal oxide towards CO_2. In this study, we employed a laser vaporization ion source to systematically produce a range of cationic clusters composed of scandium oxides with CO_2, i.e. $Sc_2O_2(CO_2)_n^+$ (n=1–4) complexes. The infrared photodissociation spectra in the wavenumber region of 2100–2500 cm^{-1} for the mass-selected cluster cations were obtained using an infrared photodissociation spectrometer. The comparison of experimental results with quantum chemical calculations facilitates the determination of geometric structures and binding motifs of cluster ions and reveals the possible role of scandium oxides in the activation of CO_2 at the molecular level, shedding new light on the design of novel catalysts with high activity in the catalytic conversion of CO_2.

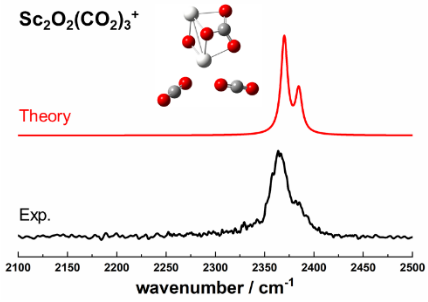

Fig. 1 The experimental infrared photodissociation spectrum of $Sc_2O_2(CO_2)_3^+$ cation complex together with the simulated infrared spectrum for a low-lying structure

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*Corresponding author: wjzhang@aiofm.ac.cn; xzhou@ustc.edu.cn

KINETIC INVESTIGATION OF PLASMA CATALYTIC SYNTHESIS OF AMMONIA

Qi Chen[1*], Jintao Sun[1], Xuteng Zhao[2], He Lin2[1]
[1] School of Mechanical, Electronic and Control Engineering, Beijing Jiaotong University, Beijing ,P. R. China
[2] Key Laboratory for Power Machinery and Engineering of Ministry of Education, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, P. R. China

Keywords

Ammonia synthesis; Plasma catalysis; Excited species, Surface kinetics/chemistry, Pathway flux analysis.

Ammonia (NH_3) is a pillar of chemical industry and widely used in the synthesis of fertilizer, synthetic fiber, hydrogen nitrate and numerous chemical compounds (Guo and Chen,2017). A green alternative for NH_3 production such as biochemical, electrochemical, photocatalysis, and plasma-catalytic synthesis with mild operating conditions is urgently needed (Cherkasov et al, 2015). Among them, plasma-catalytic synthesis is particularly attractive(Wang et al, 2019). We present a detailed chemical kinetic model of catalytic synthesis of ammonia activated by an NSD plasma, which includes a set of electron impact reactions, reactions involving excited species, ionic reactions, direct and dissociative adsorption reactions, and surface reactions. A zero-dimensional model incorporating the plasma kinetics solver is used to calculate the temporal evolution of species densities in a N_2/H_2 plasma catalysis system. The results show that the coupling of Fe/γ-Al_2O_3 catalyst with NSD plasma is much more effective in ammonia synthesis than the Fe/γ-Al_2O_3 catalyst alone and NSD plasma alone. The numerical model has a good agreement with experimental data in ammonia formation for all experimental cases. The path flux analysis shows the significant roles of excited species N(2D), H_2(v1) and N_2(v) in stimulating the formation of precursors NH, NH_2, and adsorbed N(s) through the pathways N(2D) + H_2 → NH + H, H_2(v1) + NH → NH_2 + H and N_2(v) + 2Fe(s) → N(s) + N(s), respectively. Furthermore, the results show that the adsorption reaction N + Fe(s) → N(s) and E-R interactions N(s) + H → NH(s), N + H(s) → NH(s), NH + H(s) → NH2(s) and NH_2 + H(s) → NH3(s) can kinetically enhance the formation of ammonia, which further highlights the plasma-enhanced surface kinetics/chemistry. This work provides new insights into the roles of excited species and plasma-enhanced surface kinetics/chemistry in the plasma catalytic ammonia synthesis.

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*Corresponding author: qchen@bjtu.edu.cn

Theoretical study of important reaction pathways in polycyclic aromatic hydrocarbon growth and development of kinetic model

Qian Mao[1]*, Luna Pratali Maffei[2], Raymond Langer[3], Tiziano Faravelli[2], Heinz Pitsch[3]
[1]School of Aerospace Engineering, Beijing Institute of Technology, Beijing 100081, China
[2]CRECK Modelling Lab, Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Milano, Italy
[3]Institute for Combustion Technology, RWTH Aachen University, Templergraben 64, Aachen 52056, Germany

Keywords

Polycyclic aromatic hydrocarbon, electronic structure calculation, chemical kinetics, reaction pathway.

The reaction kinetics of polycyclic aromatic hydrocarbon (PAH) growth are important in the prediction of soot in combustions. In this study, important reaction pathways in the PAH growth are revisited, and novel pathways are proposed through ab-initio studies. Reaction pathways of resonance-stabilized radical chain reactions, hydrogen abstraction carbon addition (HACA) through ethylene addition and the diacetylene addition are all investigated through high-level electronic structure calculations. The reaction kinetics and the branching ratios of these reactions are then compared against those with traditional pathways through acetylene and vinylacetylene additions. Moreover, a detailed chemical kinetic model for PAH chemistry is developed based on the above ab-initio reactions and those published in recent years, as well as experimental studies. The model development emphasizes the prediction of soot precursors starting from CH isomers up to the size of acepyrene. The proposed model was validated against a wide dataset of experimental measurements from 79 publications, including ignition delay times, laminar burning velocities, and speciation data for several fuels in various conditions. A validation against measured peak mole fractions from 31 counterflow flames demonstrates an average prediction error of aromatic species up to the size of acenaphthalene below a factor of three.

*Corresponding author: maoqian@bit.edu.cn

$CH_3O\dot{C}H_2 + O_2$: High level theory and the role of multichannel kinetics

Qian Zhao[1], Yingjia Zhang[1,]* and Zuohua Huang[1]
[1] Xi'an Jiaotong University, State Key Laboratory of Multiphase Flows in Power Engineering,
No.28 Xianning West Road, Shanxi, P. R. China

Keywords

$CH_3O\dot{C}H_2$, O_2, Low-temperature oxidation, Ab initio, kinetics, RRKM/ME.

Oxidation of organic compounds in combustion and in Earth's troposphere is mediated by reactive species formed by the addition of molecular oxygen (O_2) to organic radicals ($\dot{R}$). As an important intermediate species in atmospheric degradation of organic matter and low-temperature combustion of hydrocarbon fuels, once organic peroxy radicals ($R\dot{O}_2$) is formed, the fate of $R\dot{O}_2$ is to isomerize into QOOH. The downstream reactions of QOOH are known to profoundly fuel reactivity. Moreover, these species and their reactions with O_2 are implicated in tropospheric autoxidation that can form low-volatility, highly oxygenated organic aerosol precursors. However, both experimental measurements and high-level theoretical calculations of $R\dot{O}2$ kinetics are scarce, leading to a large gap in our understanding of $R\dot{O}_2$ fate. In this study, methoxy-methyl-peroxy ($CH_3OCH_2O\dot{O}$) is investigated as a model compound to elucidate the fate of $R\dot{O}_2$. Based on a high-level quantum chemical calculation and RRKM/master equation calculation, we report a detailed $R\dot{O}_2$ unimolecular reaction surface, as well as the corresponding temperature- and pressure-dependent rate coefficients. All the calculated results can be used to develop the global modeling of SOAs in atmospheric science, to estimate the corresponding rate coefficients of larger oxygen-centered fuels, as well as to construct the chemical kinetic model of dimethyl ether in combustion science.

*Corresponding author: yjzhang_xjtu@xjtu.edu.cn

An experimental and modeling study on the co-oxidation of ammonia and dimethyl ether: exploring the future of low-carbon combustion

Qiao Wang[1,2], Wanxiong Liao[1,2], Haodong Chen[1,2], Bin Yang[1,2 *]
[1] Center for Combustion Energy and Department of Energy and Power Engineering,
Tsinghua University, Beijing, 100084, China
[2] Key Laboratory for Thermal Science and Power Engineering of MOE, International Joint Laboratory on Low Carbon Clean Energy Innovation, Tsinghua University, Beijing 100084, China

Keywords

Ammonia, Dimethyl ether (DME), Kinetic mechanism, Jet stirred reactor (JSR) experiments, SVUV-PIMS.

The global energy revolution and climate-related issues motivate the search for more environmentally friendly fuels and combustion techniques (Kohse-Höinghaus, 2023). Ammonia (NH_3), as a carbon-free fuel, has recently received extensive attention from both academic research and industry (Kobayashi et al., 2019). The combustion of renewable ammonia for power generation and transportation sector is beneficial to meet the decarbonization target and address the climate challenges (Valera-Medina et al., 2018). The low reactivity of ammonia, however, hinders its direct usage as a combustible fuel. A feasible way is to co-fire ammonia with other reactive, also low-carbon fuels including hydrogen (H_2), methene (CH_4), and dimethyl ether (DME) (Chai et al., 2021). Understanding the kinetics of ammonia and the chemical interaction with those low-carbon fuels is becoming increasingly important to a growing variety of applications. In this work, oxidation properties of ammonia were investigated by blending it with various proportions of dimethyl ether using a jet-stirred reactor (JSR) over a wide range of experimental conditions. Numerous intermediate species were detected and quantified using gas chromatograph (GC), Fourier transform infrared (FTIR), and synchrotron vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS). The results were interpreted in terms of an updated detailed chemical kinetic model, drawing on the latest progress on the combustion kinetics of the two fuels. Sensitivity and reaction pathway analyses were performed to reveal the most important reactions controlling the consumption of ammonia and the interaction with dimethyl ether. The results show that the NH_3 & DME combination is a promising low-carbon fuel blend to drive a cleaner combustion in the future. Moreover, the interaction chemistry between the nitrogen-based fuels and carbon-based fuels is still an open question and is important to predict the key combustion properties as well as emission generation of various applications.

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*Corresponding author: byang@tsinghua.edu.cn

Bayesian analysis for RRKM/Master equation based kinetic predictions: A case study of ethyl with oxygen

Qifeng Hou[a], Yiru Wang[b], Keli Lin[b], Can Huang[b], Bin Yang[a], Feng Zhang [a,*]
[1]*Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, 230026, P. R. China.*
[2]*Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, P. R. China*

Keywords

Uncertainty analysis, RRKM/ME model, Bayesian method, ethyl+oxygen

In order to understand the sources of errors in mechanisms and enhance their predictive capabilities, it is necessary to investigate the factors affecting the predictive ability of mechanisms and conduct optimization. Uncertainty analysis aim to quantitatively evaluate the sources of uncertainty in detailed combustion reaction kinetics mechanisms and primarily consist of forward and reverse uncertainty analysis methods. In this work, we propose a research framework based on the RRKM/master equation model to investigate the sources of uncertainty in rate constants and constrain the input parameters of RRKM/master equation model. We illustrate this process through an example calculation of ethyl+oxygen [1]. This work focuses on optimizing two different targets, namely the branching ratio for the $C_2H_5 + O_2 = C_2H_4 + HO_2$ reaction and total rate constant of $C_2H_5+O_2$. Firstly, global sensitivity analysis and sensitivity entropy calculations were conducted to analyze the important parameters in the model and select the optimal operating conditions. Secondly, based on experimental values from the literature and prior distributions of parameters (uniform and Gaussian distributions), the posterior probability distributions of the parameters were obtained using the MCMC algorithm.When the optimization target is the branching ratio, a more accurate TS2 energy recommendation value was obtained. When the prior distribution was Gaussian distribution, the uncertainty range of the model-predicted branching ratio was reduced in a wide range of operating conditions, improving the predictive performance of the combustion reaction mechanism. When the prior distribution was a uniform distribution, a more accurate TS2 energy recommendation value was also obtained, but the uncertainty range of the model prediction was not significantly reduced. When the optimization target was the total rate constant and the prior distribution of input parameters was a Gaussian distribution, the RRKM/master equation model had higher predictive accuracy than experimental values, and further optimization was not possible. Based on the uniform distribution prior, the model optimization obtained a more accurate energy transfer parameter, but did not reduce the uncertainty range of the model prediction.

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*Corresponding author: feng2011@ustc.edu.cn

Exploring the chemistry behind low temperature auto-ignition of isopropyl nitrate in an RCM: an experimental and kinetic modeling study

Qifeng Hou[1], Weitao Liu[1], Zhaohan Chu[2], Xiaoqing Wu[1,3], Mengqi Wu[1], Zhongkai Liu[2], Shiyao Niu[1,4], Feng Zhang[1,*]
[1]Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China
[2]Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, P. R. China
[3]National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China
[4]School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

Keywords: Isopropyl nitrate (iPN); Ignition delay time; Rapid compression machine; Kinetic modeling.

The low-temperature auto-ignition chemistry of isopropyl nitrate (iPN) was experimentally and numerically investigated in the present study. The ignition delay times (IDTs) of iPN were measured stoichiometrically over a temperature range of 560-600 K at effective pressures of 5 and 10 bar in a rapid compression machine. A two-stage ignition phenomenon of iPN was observed. Both the first-stage IDTs and total IDTs vary rapidly within the narrow temperature range investigated (~40 K). A recent iPN kinetic mechanism proposed by Fuller and Goldsmith [1] for pyrolysis studies was extended. The reaction kinetics of CH_3CHO + NO_2 has been theoretically calculated at 500-1500 K and 0.01-100 atm. The rate information of $CH_3 + NO_2$ was updated based on previous theoretical results. The O_2-addition channel of acetyl radical (CH_3CO), which accounts for the first-stage IDT, was also considered in the present work. The extended iPN kinetic model predicts the two-stage IDTs well. Simulation results suggest that the IDTs are most sensitive to the following two reactions: (1) $CH_3 + NO_2 = CH_3O + NO$; (2) $CH_3 + NO_2 = CH_3NO_2$. The former promotes the overall reactivity by yielding the reactive methoxy radical, while the latter forms a relatively stable product (i.e., CH_3NO_2). The reaction of $CH_3CHO + NO_2 = CH_3CO + HONO$ supplements the formation of CH_3CO. The different consumption channels of CH_3CO radicals (the O_2-addition reaction and the decomposition reaction) lead to different chain reactions yielding OH radicals with increasing temperature in the ignition process. The “NO-NO_2 loop” is the main route for OH formation in the studied conditions, which is mainly responsible for the iPN ignition.

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*Corresponding author: feng2011@ustc.edu.cn

A Comparative Study on Flow Reactor Pyrolysis and Laminar Flame Propagation of Flame Synthesis Precursors: Tetraethoxysilane and Its Oxygenated Hydrocarbon Counterpart

Qilong Fang, Yan Zhang, Wei Li and Yuyang Li*
School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

Keywords

Tetraethoxysilane, Tetraethyoxymethane, Flow reactor pyrolysis, Laminar flame propagation, Kinetic model

Silica (SiO_2) nanoparticle is a kind of important inorganic chemical material, which has been widely adopted in catalysts, biomedicine, and lithium-ion batteries fields. Silicon-based organic compounds such as tetraethoxysilane (TEOS) generally serve as flame synthesis precursors of SiO_2 nanoparticles (Li et al. 2016). A deep understanding of their combustion characteristics is of great significance for regulating the synthesis processes of SiO_2 nanoparticles (Schulz et al. 2019). Only a limited number of experimental and kinetic model studies were performed, while most of them focused on the thermal decomposition of TEOS (Nurkowski et al. 2015; Herzler et al. 1997). Moreover, the critical consumption pathways for the key silicon-containing intermediates were ignored in the published kinetic models of TEOS, resulting in the failure of their predictions.

In this work, the flow reactor pyrolysis at 794-1085 K, 1 atm and laminar burning velocity (LBV) measurements at 423 K, 1 atm were carried out for TEOS. Furthermore, a comparative study between TEOS and its oxygenated hydrocarbon counterpart tetraethyoxymethane (TEOM) was also performed to explore the congener substitution effects between Si and C elements. Pyrolysis species such as methane, ethanol, ethylene, acetaldehyde, ethane, and carbon dioxide were detected by gas chromatography, and their mole fraction profiles versus the heating temperature were also obtained. It is observed that TEOS decomposes about 100 K slower than TEOM, showing a weaker pyrolysis reactivity. Great differences on the peak positions and values of the laminar burning velocities are also observed for the two fuels. Compared to TEOM with LBV peak located at $\phi = 1.35$, the peak of measured LBVs of TEOS is located at $\phi = 1.2$. Their LBVs intersect with each other at $\phi = 1.1$, and TEOM propagates much faster than TEOS under richer conditions. Combustion kinetic models of TEOS and TEOM were also constructed and validated against the newly obtained experimental data. Based on the rate of production analysis and sensitivity analysis, the critical pathways in the pyrolysis and flames of TEOS and TEOM were revealed. The fictitious diluent gas method was adopted to provide insight into the remarkable congener substitution effects on the LBVs of TEOS and TEOM.

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*Corresponding author: yuygli@sjtu.edu.cn

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*Corresponding author: yuygli@sjtu.edu.cn

Experimental and kinetic model studies on the pyrolysis of Hydroxylamine Nitrate Ionic Liquid and Hydroxylamine

Qingbo Zhu [1], Bingzhi Liu [1], Zhihong Hu [1], Qiang Xu [1], Yixuan Jing [1] and Zhandong Wang [1,2*]
[1] National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, PR China
[2] State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China

Abstract: Hydroxylamine nitrate is a promising green propellant, that has been studied as a substitute for hydrazine. However, there is still a great deal of uncertainty about the mechanism of hydroxylamine nitrate decomposition, which requires further fundamental investigations. In this work, the pyrolysis experiment of hydroxylamine nitrate in a low-pressure flow reactor was carried out (temperature range: 380-680 K, pressure: 200 Torr). It was found that hydroxylamine nitrate has strong low-temperature reactivity and begins to decompose at ca. 450 K. Some significant pyrolysis products were identified and quantified using synchronous vacuum ultraviolet photoionization mass spectrometry, including NH_3, H_2O, NO, HNO, NH_2OH, N_2O, HONO, and HNO_3. A detailed chemical kinetic model was updated to describe the thermal decomposition of hydroxylamine nitrate. The primary step in the decomposition of hydroxylamine nitrate is the proton transfer from the cation (NH_3OH^+) to the anion (NO_3^-), resulting in the formation of hydroxylamine and HNO_3. The updated model can well predict the experimental results of hydroxylamine and nitric acid, but for NH_3, NO, and other products, the prediction of the model is quite different from the experimental results. Thus, to further explore the decomposition kinetics of HAN, we carried out the pyrolysis experiment of hydroxylamine and used synchronous vacuum ultraviolet ionization mass spectrometry analysis and gas chromatography analysis to identify and quantify the pyrolysis products. Further update based on the above model. The kinetics analysis shows that the unimolecular dissociation of hydroxylamine is the main way of hydroxylamine consumption and the main source of NH_2 and OH. NH_2/OH radicals also play an important role in the consumption of hydroxylamine. The experimental results and model development of this work are expected to contribute to further investigation of the chemical kinetics of HAN and hydroxylamine.

***Keywords**:* Ionic liquids; Hydroxylamine nitrate; Pyrolysis; Unimolecular dissociation; Low-temperature reactivity

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*Corresponding author: E-mail: zhdwang@ustc.edu.cn (Z. Wang)

Quantum Chemical Study on the Enantioselective Sulfoxidation Catalyzed by Vanadium-Dependent Bromoperoxidase

Qinrou Li[1], Xiang Sheng[1]*
[1] Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Keywords

Sulfoxidation, Vanadium-Dependent Bromoperoxidase, Reaction mechanism, Quantum chemistry.

Chiral sulfoxides hold many attractive interests including biological activity and the potential of chiral auxiliaries, which will aid in the production of chiral drugs, agrochemicals, and other fine chemicals. Therefore, the synthesis of chiral sulfoxides is an active area of research. Due to the low enantioselectivities and yield, traditional chemical methods face some tough challenges in the synthesis of chiral sulfoxides. [Han et al., 2018] However, the biosynthesis of sulfoxidation could provide new possibilities to solve those problems. The vanadium-dependent bromoperoxidase (VBPO) belonging to haloperoxidases can catalyze the oxidation of organic sulfides to sulfoxides by means of “green” oxidant hydrogen dioxide. [Brink et al., 1998] The high stability in organic solvents and the ability to withstand high temperatures demonstrate that VBPO has great potential in biocatalysis. Owing to the ambiguous reaction mechanism and the unclear reasons for the stereo-preference in the different sources of VBPO, limited applications were reported for VBPO compared to other enzymes which successfully apply to the synthesis of chiral sulfoxides. In the current work, by using the quantum chemical cluster approach, mechanisms of the oxidation of sulfides and the selectivity of VBPO from the brown alga *Ascophyllum nodosum* (An-VBPO) and the red alga *Corallina pilulifera* (Cp-VBPO) have been investigated. The key residues Trp338 and Phe315 in An-VBPO along with Arg396 and Phe372 in Cp-VBPO have been indicated to play important roles in controlling the enantioselectivities. The promising results obtained in this work will promote the rational design of biocatalytic and biomimetic catalysts of VBPO.

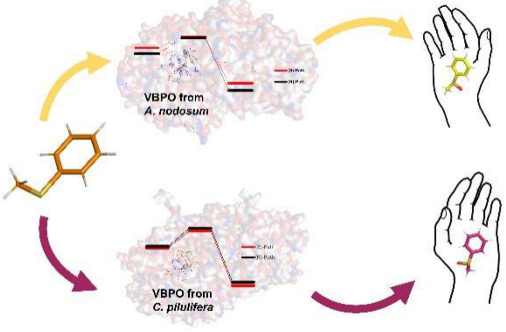

***Figure.** The VBPO from Ascophyllum nodosum and Corallina pilulifera can catalyze the oxidation of methyl p-tolyl sulfide to the different enantioselectivities of the sulfoxide.*

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*Corresponding author: shengx@tib.cas.cn

MODELING NONTHERMAL REACTIONS IN COMBUSTION

Raghu Sivaramakrishnan[1,*]
[1] CSE Division, Argonne National Laboratory, 9700 S. Cass Avenue, Lemont, IL-60439, USA

Keywords

Prompt Dissociations, Termolecular Reactions, Master Equation, Dynamics, Flames.

Kinetics models for practical applications such as in combustion have traditionally included networks of elementary reactions where the products from each of these are assumed to be thermalized before undergoing subsequent reactions. One common exception to this scenario that has been well-characterized are chemically activated reactions (Rabinovitch and Flowers) of energized intermediates. These reactions occur on the same potential energy surface as that of the incipient reaction that is the source of the energized intermediates. In recent years, motivated by experimental and theoretical studies (Glowacki et al., Burke et al., Labbe et al., Sivaramakrishnan et al.), we have been characterizing nonthermal reactions (prompt dissociations, termolecular reactions) of energized intermediates occurring on a different potential energy surface than the reaction that is the source for the initial ro-vibrational excitation (of the intermediates of interest). Here we would like to discuss some recent efforts on characterizing prompt dissociations of resonantly stabilized and carbonyl centered radicals and identifying criteria for their relevance in flame chemistry. Additionally, we would also like to highlight the potential for termolecular chemistry induced in radical recombinations and methods to adequately represent such nonthermal reactions in practical simulations.

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*Corresponding author: raghu@anl.gov

AUTOMATING THE GENERATION OF KINETIC MODELS FOR HALOGENATED HYDROCARBONS

Richard H. West[1,*]
[1] Department of Chemical Engineering, Northeastern University, Boston MA, USA

Keywords

Automated mechanism generation, combustion, halogenated hydrocarbons.

Halogenated hydrocarbons have long been used as flame suppressants and as refrigerant working fluids, applications in which their combustion is a critical safety concern. Due to environmental concerns there is now a search for a new generation of compounds that have both a low ozone depleting effect and a low global warming potential. Unfortunately, the proposed compounds are much more flammable, and can display curious combustion behaviors such as extinguishing flames at some conditions but accelerating them at others. To accelerate the development of new compounds and mixtures, we must build kinetic models of the combustion that can explain and predict the behavior. The open-source Reaction Mechanism Generator (RMG) software is well known for generating detailed kinetic models of combustion kinetics. We have now added the ability to predict halogenated hydrocarbons.

High quality (G4) thermochemistry data for over 16,000 halocarbons were calculated with an automated workflow, and used to train a group-additive scheme that can predict novel molecules and radicals (Farina et al., 2021). Existing reaction families in RMG were updated and new families specific to halogens were created. Over 1,000 reaction rates were calculated via (somewhat automated) transition state theory calculations. These rates, combined with literature values, were used to train decision-tree estimators for novel reactions (Farina et al. 2023). Halogen-containing groups were added to the vibrational frequency estimation routines used by RMG to get densities of states for automated Master Equation calculations of pressure-dependent reactions, and to the estimators of transport properties needed for flame speed calculations.

The updated version of RMG was tested on some known compounds, then used to study binary blends of halogenated hydrocarbons, showing the effect of cross-reactions that might be omitted when merging combustion models for two different compounds. Model truncation error (omitting pathways) is shown to be an important challenge for these systems.

Automating the generation of detailed halocarbon kinetic models through RMG helps screening for the next generation of environmentally-friendly refrigerants and flame suppressants, a task that would be both slow and expensive if conducted without automation.

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*Corresponding author: r.west@northeastern.edu

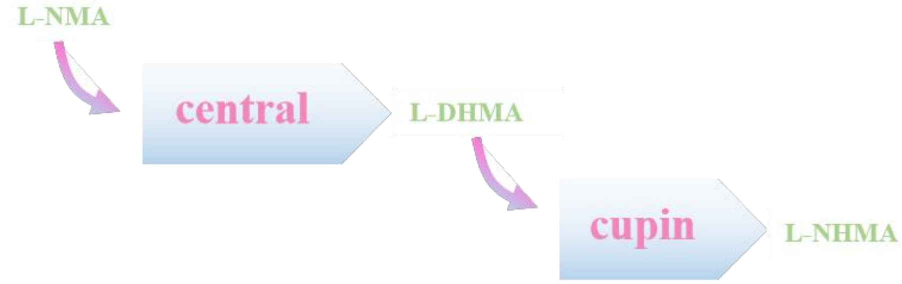
Theoretical Study on Catalytic Mechanism of Diiron Cofactor in Metalloenzyme SznF

Rui-ning Li[1], Shi-lu Chen[1,*]
[1] Beijing Institute of Technology, School of Chemistry and Chemical Engineering, No. 5 South Street, Zhongguancun, Beijing, P. R. China

Keywords

Non-heme dirron enzymes, Density functional theory, reaction mechanism.

Heme-oxidase-like diiron oxidase and oxygenase (HDO) are an emerging family of enzymes containing diiron cofactors. Enzymes with dinuclear iron cofactors coordinated by histidine and carboxylate ligands catalyze biologically, biomedically, and environmentally important reactions in organisms ranging from bacteria to humans (Bollinger et al., 1991, Rajakovich et al., 2020). SznF, a new member of this family discovered, sequentially hydroxylates the two unmethylated guanidinium nitrogen atoms of N^{ω}-methyl-L-arginine (L-NMA) in its central domain, and then the cupin domain oxidatively rearranges the modified L-DHMA to N^{δ}-hydroxy-N^{ω}-methyl-$N^{\omega'}$-nitroso-L-citrulline, which is the source of the N-nitrosourea pharmacophore of streptozotocin (SZN) as a precursor (Ng et al., 2019). In this work, we investigate the catalytic mechanism of SznF by density functional theory. Our results enrich the understanding of the synthesis of N-nitroso group and can also provide a theoretical basis for the exploration of the structural and functional features of the emerging family of diiron enzymes.



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*Corresponding author: **shlchen@bit.edu.cn**

Kinetic study of the tropospheric reaction of OH with $CF_3CHFCF_2OCH_3$ (HFE-356mec3) and $CHF_2CHFOCF_3$ (HFE-236ea1) between 263 and 353 K

Sara Espinosa[1,2], José Albaladejo[1,2] and Elena Jiménez[1,2,*]
[1] Departamento de Química Física, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha (UCLM), Avda. Camilo José Cela 1B, 13071, Ciudad Real, Spain.
[2] Instituto de Investigación en Combustión y Contaminación Atmosférica (ICCA), UCLM, Camino de Moledores s/n, 13071, Ciudad Real, Spain.

Greenhouse gases; HFC replacements; atmospheric lifetime; radiative efficiency; kinetics; laser induce fluorescence

Hydrofluoroethers (HFEs) have been developed as new alternatives to high global warming potential (GWP) compounds, such as hydrofluorocarbons (HFCs), in many industrial applications standing out as heat transfer agents in refrigeration. To assess the suitability of HFEs as potential candidates for replacing high GWP species is essential to evaluate their expected impact on climate change prior to their widespread. For that purpose, the rate coefficient for the reaction of a certain HFE with OH radicals (k_{OH}) the main diurnal atmospheric oxidant, and their infrared (IR) absorption cross sections must be determined. Thus, the present study investigates for first time the temperature dependence of the absolute OH-rate coefficient as a function of temperature, ($k_{OH}(T)$ in $cm^3 molecule^{-1} s^{-1}$), in the range of 263-353 K and 100 Torr of the $CF_3CHFCF_2OCH_3$ (HFE-356mec3) and $CHF_2CHFOCF_3$ (HFE-236ea1). The observed preliminary T-dependences of $k_{OH}(T)$ are well described by the following Arrhenius expressions:

HFE-356mec3: $k_{OH}(T) = (1.18\pm1.07)\times10^{-12} \exp[-(1046\pm27)/T]$

HFE-236ea1: $k_{OH}(T) = (7.76\pm4.26)\times10^{-13} \exp[-(1417\pm28)/T]$

To determine $k_{OH}(T)$ the pulsed laser photolysis/laser-induced fluorescence technique was used (Blázque et al., 2022). From these results atmospheric lifetimes due to OH-reaction are 1.2 years for HFE-356mec3 and 5.5 years for HFE-236ea1. In addition, Fourier transform IR spectroscopy was used to determine the IR absorption cross sections between 600 and 4000 cm^{-1} (Blázquez et al., 2022). Radiative efficiencies (REs) corrected with lifetime for these species were calculated to be 0.26 W $m^{-2}ppbv^{-1}$ for HFE-356mec3 and 0.39 W $m^{-2}ppbv^{-1}$ for HFE-236ea1. The GWPs at 100-yrs time horizon are 118 and 885 for HFE-356mec3 and HFE-236ea1, respectively. Therefore, the contribution of HFE-356mec3 and HFE-236ea1 to global warming of Earth could be significant if the use of these HFEs becomes more widespread and their emissions to the atmosphere increase. However, these HFEs contribute to the global warming of Earth in much lesser extent than HFCs with similar structures, which have GWP of 804-8060.

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*Elena.Jiménez@uclm.es

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*Elena.Jiménez@uclm.es

Single-atom catalysis: mechanism and dynamics

Sen Lin
University of Fuzhou University, State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou, P. R. China

Keywords: Single-atom catalysis; density functional theory; reaction mechanism; dynamics

Single-atom catalysis involves complex reactions and dynamic processes, lacking an accurate understanding of the correlation between the coordination environment and single atoms, as well as the structure of the active center and the dynamics of the reaction intermediates. Our group has recently made significant progress in the development of new catalyst models and theoretical studies on the regulation of the coordination environment and reaction mechanisms, including: (1) the development of a "single-atom promoter" model that clarifies the multiple roles of single atoms in catalysis; (2) the discovery of the importance of post-transition state dynamics on selectivity and the construction of the first potential energy surface for single-atom catalysis to understand the dynamics of hydrogen spillover; and (3) the discovery of the important influence of the outer coordination environment on single-atom performance.

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*Corresponding author: slin@fzu.edu.cn

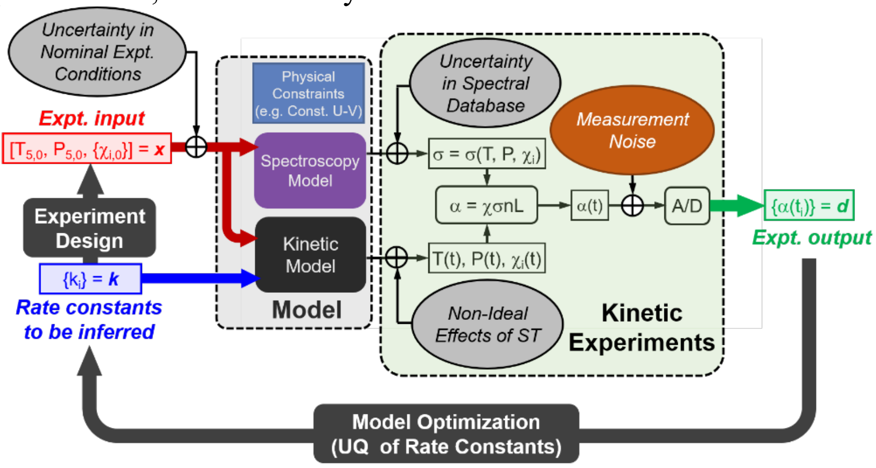
Information-Driven Experiment Design for Shock Tube and Laser Absorption Measurements of Fundamental Reaction Rate Constants

Shengkai Wang[1,2*]
[1] State Key Laboratory for Turbulence and Complex Systems, Department of Mechanics and Engineering Science, College of Engineering, Peking University, Beijing, 100871, P.R. China
[2] Joint Laboratory of Marine Hydrodynamics and Ocean Engineering, Laoshan Laboratory, Shandong, 266299, P.R. China

Keywords

Shock Tube, Laser Diagnostics, Chemical Kinetics, Experimental Design, Bayesian Analysis

Shock tube experiments, paired with precision laser diagnostics, are ideal venues to generate kinetics data critically needed for the development, validation and optimization of modern combustion kinetics models. However, to design feasible, sensitive and information-rich experiments that may yield such data often requires sophisticated planning. This study presents a mathematical framework to guide such experimental design, together with a quantitative approach to pin-point the optimal conditions for specific experimentation under realistic constraints of the shock tubes and diagnostic tools involved. Specifically, this study utilizes a Bayesian approach to maximize the expected prior-posterior information gain regarding the rate constants to be inferred from the intended experiment. Demonstrative studies on three main types of shock tube kinetic experiments, including ignition delay time measurement, species yield analysis and direct determination of fundamental reaction rate constants (as in Wang et al., 2022), are presented. Based on the current framework, an iterative procedure involving information-driven, alternating steps of experiment design and model optimization is also proposed (see Fig. 1), with an aim to potentially automating the cycle of developing detailed kinetic models. Perspectives on the challenges and opportunities regarding a few advanced topics, such as asymptotic convergence, detection of model-form error, model comparison and selection, rejection of spurious data, are also briefly discussed.



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*Corresponding author: sk.wang@pku.edu.cn

A Large-Scale High-Quality Dataset for Predicting Activation Energy for Alkene Radical Reactions

Shih-Cheng Li[1,2], Xiaorui Dong[1], Yi-Pei Li[2,*], and William H. Green[1,*]
[1] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States
[2] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

Keywords: Activation energy, Radical reaction, Machine learning

Light alkenes serve as reaction intermediates in the combustion chemistry for a range of fuels, so predicting activation energy for radical reactions of alkenes is crucial for building kinetic mechanisms to model combustion systems. Conventionally, kinetic parameters were fit to a specific experimental dataset, which may limit their applicability to systems under distinct conditions and potentially lead to inaccuracies in kinetic models. To address this issue, the estimation of kinetics has gradually shifted from postdictive to predictive modeling approaches recently. However, the lack of high-quality experimental and quantum mechanical data hinders the ability to obtain reliable kinetic parameters. In this work, we utilized an automated workflow to generate approximately 6,000 radical reactions calculated at CCSD(T)-F12/cc-pVDZ-F12//ωB97XD/def2-TZVP. To the best of our knowledge, this is the largest high-quality radical reaction dataset published to date. A directed message passing neural network (D-MPNN) was trained on this dataset to predict activation energy, and it showed a testing MAE of 3.07 kcal/mol with respect to the coupled-cluster values. This poster will showcase the automatic pipeline for dataset generation using equivariant graph neural networks and semiempirical quantum mechanics. Additionally, a comparison of performance between the D-MPNN model and tree-based kinetic estimators will be presented.

*Corresponding authors: Yi-Pei Li (yipeili@ntu.edu.tw), William H. Green (whgreen@mit.edu)

Quantum chemical modeling of enzymatic reactions in extremophiles

Shi-Lu Chen
School of Chemistry and Chemical Engineering, Beijing Institute of Technology, China

Keywords

Enzyme catalysis; Reaction mechanism; Density functional calculations; Extremophiles; Methanogen

The extremophiles are the microbes living in special environments, such as hot spring, mine drainage, and hydrothermal vent. They often have special metabolisms. The mechanisms of their enzymatic reactions are important for understanding the metabolism of matter and energy in microbes and the biogeochemical element cycles, and also are the important prototypes for biomimetic catalysis. Using the quantum chemical modeling method, we have investigated a lot of enzymatic reactions in extremophiles, such as methanogenic archaea, perchlorate-reducing bacteria, and anaerobic ammonium oxidation bacteria. This talk will focus on the partial enzymatic reactions in methanogenic archaea (Wu et al., 2022; Chen et al., 2014; Chen et al., 2012; Chen et al., 2009).

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*Corresponding author: shlchen@bit.edu.cn

Theoretical investigation on the reaction mechanism of CO_2 hydrogenation by the artificial enzyme LmrR

Shi-Ping Wang[1], Su Hao[1] and Sheng Xiang[1,*]
[1] Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Keywords

Homogeneous catalysis, Biocatalysis, Reaction mechanism, Quantum chemistry.

Hydrogenation of CO_2 is one of the important routes of carbon capture, storage and utilization (Atsbha et al., 2021). The hydrogenation of CO_2 promoted by the traditional chemical catalysts usually requires high temperature and pressure and heavy metals. Enzymatic hydrogenation of CO_2 provides a green alternative to the chemical method. However, the known biocatalytic CO_2 hydrogenation have low catalytic efficiency. To combine the advantages of chemical catalysts and biocatalysts, the most direct way is to introduce chemically homogeneous catalyst into the protein. In a recent study, an artificial metalloenzyme was designed by combining the $Rh(PNP)_2$ homogeneous catalyst and the lactococcal multidrug resistance regulator (LmrR) protein (Laureanti et al., 2019). This metalloenzyme shows catalytic activity of the hydrogenation of CO_2, but its catalytic efficiency is extremely low and the reaction mechanism is still ambiguous. In the present work, the detailed reaction mechanisms of $Rh(PNP)_2$ catalyst and LmrR@$Rh(PNP)_2$ metalloenzyme are revealed by the theoretical investigation with quantum chemistry and molecular dynamics methods. The differences between the metalloenzymatic catalysis and the homogeneous catalysis are analyzed, and the effects of the surrounding residues on catalytic efficiency are revealed. The present study can provide useful information for the rational design of more efficient artificial metalloenzyme for CO_2 hydrogeneration.

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*Corresponding author: shengx@tib.cas.cn

Development of an autogenerated and rate-rule optimized combustion kinetic model for the isomers of pentane

Sirio Brunialti[1], Xiaoyuan Zhang[1], S. Mani Sarathy[1], Tiziano Faravelli[2], Alessio Frassoldati[2],
Pengzhi Wang[3], Henry J. Curran[3], Máté Papp[4], Tamás Turányi[4], Tibor Nagy[5,*]

[1] Clean Combustion Research Center, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia
[2] Department of Chemistry, Materials, and Chemical Engineering, Politecnico di Milano, Piazza Leonardo da Vinci, 32, Milano 20133, Italy
[3] Combustion Chemistry Centre, School of Biological and Chemical Sciences, Ryan Institute, MaREI, University of Galway, Galway, Ireland
[4] Institute of Chemistry, Eötvös Loránd University, 1117, Pázmány P. stny. 1/A, Budapest, Hungary
[5] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, 1117, Magyar tudósok krt. 2, Budapest, Hungary

Keyword: mechanism; Rate rules; Mamox++; Alkanes; Optima++, Foctopus

The Optima++ kinetic parameter optimization code (Turányi et al, 2012) (Goitom et al, 2022) (Papp et al, 2023) has been extended to rate rules and its application is demonstrated on the autogenerated combustion mechanisms of pentane isomers. A suitably modified version of Mamox++ (Ranzi et al., 1995) (Brunialti et al., 2022) was used for mechanism auto-generation based on rate rules collected from the literature for the most important reaction classes (Brunialti et al., 2022) (Wang et al., 2023). Submechanisms for all pentane isomers have been generated and merged with the C_{0-4} core part of the NUIGMech 1.3 mechanism (Panigrahy et al. 2022). Thermodynamic data of species were taken from the paper of (Elliott et al, 2023) and, in case of unavailability, they were automatically computed by Mamox++ using Benson's group additivity method (Benson and Buss, 1958). Forward and backward rate coefficients of reaction classes were defined separately to eliminate the impact of thermodynamic data uncertainty on the accuracy of backward rate coefficients. Important rate rules were identified using a recently proposed active parameter selection strategy (Kovács et al., 2022), which is based on the principal component analysis of a scaled local sensitivity matrix. The analysis was carried out on a representative subset of experimental data collection, which included ignition delays from shock tube and rapid compression machine experiments, and species concentrations from jet-stirred reactors covering wide ranges of conditions. The Arrhenius parameters of the influential rate rules were optimized within their prior uncertainty range while considering the whole data collection as a target. Significant improvement was achieved in the accuracy of the model, while at the same time, the rate coefficients of the rules could also be constrained.

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EFFECT OF MULTI-STRUCTURE ON KINETICS OF PEROXY RADICAL HYDROGEN MIGRATION REACTION OF DIETHOXYMETHANE (DEM)

Siyu Chen[1], Zerong Li[2] and Quan Zhu[1,3*]
[1] College of Chemical Engineering, Sichuan University, Chengdu 610065, PR China
[2] College of Chemistry, Sichuan University, Chengdu 610064, PR China
[3] Engineering Research Center of Combustion and Cooling for Aerospace Power, Ministry of Education, Sichuan University, Chengdu, Sichuan 610065, PR China

Keywords

Quantum chemical calculation, Kinetics, H-migration, Multi-structure, Anharmonicity

Diethoxymethane (DEM) is a potential carbon-neutral fuel with high reactivity at low temperatures. The peroxy radical hydrogen migration reactions can be seen as a committed step in the low-temperature oxidation mechanism. The 1,5 and 1,7 H-migration reactions for a peroxy radical of DEM ($CH_3CH(OO)OCH_2OCH_2CH_3$) were studied using theoretical methods. To investigate the multi-structure effect on the energy barriers and rate constants, an exhaustive structural search was conducted for the reactants, transition states and products. The multi-conformation effect caused by bond rotations was treated as the anharmonicity effect. The inter-conversion of cyclic transition states and the position of the substituent in the cyclic transition state caused four types of transition states to be treated as multiple pathways in rate estimation. The energy barriers and the rate constants of different pathways caused by configurations of transition states proved that the 1,5 H-migration reactions with chair structures of transition states are much faster than those with boat structured transition states. And for 1,7 H-migration transition states, the boat-chair structure with a substituent in the equatorial position is the lowest energy structure, but the rate constants of the four reaction pathways are close to each other. The calculated rate constants indicate that different choices of pathways may change the competition between 1,5 and 1,7 H-migration reactions. Concerning multi-structure, tunneling and variational effects, more accurate rate constants were obtained. And the computed results show that the anharmonicity effect has a more significant influence on the rate constants of H-migration and makes the 1,5 H-migration reaction faster than the 1,7 H-migration. The pressure-dependent rate constants show that the falloff effect of the 1,5 H-migration reaction is more obvious than that of the 1,7 H-migration reaction. The thermodynamics and kinetics represented in this study may be helpful to understand the low-temperature oxidation mechanism of DEM and are important for future comprehensive autoignition behavior.

Table 1. The range of multi-structure torsional anharmonicity factor (F), tunneling transmission coefficient (κ) and recrossing transmission coefficient (Γ) for R1 and R2 at 500-1500K.

	R1	R2
F	0.1056~0.0883	0.0158~0.0099
κ	5.03 ~1.13	4.72~1.17
Γ	0.995~0.548	0.894~0.548

*Quan Zhu: qzhu@scu.edu.cn

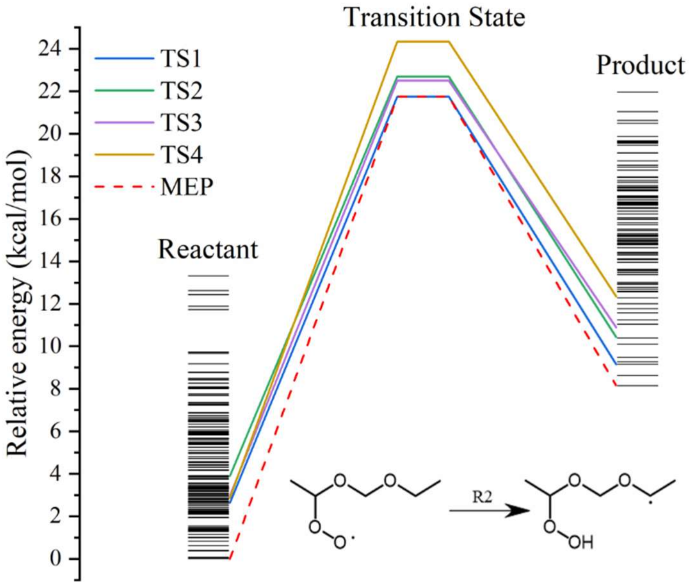

Figure 1. Potential energy profiles of R2 for different structures of transition states.

*Quan Zhu: qzhu@scu.edu.cn

Untangling the molecular complexity of interstellar ices in a synchrotron-based space simulation machine

Tao Yang
tyang@lps.ecnu.edu.cn
State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062,
P. R. China

It is essential to untangle the formation of complex organic molecules (COMs) on interstellar grains, which might eventually contribute to establishing predictive astrochemical reaction networks and recognizing evolution stages of molecular clouds and star-forming regions. Within the framework of research collaboration between East China Normal University, University of Hawaii, and University of Science and Technology of China, I present here a novel space simulation machine featured in synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS). By replicating the conditions of ice-coated interstellar grains (ice type and thickness, temperature, electron irradiation dose), the apparatus affords an explicit isomer-selective identification of COMs upon their sublimation into the gas phase via tunable, fragment-free vacuum ultraviolet photoionization. Such a space simulation system with rapid extraction of molecular complexity can be of potential use in exploring the underlying formation pathways of COMs in astrophysically relevant interstellar ices.

Keywords: Complex organics molecules (COMs), interstellar ices, synchrotron vacuum ultraviolet photoionization (SVUV-PI), photoionization efficiency (PIE) curves

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A NOVEL ACTIVE PARAMETER SELECTION STRATEGY FOR THE EFFICIENT OPTIMIZATION OF COMBUSTION MECHANISMS

Márton Kovács[1], Máté Papp[1], Tamás Turányi[1,*], Tibor Nagy[2,*]
[1] Institute of Chemistry, Eötvös Loránd University, 1117, Pázmány P. stny. 1/A, Budapest, Hungary
[2] Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, 1117, Magyar tudósok krt. 2, Budapest, Hungary

Keywords

Parameter optimization, Sensitivity analysis, Uncertainty of parameters, Uncertainty of experimental data, Methanol/NOx combustion

Optimization of large combustion mechanisms means that a few dozen parameters (called active parameters) are optimized within their uncertainty limits to achieve a better reproduction of the experimental data, which is usually measured by a mean square error function. In previous studies, the active parameters were selected based either on their local sensitivity coefficients (strategy S) or on the products of local sensitivity coefficient and a corresponding uncertainty parameter (strategy SU). This latter measure is known by various names: optimization potential, sensitivity-uncertainty index or uncertainty-weighted sensitivity coefficient. In this work, we proposed three novel active parameter selection strategies of increasing complexity (PCA-SU, PCA-SUE, PCALIN) and demonstrated their superior performance in the optimization of pre-exponential factors (A) in a methanol/NOx combustion mechanism (562 reaction steps of 70 species) against 2360 data measured in shock tube, JSR and flow reactor experiments (Kovács et al., 2022). The novel methods are based on the principal component analysis (PCA) of sensitivity matrices scaled by the uncertainties of parameters (U) and the uncertainty of the experimental data (E). These PCA-based methods take into account parameter correlations and designate parameters groups and corresponding relevant subsets of experimental data, thereby a factor of 4-7 savings in optimization time was achieved over the S and SU methods. PCA-SUE method performed better than the PCA-SU as it also considered the uncertainty of the experimental data. The PCALIN strategy is similar to PCA-SUE, but it also considers the linear change (LIN) of the error function, which depends on the simulation error of experimental data, and thereby it could provide the most accurate models as a function of the number of active parameters. Based on the PCALIN strategy, fitting all three Arrhenius parameters resulted in further improvements, however, it provided moderate improvements over simple A-factor tuning and required significantly more computer time.

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*Corresponding author: turanyi@chem.elte.hu, nagy.tibor@ttk.hu

Automated Generation of Combustion Reaction Mechanisms

Tong Zhu[1,2*]
[1]School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, China
[2]NYU-ECNU Center for Computational Chemistry at NYU Shanghai, Shanghai, China

Combustion Mechanism; Reaction Network; Machine Learning; Rate constant

Aviation fuel is a complex mixture with extremely complicated thermal decomposition and combustion reaction pathways. It is difficult to systematically understand the combustion mechanisms of complex kerosene fuels relying solely on current experimental methods and computational techniques. Guessing and providing all possible reaction pathways manually is difficult to achieve, and calculating each reaction pathway using quantum chemistry methods is even more impractical. Driven by the goals of carbon peak and carbon neutrality, people are constantly exploring new low-carbon and zero-carbon fuels, which puts forward a more urgent demand for the efficient construction of high-precision combustion mechanisms. Here we report some recent progress we have made in this direction. By fully integrating machine learning and physical models, we have achieved rapid searching of combustion reaction pathways and fast prediction of rate constants. The introduction of machine learning methods ensures the efficiency of the method, while the physical model fully guarantees its accuracy and extrapolation capability. The development of this method is expected to provide more reliable and efficient tools for the rapid construction of combustion reaction mechanisms.

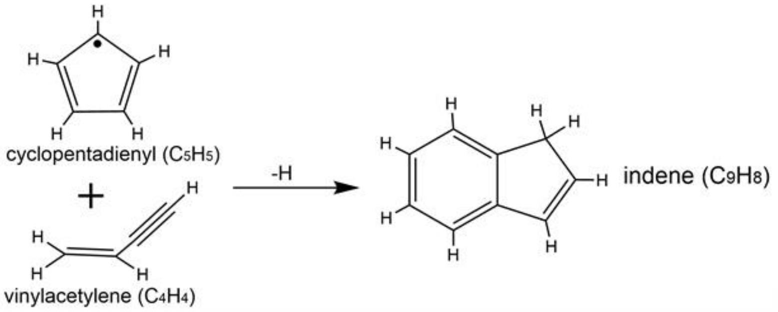
*tzhu@lps.ecnu.edu.cn

VUV photoionization study of the gas formation of indene-a molecular building block of nonplanar PAHs

Wang Li[1], Yi-Fan Zhang[1] Chang-Yang Wang,[1] Jiu-Zhong Yang,[1] Long Zhao[1,2]*
[1] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China*
[2] *School of Nuclear Science and Technology, University of Science and Technology of China, Hefei, Anhui 230027, China*

Keywords
gas-phase reactions, reaction mechanism, reactive intermediates, ab initio calculations.

The indene (C_9H_8) molecule, carrying five- and six-membered rings, represents the simplest molecular building block of polycyclic aromatic hydrocarbons (PAHs) with stereo-configurations (e.g. corannulene etc.). The reactions involved [C1 + C8], [C2 + C7], and [C3 + C6] systems leading to indene formation have been investigated experimentally and theoretically. Cyclopentadienyl ($C_5H_5•$), as a typical resonantly stabilized free radical (RSFR), is contemplated as the reactive intermediate in molecular mass growth processes leading to PAHs. Exploiting a chemical microreactor in combination with an isomer-selective product identification through fragment-free photoionization utilizing tunable vacuum ultraviolet (VUV) light in tandem with the detection of the ionized molecules by a high resolution reflection time-of-flight mass spectrometer (Re-TOF-MS),[1] along with quantum theoretical calculations, the present investigation provides compelling evidence on the formation of indene through cyclopentadienyl ($C_5H_5•$) reacting with vinylacetylene (C_4H_4). Our findings reveal hitherto a novel rapid [C5+C4] formation pathway of indene at elevated temperature, which supplements the indene synthesis network in combustion and interstellar environments.



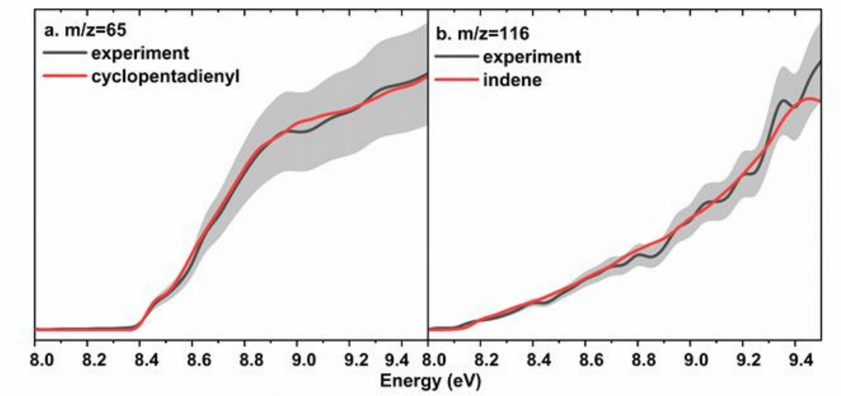


Figure. Experimental photoionization efficiency curve of m/z=65 and 116.

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* Long Zhao <zhaolong@ustc.edu.cn

An experimental and kinetic investigation on the two-stage ignition behavior of NH_3/H_2 mixtures in an RCM

Wanxiong Liao[1], Yiru Wang[1], Zhaohan Chu[1], Chenyue Tao[1] and Bin Yang[1,*]
[1] Tsinghua University, Center for Combustion Energy and Department of Energy and Power Engineering, 30 Shuangqing Road, Beijing, P. R. China

Keywords

Ammonia; Hydrogen, Two-stage ignition, Rapid compression machine, Ignition delay time.

The two-stage ignition behavior of NH_3/H_2 mixtures was studied using an RCM. Ignition delay times and first-stage ignition delay times for NH_3/H_2 mixtures were measured under temperatures ranging from 881 to 1127 K, pressures of 15 and 25 bar, and equivalence ratio (ϕ) of 1.0 and 1.5. H_2/NH_3 ratios ranged from 10% to 50% in fuel mixtures. Two-stage ignition behavior was observed in some test mixtures: a 10% H_2 blend at $\phi = 1.0$ and a 25% H_2 blend at $\phi = 1.5$. Time-resolved species concentrations were recorded during the single- and two-stage ignition process of NH_3/H_2 mixtures using a fast sampling system combined with the GC method. Species evolution suggested that the consumption of NH_3 and H_2 separated during the two-stage ignition process. The oxidation of H_2 primarily occurred at the first-stage ignition point while NH_3 oxidation occurred at the total ignition point. The kinetic model optimized in this work can well predict the two-stage ignition behavior of NH_3/H_2 and the species profiles.

The oxidation of H_2 was found to be the main initiator of NH_3 oxidation and the resulting heat release. For NH_3/H_2 mixtures with 50% H_2 content, H_2 oxidation can trigger the total combustion of NH_3, exhibiting the characteristics of single-stage ignition. In contrast, a small amount of H_2, such as 10%, can only initiate the partial consumption of NH_3, leading to the two-stage ignition behavior. Different sensitivity distributions were observed in the total ignition delay time and the first-stage ignition delay time. The first-stage ignition delay time was more sensitive to NH_3 reactions with HO_2, OH, and H radicals, while the total ignition delay time was more sensitive to NO_2-involved reactions. The observations demonstrated that the co-oxidation of fuels in the first-stage ignition was primarily dominated by H_2 oxidation chemistry, while NH_3 oxidation became dominant after the first-stage ignition.

Factors influencing the ignition behavior of NH_3/H_2 mixtures were discussed through simulation studies under various operating conditions. It was observed that there was a threshold temperature and pressure that distinguishes between single-stage and two-stage ignition phenomena. The temperature range for the two-stage ignition behavior was limited and depended on the relative reactivity of NH_3 and H_2 in the mixture. The H_2 fraction significantly affected the ignition behavior, with an increase in H_2 fraction leading to an increase in the intensity of the first-stage ignition and a decrease in the distance between the first-stage and total ignition points. When the H_2 fraction exceeded a certain threshold, two-stage ignition disappeared, and a fusion of the first-stage and total ignition occurred. By identifying these thresholds, it is possible to better understand the factors that contribute to the ignition behavior of NH_3/H_2 mixtures and to develop strategies for controlling and optimizing the combustion process.

*Corresponding author: byang@tsinghua.edu.cn

Systematic construction of combustion reaction models for large hydrocarbon fuels based on a two-step reaction scheme

Wei Shen[1], Jiyu Liao[2], Xingyu Liang[1], Kun Wang[1*]
[1] State Key Laboratory of Engines, Tianjin University, Tianjin 300350, China
[2] CISDI Information Technology (Chongqing) Co., Ltd, Chongqing 400000, China

Keywords

Automatic generation of combustion reaction model, two-step reaction scheme, high-temperature combustion, large hydrocarbon fuels.

Understanding the combustion chemistry of large hydrocarbons contained in practical gasoline, diesel and jet fuels is critical for the reduction of pollutant emissions and increase of fuel/engine efficiencies. The primary objective of the present study was to illustrate the methodology and applications of a simplified modeling approach based on a two-step reaction scheme (TSRS) for describing the combustion chemistry of large hydrocarbon fuels under engine-relevant high-temperature conditions. Under such conditions, the combustion process of large hydrocarbons consisted of two distinct, subsequent reaction steps: the first step was the prompt fuel decomposition, converting the parent fuel to several intermediate products; the second step was the oxidation reactions of the decomposed products. Particularly, the second step was slower, thus rate-limiting and controlling the heat release and formation of final combustion products of the entire combustion reaction process. Firstly, an automatic analysis by mathematical methods was performed to obtain a unified treatment for hydrocarbons with different molecular sizes. Based on the analysis of characteristic time scale of elementary reaction and steady-state assumption, TSRS used a fuel decomposition sub-model to convert the fuel into several major products, including ethene, propene, butene and methane for n-alkanes, which was then described by a detailed foundational fuel chemistry mechanism. Through this scheme, reaction models for large hydrocarbons were compact and with similar size of ~110 species and ~800 reactions. Next, one common simplified combustion reaction model was created for several selected large hydrocarbons ranging from C_8-C_{16}, and validated by comprehensive datasets from literature, including speciation, ignition delay times and laminar flame speeds. Good agreements were achieved, showing the robustness of simplified modeling by the two-step reaction scheme. Then, model analysis was performed to unveil the inherent similarities and differences among these fuels with molecular sizes. Lastly, the thus-developed model was shown still subject to reduction to further shrink the size that may satisfy the needs of advanced computational fluid dynamic (CFD) simulations.

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*Corresponding author: kwang5@tju.edu.cn

Sabatier Principles of Metal-Support Interaction for Growth of Supported Nanocatalysts

Wei-Xue Li[1,*]
[1] University of Science and Technology of China, 96 Jinzhai Road, Hefei, P. R. China

Keywords

Metal-Support Interaction, Scaling Relationship, Growth, Metal Nanocatalyst

The stability of supported nanocatalysts is crucial to meeting environmental and energy challenges and necessitates fundamental theory to relieve trial-and-error experimentation and accelerate lab-to-fab translation. Among others, metal-support interaction is thought as one of the most fundamental concept and vital to the overall stability of supported nanocatalysts. In particularly, strong metal-support interaction received long standing attention since it was proposed in 1969, though the description was limited to the phenomenal and qualitative aspects. Here we report a Sabatier principle of metal-support interaction for stabilizing metal nanocatalysts against sintering based on the kinetic simulations of 323 metal-support pairs using scaling relations from 1252 energetics data (Hu and Li (2021)). Too strong of an interaction is shown to trigger Ostwald ripening (Hu and Li (2018)) whereas too weak of an interaction stimulates particle migration and coalescence (Hu and Li (2019)). High-throughput screening of supports enables the sintering resistance of nanocatalysts to reach the Tammann temperature on homogeneous supports and far beyond it on heteroenergetic supports. This theory is substantiated by first-principles neural network molecular dynamics simulations, enable to quantify when strong metal-support interaction is strong metal-support interaction and paves the way for the design of ultrastable nanocatalysts.

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*Corresponding author: e-mail address

Sulfur-Induced Dynamic Reconstruction of Iron-Nitrogen Species for Highly Active Neutral Oxygen Reduction Reactions

Wenjie Wang[2], Tianpei Zhou[1], Kai Zhang[1], Chun Wang[1], Xiang Shi[1], Lin Wang[1], Qinghua Liu[2], Yang Wang[1], Qiyang Jiao[1], Guixin Ma[3], Chen Ye[3], Yi Xie[1,3], Xiaojun Wu[1], Wangsheng Chu[2] * and Changzheng Wu[1,3*]

[1] *School of Chemistry and Materials Science, CAS Center for Excellence in Nanoscience, University of Science & Technology of China, Hefei 230026, P. R. China.*

[2] *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China*

[3] *Institute of Energy, Hefei Comprehensive National Science Center, Hefei, China*

Keywords:

Neutral oxygen reduction reaction, zinc-air battery, density-functional theory, operando synchrotron radiation techniques.

The neutral oxygen reduction reaction (ORR) has attracted tremendous attention for its broad prospects in next-generation power storage systems. However, the extremely sluggish cathodic reaction process and the limited cognition of the reaction mechanism greatly hinder its practical application. Here, we demonstrate a dynamic reconstruction behavior induced by sulfur of the Fe-N_x species in neutral solution. Our developed FeS_1N_3-OH configuration effectively optimizes the reaction kinetics by regulating the adsorption energy of oxygen intermediates for central catalytic sites. Consequently, this structure exhibits over 363% enhancement in ORR mass activity compared to the pristine FeN_4 sites under neutral electrolyte. Moreover, a neutral zinc-air battery assembled with this electrocatalyst reached an ultrahigh peak power density (81.2 mW cm^{-2}), robust stability (more than 100 h) as well as superior tolerance to extreme environments (operating between -20 ℃ and 60 ℃), representing a critical breakthrough for neutral ORR exploration and application.

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*Corresponding author: e-mail address

Accelerating Variable Reaction Coordinate Transition State Theory (VRC-TST) Calculations Using Gaussian Process Regression (GPR)-based Surrogate Potential Energy Surface

Wenqi Chen[1], Xuefei Xu[1,*]
[1] Center for Combustion Energy, Department of Energy and Power Engineering, and Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

Keywords

variable reaction coordinate transition state theory, gaussian process regression, machine learning, barrierless reaction, rate constants.

The VRC-TST method (Klippenstein 1992), which serves as a benchmark methodology for treating loose transition states and calculating rate constants for barrierless reactions in the gas phase, often encounters significant computational costs in the Monte Carlo (MC) sampling of the long-range potential energy surface (PES), thereby limiting its applicability. In this work, an application of the GPR (Williams and Rasmussen, 2006) method for accelerating VRC-TST calculations is presented. By training on limited MC samplings, the GPR-based surrogate PES can describe well the long-range interaction between two species. Moreover, through this strategy, the number of explicit electronic energy calculations required for the VRC-TST is greatly reduced, and the barrierless reaction rate constants obtained by this strategy have a small average error from the reference values over a wide temperature range.

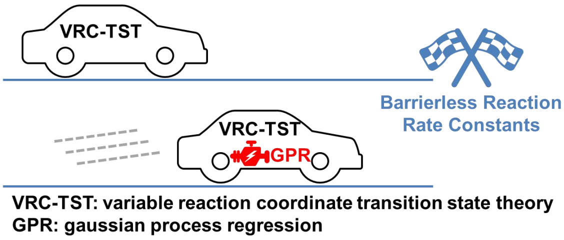

Fig. 1 Table of contents

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*Corresponding author: xuxuefei@tsinghua.edu.cn

Kinetics of Criegee Intermediate Relevant Reactions

Yang Chen[1], Haotian Jiang[1], Siyue Liu,[1] Jiayu Shi,[1] Yuqi Jin,[1] Xueming Yang[1,2,3] and Wenrui Dong[1,2*]
[1] Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, P. R. China
[2] Hefei National Laboratory, 96 Jinzhai Road, Hefei, P. R. China
3 Department of Chemistry, Southern University of Science and Technology, 1088 Xueyuan Avenue, Shenzhen, China

Keywords: Criegee Intermediate, Atmospheric effect, Laser-induced Fluorescence, reaction kinetics.

Alkenes in the atmosphere can react with ozone to form primary ozonide (POZ) and rapidly decompose to produce carbonyl compounds and Criegee Intermediates. (Criegee, 1975) Criegee Intermediates and their atmospheric implications have become a frontier research topic nowadays since they could oxidize many atmospheric pollutants as well as being one of the significant sources of OH radicals in the earth’s atmosphere. The reaction of Criegee intermediates in the troposphere significantly impacts the greenhouse effect and global climate.

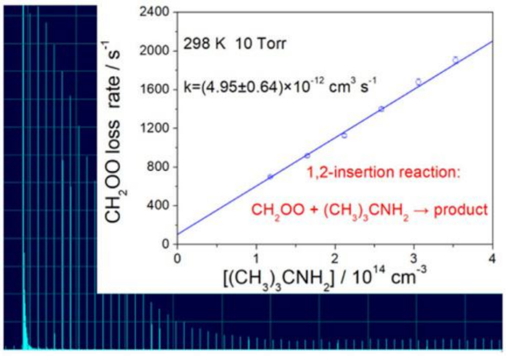

Figure 1. Loss rate of CH_2OO were plotted against the concentration of *tert*butylamine. (Chen et al., 2023)

We will present our recent work on Criegee Intermediates (CH_2OO and *syn*-CH_3CHOO) reactions with aldehydes and amines. The reactions in a flow tube were studied with laser-induced fluorescence method. The temperature- and pressure- dependent rate coefficients were measured, and the atmospheric effect of these reactions were discussed.

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*Corresponding author: wrdong@dicp.ac.cn

*Corresponding author: e-mail address

Mesokinetics as a Tool Bridging the Microscopic-to-Macroscopic Transition to Rationalize Catalyst Design

Wenyao Chen, Xuezhi Duan* and Xinggui Zhou
[1] State Key Laboratory of Chemical Engineering, East China University of Science and Technology,
Shanghai 200237, China

Keywords

Mesokinetics, Active site, Descriptor, Modeling, Mechanism.

Heterogeneous catalysis is the workhorse of the chemical industry, and a heterogeneous catalyst possesses numerous active sites working together to drive the conversion of reactants to desirable products. Over the decades, much focus has been placed on identifying the factors affecting the active sites to gain deep insights into the structure-performance relationship, which in turn guides the design and preparation of more active, selective, and stable catalysts. However, the molecular-level interplay between active sites and catalytic function still remains qualitative or semiquantitative, ascribed to the difficulty and uncertainty in elucidating the nature of active sites for its controllable manipulation. Hence, bridging the microscopic properties of active sites and the macroscopic catalytic performance, that is, microscopic-to-macroscopic transition, to afford a quantitative description is intriguing yet challenging, and progress toward this promises to revolutionize catalyst design and preparation.

In this regard, we propose mesokinetics modeling as a versatile tool to rationalize catalyst design. In comparison with the widely used microkinetics modeling that somewhat neglects the complexity of catalyst structure by the approximations in the description of an active site, mesokinetics modeling captures the active site characteristics and the related mechanistic information on a real catalyst to bridge the microscopic-to-macroscopic transition. We begin with the kinetics-based methodology to identify and quantify the number (N_i) of the dominating active site and the catalytic descriptor (d) for its quantitative determination of turnover frequency (TOF_i). Next, substituting the statistical correlations of N_i and TOF_i into the rate equation ($R = \Sigma N_i \times TOF_i$) offers the mesokinetics model, which links the microscopic properties of active sites with the macroscopic catalytic performance. Finally, based on the disentanglement of the factors underlying Pt electronic structures, we demonstrate a de novo strategy to map the unified mechanistic and kinetics picture of reaction based on the proposed mesokinetics modeling. Moreover, the developing trends of this mesokinetics

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*xzduan@ecust.edu.cn

Probing the kinetic sensitization effect of NO_2 on ethylene oxidation

Wuchuan Sun[1], Congjie Hong[1], Qian Zhao[1], Yingjia Zhang[1,]* and Zuohua Huang[1]
[1] Xi'an Jiaotong University, State Key Laboratory of Multiphase Flows in Power Engineering,
No.28 Xianning West Road, Shanxi, P. R. China

Keywords

C_2H_4, NO_2, Auto-ignition, Kinetic modeling, Sensitization effect.

Exhaust gas recirculation (EGR) has been widely equipped in current engines for pollutant emission abatement. NO_x present in EGR can greatly influence fuel combustion properties in engine operation. Ethylene (C_2H_4) is well-known a critical intermediate formed *via β*-scission reactions of alkyl radicals in the pyrolysis and oxidation of hydrocarbons, thus investigating the mutual effects of C_2H_4 and NO_x is beneficial to engine design as well as hierarchically developed strategy of chemical kinetic model. In *this study*, the auto-ignition behavior of C_2H_4/air mixtures doped with NO_2 (0 ppm, 200 ppm, 500 ppm, 3000 ppm) was investigated in a high-pressure shock tube at pressures of 1 atm and 24 atm, temperatures of 820 – 1300 K and different equivalence ratios of 0.5, 1.0 and 2.0. Pronounced promotion was observed with the addition of 200 ppm, 500 ppm and 3000 ppm NO_2 at the high pressure, while at low pressure, only limited effects were shown with the addition of 3000 ppm NO_2 in the temperature range of 1000 to 1177 K. A detailed kinetic mechanism was proposed based on the hierarchically developed strategy and modeling points of view. The proposed model was used to reproduce the measurements, with a good agreement between experimental data and model predictions over the entire test conditions. Flux and sensitivity analyses were then implemented to explore the sensitization effect of NO_2 addition on the ignition kinetics of C_2H_4. It was found that the additional $\dot{O}H$ radicals produced by new consumption routes of $\dot{C}H_2CHO$ radicals accelerated the oxidation of C_2H_4.

*Corresponding author: yjzhang_xjtu@xjtu.edu.cn

Dimeric Product of Peroxy Radical Self-Reaction Probed with VUV Photoionization Mass Spectrometry

Xiaofeng Tang
Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, China

Keywords

Peroxy radical (RO_2), Self-reaction, Dimeric product, Photoionization mass spectometry.

Organic peroxy radicals (RO_2) as key intermediates in tropospheric chemistry exert a controlling influence on the cycling of atmospheric reactive radicals and the production of secondary pollutants like ozone and secondary organic aerosols (SOA). In this talk, I will present our recent study of the self-reaction of alkyl peroxy radicals by using advanced vacuum ultraviolet (VUV) photoionization mass spectrometry in combination with theoretical calculations. A VUV discharge lamp and synchrotron radiations (Hefei, SOLEIL and the Swiss Light Source) are utilized as photoionization light sources in experiments. The dimeric product ROOR, as well as RO radicals, ROH and R_{-H}=O, formed from the self-reaction are clearly observed in photoionization mass spectra. Two kinds of kinetic experiments have been performed by either changing the reaction time or the initial concentration of peroxy radicals to confirm the origins of the products and to validate the reaction mechanisms. Based on the fitting of kinetic data with theoretically calculated results and the peak area ratios in the photoionization mass spectra, the branching ratio of the dimeric product is measured. In addition, the adiabatic ionization energy (AIE) of ROOR is determined in photoionization spectrum with the aid of Franck-Condon calculations and its structure is revealed. This study provides a new insight into the direct measurement of the elusive dimeric product ROOR and demonstrates its non-negligible branching ratio in the self-reaction of small RO_2 radicals.

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E-mail: tangxf@aiofm.ac.cn

Theoretical investigation on the mechanisms of naphthalene oxidation by hydroxyl radicals and oxygen in atmosphere

Xiaoqing Wu[1] and Feng Zhang[2,*]
[1]China Jiliang University, College of Information Engineering, 258 Xueyuan Road, Hangzhou, P. R. China
[2]University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China

Keywords: Naphthalene, Hydroxyl radical, Oxygen, Reaction kinetics, Branching ratio

Given the most abundant polycyclic aromatic hydrocarbon and its high secondary organic aerosol (SOA) yield, naphthalene has been identified as a major source of SOA in urban areas and downwind as supported by both model simulations and ambient observations. It's identified that naphthalene is primarily attacked by OH radical and then associate with O_2 to form the pivotal reactive intermediate—peroxyl radical (ROO). The complex mechanism during the atmospheric sink of naphthalene requires to be revealed by state-of-the-art statistical theories. In present work, the reaction kinetics of initial OH oxidation and subsequent O_2 oxidation was extensively studied using high-level quantum chemical methods (DLPNO-CCSD(T)/aug-ccpVQZ//M052x-D3/6-311++G(d,p)) combined with RRKM/master equation simulations. The reactions mainly proceed through electrophilic addition to the aromatic ring and H-atom abstraction from the aromatic ring of naphthalene by OH/O_2. The total rate coefficient of naphthalene + OH at ~300 K and 1 atm from our calculation (9.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) agrees well with previous measurements. The largest yield of add1 producing the major precursor of ROO from naphthalene + OH is computed to be more than 90% in the ambient environment. The dominant ROO from secondary reactions for intermediate add1 with O_2 is add1-OO-4cis (67%), which can be further oxidized to form 1,4-naphthoquinone, affecting the redox behavior and toxicity of ambient particles. Furthermore, the unimolecular reaction (cyclization and rearrangement) of ROO and their reactions with HO_2, NO and NO_2 are responsible for the formation of SOA. The detailed reaction kinetics information reported in this work is also useful for models to accurately capture the evolution of naphthalene-SOA and evaluate their climate effects.

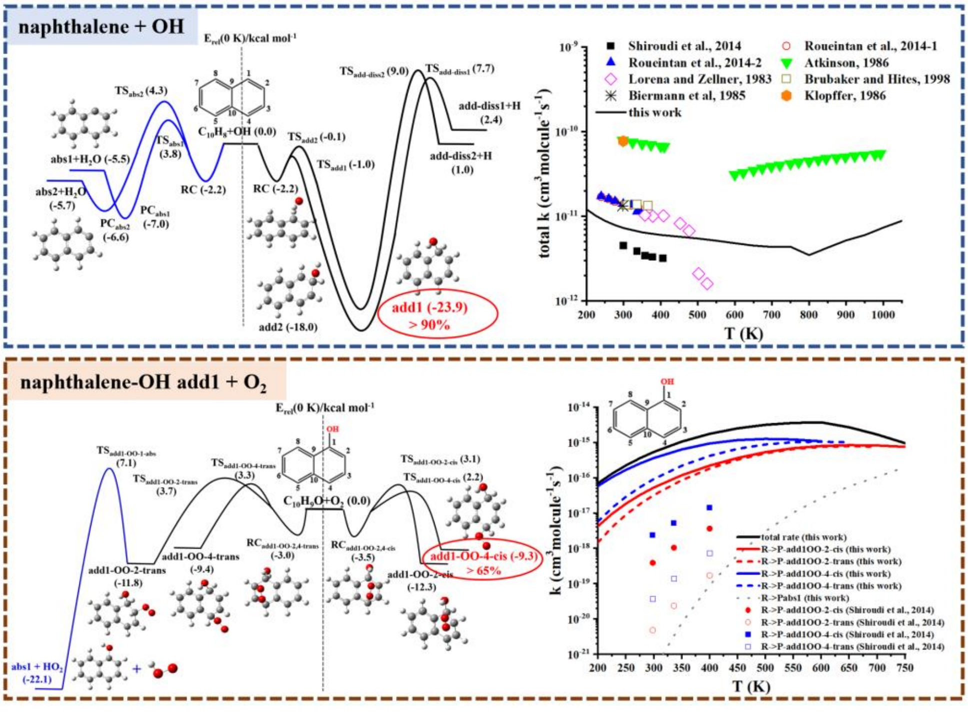

Fig. the potential energy surface of naphthalene + OH and naphthalene-OH add1 + O_2 by DLPNO-CCSD(T)/aug-cc-pVQZ// M052x-D3/6-311++G(d,p) (left); the comparison of rate coefficients from previous and present studies (right). Shiroudi et al., 2014: transition state theory (TST), CBS-QB3; Roueintan et al., 2014: relative rate technique (RR); Atkinson, 1986: RR; Lorena and Zellner, 1983: time resolved resonance fluorescence; Brubaker and Hites, 1998: gas chromatograph.

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*Corresponding author: feng2011@ustc.edu.cn

Effects of iron addition on soot formation characteristics

Xiaoqing You,* Yuxin Zhou, and Qingyan He
Center for combustion energy, Tsinghua University, Beijing, P. R. China

The effects of iron addition on soot formation are stuided in both premixed ethylene flames and ethylene pyrolysis in a laminar flow reactor by measuring particle size distribution, morphology, and chemical compostion. Ferrocene (~60 ppm in mole basis) was added in flames while iron (III) chloride ($FeCl_3$) (~10 ppm) was added in the flow reactor. In addition, to understand the experimental results better, the influence of iron addition on the coagulation of polycyclic aromatic hydrocarbon (PAH) clusters, the analogue of incipient soot particles, is further investigated using molecular dynamics simulations. It is found that the growth in soot particle size is promoted in both cases but for different reasons. Ferrocene addition promotes the growth in soot particle size due to enhanced particle coagulation, while the addition of $FeCl_3$ causes iron-containing particles to have an overall higher charge fraction, hindering the agglomeration of iron nuclei but promoting the formation of core-shell particles.

Keywords

Soot formation, Iron, Particle coagulation, MD simulation

*Corresponding author: xiaoqing.you@tsinghua.edu.cn

Direct Nonadiabatic Dynamics of Ammonia: An Example of Severe Population Leaking in Trajectory Surface Hopping Due to Long-Time Simulations and Frustrated Hops

Xiaorui Zhao[1,2], Yinan Shu[3], Linyao Zhang[4,*], Xuefei Xu[1,5,*], and Donald G. Truhlar[3,*]

[1] Center for Combustion Energy, Tsinghua University, Beijing 100084, P. R. China
[2] School of Aerospace Engineering, Tsinghua University, Beijing 100084, P. R. China
[3] Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455-0431, USA
[4] School of Energy Science and Engineering, Harbin Institute of Technology, Harbin 150001, P. R. China
[5] Department of Energy and Power Engineering, and Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Tsinghua University, Beijing 100084, P. R. China

Keywords

Nonadiabatic dynamics, trajectory surface hopping, frustrated hops, the fewest switches with time uncertainty algorithm, curvature-driven coherent switching with decay of mixing

Electronically nonadiabatic processes involving multiple electronic states are essential for understanding the behavior of molecules and materials upon electronic excitation. Mixed quantum–classical nonadiabatic dynamics is widely used to simulate the nonadiabatic processes, in which nuclear motion is treated classically while electrons are treated quantum mechanically (Jasper et al., 2004). Two main categories of mixed quantum-classical nonadiabatic dynamics algorithms are trajectory surface hopping (TSH) and self-consistent-potential (SCP) methods. In TSH, the trajectory propagates on a single potential energy surface interrupted by hops (Tully, 1990); in SCP, such as semiclassical Ehrenfest (SE) and coherent switching with decay of mixing (CSDM), propagation occurs on a mean-field surface without hops (Zhu et al. 2004). In this work (Zhao et al., 2023), we illustrate an example of severe population leaking in TSH, the nonadiabatic dynamics of ammonia - a typical photodissociation reaction. Such leaking is a combined effect of frustrated hops and long-time simulations that drive the final excited-state population toward zero as a function of time. We further show that the fewest switches with time uncertainty TSH algorithm (here implemented in the SHARC program) can alleviate this issue in a certain extent by greatly reducing the number of frustrated hops (Jasper et al., 2002). The population leaking is not present in CSDM methods. We also find good agreement of the original CSDM algorithm with its variants, time-derivative CSDM (tCSDM) and curvature-driven CSDM (κCSDM) (Shu et al., 2022), in both the ensemble electronic states population and the individual trajectory behavior, although in κCSDM only information on potential energies and gradients are needed for propagating trajectories.

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* Linyao Zhang: zhanglinyao1209@gmail.com
* Xuefei Xu: xuxuefei@tsinghua.edu.cn
* Donald G. Truhlar: truhlar@umn.edu

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* Linyao Zhang: zhanglinyao1209@gmail.com
* Xuefei Xu: xuxuefei@tsinghua.edu.cn
* Donald G. Truhlar: truhlar@umn.edu

Theoretical Kinetics of the Reactions HO + SO ↔ H + SO_2 on an Accurate Full-Dimensional Potential Energy Surface

Xiaoshan Huang[1], Jie Qin[1], and Jun Li[1*]
[1]School of Chemistry and Chemical Engineering & Chongqing Key Laboratory of Theoretical and Computational Chemistry, Chongqing University, China

Keywords

Potential energy surface; sulfur-containing reaction; RRKM theory; Master equation; Kinetic isotope effect

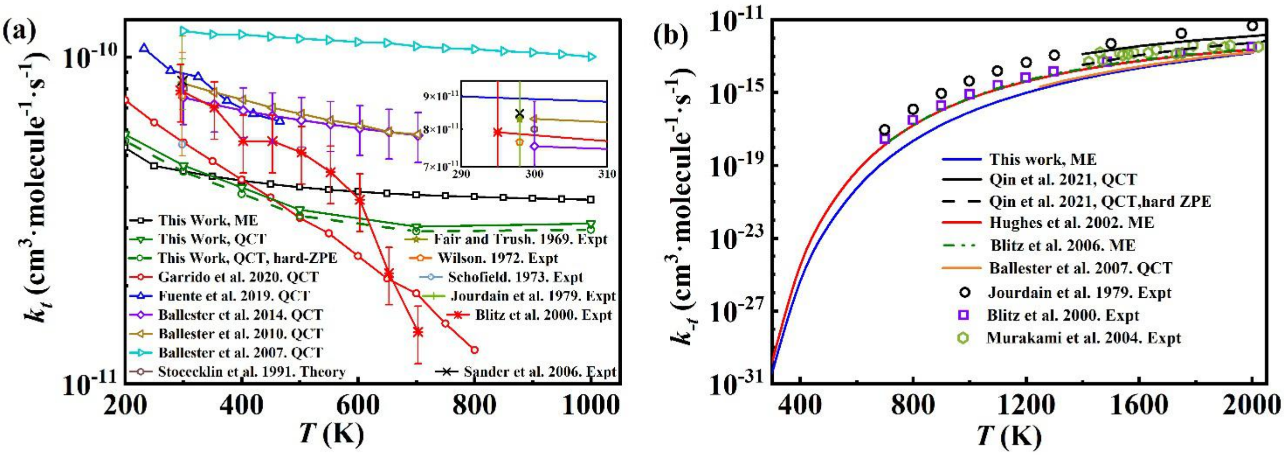

Figure 1. (a) Temperature dependent rate coefficients for the overall reaction Rt obtained by ME at 0.13 atm and QCT. (b) Rate coefficients determined by ME at 1 atm and QCT for the reaction R-t.

The gas phase reactions, HO + SO → H + SO_2 (R_t) and its reverse (R_{-t}) play an important role in environment and the combustion of sulfur-containing fuels. In this work, we report comprehensive theoretical kinetics of the reactions of R_t and R_{-t} based on a globally accurate full-dimensional potential energy surface (PES-2020) at UCCSD(T)-F12a/AVTZ level. This highly accurate PES-2020 is interfaced with the software Gaussian to obtain electronic structure information with very low time cost. The temperature- and pressure-dependent rate coefficients of title reactions are derived by the RRKM-based master equation with hindered rotor and free rotor model considered. Note that, the reaction precursor in the entrance channel of HO + SO system has never been considered in previous kinetics calculations. In addition, the effect of isotope substitution for the hydrogen is investigated on the reaction kinetics. Meanwhile, the quasi-classical trajectory (QCT) calculation is performed on the PES to obtain the temperature-dependent reaction kinetics. As shown in **Figure 1**, R_t is negatively related to temperature and slightly negative pressure dependent. For R_{-t}, the rate coefficients show positive temperature dependence and marginally negative pressure dependence.

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*Corresponding author: jli15@cqu.edu.cn

MAKING USE OF THE KINETIC INFORMATION FROM ReaxFF MOLECULAR DYNAMICS

Xiaoxia Li*[1,2], Mo Zheng[1,2], Shanwen Yang[1,2], Han Liu[1,2], Chunxing Ren[1]
[1] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P. R. China
[2] School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Keywords
ReaxFF molecular dynamics, Hydrocarbon fuel pyrolysis, Machine learning, Composition refinement, skeleton reaction exraction.

This presentation overviews the methodology development and applications of large scale ReaxFF MD in my group (Xiaoxia Li et al., 2021) to unravel pyrolysis reactions and kinetics of hydrocarbon fuel. The method combines high performance computing of GPU (graphics processing unit) for simulation and cheminformatics approach for reaction analysis from simulation trajectories. The GPU-enabled code (GMD-Reax) enables efficient simulation of fuel models ~10, 000 atoms on a single GPU. The unique tool of VARxMD (Visualization and Analysis of Reactive Molecular Dynamics) were developed to get the overall reaction list and reaction network with reaction site details.

The ReaxFF MD methodology was found useful in revealing the initial chemistry of soot nanoparticle formation in RP-1 oxidation and of pyrolysis for RP-1, RP-3 and JP-10 (Han Liu et al., 2022). Taking the advantage of a 45-component RP-3 model as a baseline, reactivity differences were unraveled between the real fuel and surrogate models of 3-component or 4-component for RP-3 in terms of weight loss and product yields of ethylene and propylene. The kinetic chemistry information of species concentration and weight loss obtained from ReaxFF MD simulations of hydrocarbon fuel pyrolysis are key to a new computational approach for evaluating reactivity differences of hydrocarbon fuels, which is also the very basis to refine the composition of RP-3 surrogate model with machine learning method (Song Han et al., 2020).

The machine learning based attempt for extracting the skeleton reactions from the massive detailed reactions of ReaxFF MD undergoing in my group (Shanwen Yang et al., 2022) should be a step forward to a new approach in building kinetic model fully on theoretical basis of ReaxFF MD for numerical engine simulation.

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*Corresponding author: xxia@ipe.ac.cn

Cl-initiated Oxidation Reactions of Nopinone and Methacrolein

Xiaoxiao Lin[1], Zuoying Wen[2] and Xiaofeng Tang[1,*]
[1] Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei, 230031 Anhui, China

Keywords

Chlorine radicals, nopinone, methacrolein, oxidation mechanisms, photoionization mass spectrometry.

The Cl-initiated oxidation reactions of nopinone ($C_9H_{14}O$) and methacrolein (MACR, C_4H_6O) under NOx-free conditions have been investigated in a fast flow tube by using a home-made vacuum ultraviolet (VUV) photoionization mass spectrometer complemented by high-level theoretical calculations. The key species such as intermediates and radicals together with products involved in the oxidation are observed online and confirmed in photoionization mass spectra. The reaction of Cl-initiated nopinone first undergoes a hydrogen abstraction channel to produce the radical $C_9H_{13}O$. After the addition of O_2, $C_9H_{13}O$ reacts with O_2 to produce product $C_9H_{12}O$ and the peroxyl radical $C_9H_{13}OO_2$. For the reaction of Cl + MACR, it starts to generate the C_4H_5O and C_4H_6OCl radicals via hydrogen abstraction and the addition of Cl atom to the C=C double bond, respectively. For the first time, the transient C_4H_5O and C_4H_6OCl radicals are experimentally detected. The C_4H_5O and C_4H_6OCl radicals can react with O_2 to produce the corresponding peroxy radicals $C_4H_5OO_2$ and $C_4H_6OClO_2$. Under low NOx conditions, these peroxy radicals will perform bimolecular reactions with themselves and the HO_2 radicals. Combined with theoretical calculations, the resulting specific products have been clearly identified in the photoionization mass spectra. Moreover, the time evolutions of products were measured by kinetic experiments and compared with theoretical model results.

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*Corresponding author: tangxf@aiofm.ac.cn

MACHANISM AND KINETICS OF PRYPYLENE EPOXIDATION BY H_2 AND O_2 ON Au-Ti CATALYSTS

Wei Du[1], and Xinggui Zhou[1,*]
[1] East China University of Science and Technology, State Key Laboratory of Chemical Engineering, 230 Meilong Road, Shanghai, P. R. China

Keywords

Kinetics, Tandem catalysis, Gold, TS-1, Propylene epoxidation.

Propylene oxide (PO) is a crucial chemical that finds extensive use in the production of polyurethane polyols, glycol ethers, dipropylene glycol, and other materials. The hydrogen and oxygen-driven propylene epoxidation (HOPO) process is an efficient, environmentally friendly, and highly selective method for PO production. Over the years, several Au-Ti bifunctional catalysts, including Au/TiO_2, Au/TS-1, Au/Ti-TUD, and Au/TS-1, have been developed for the HOPO reaction (Hayashi et al., 1998). Typically, the Au site is responsible for hydroperoxide species (HOOH and *OOH) formation, while the Ti site (isolated and tetracoordinated Ti species) is responsible for propylene epoxidation using the peroxides. The proximity of Au-Ti has been considered to be crucial for PO formation on Au/TS-1 (Harris et al., 2018).

For the catalyst with uncalcined TS-1 (TS-1-B), the Ti sites in close proximity to Au are only a small fraction of the total Ti sites, while the majority of Ti sites are positioned further away from Au. However, the role of the abundant remote Ti sites in PO formation is still unclear. We propose that these remote Ti sites catalyze epoxidation via a tandem mechanism that involves HOOH species migration in the gas-phase. To investigate this, we created a tandem catalyst (Fig. 1a) by physically mixing uncalcined S-1-B supported Au (Au/S-1-B) catalyst and uncalcined TS-1 (TS-1-B), which had fewer Au-Ti proximity sites. The catalytic performance of the tandem catalyst was comparable to that of the Au/TS-1-B catalyst (Fig. 1b), indicating that the tandem mechanism is also responsible for PO formation.

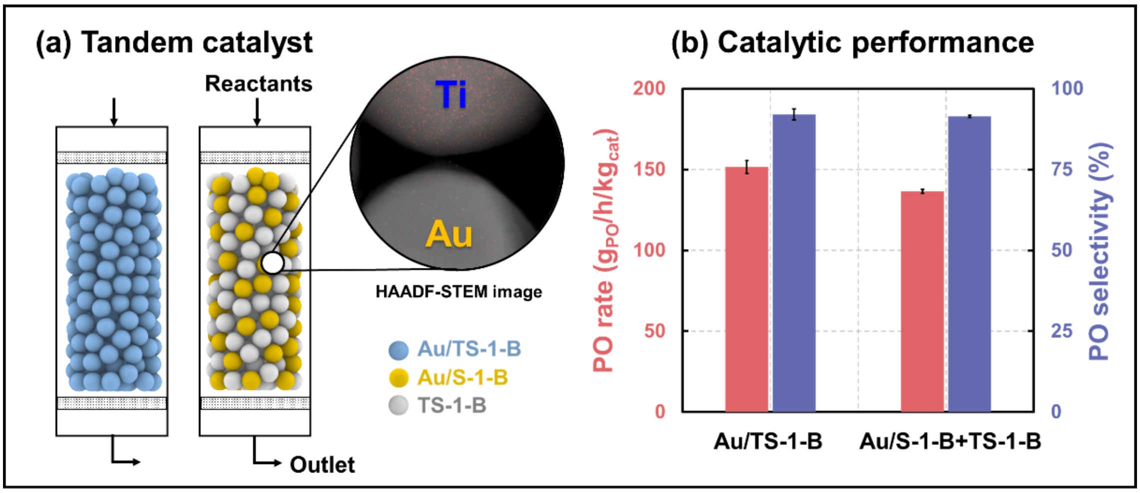

Fig. 1 (a) Supported catalyst (Au/TS-1-B) and tandem catalyst (physical mixture of Au/S-1-B and TS-1-B), (b) corresponding catalytic performance in PO formation.

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*Corresponding author: xgzhou@ecust.edu.cn

Moreover, the mechanism is clarified through a combination of the H_2/D_2 exchange experiment, in-situ diffuse reflectance infrared Fourier transform spectroscopy, and kinetic modeling. The experimental results are best explained by a kinetic model that incorporates both the tandem mechanism on remote Ti sites and the simultaneous mechanism on the Au-Ti proximity. The tandem mechanism is found to contribute more significantly to PO formation than the simultaneous mechanism on the Au/TS-1-B catalyst, which features Au nanoparticles on the external surface. However, on the Au/TS-1 catalyst with intraporous tiny Au clusters, PO formation is predominantly driven by the simultaneous mechanism (Fig. 2) due to the dissociation of HOOH species in the micropores.

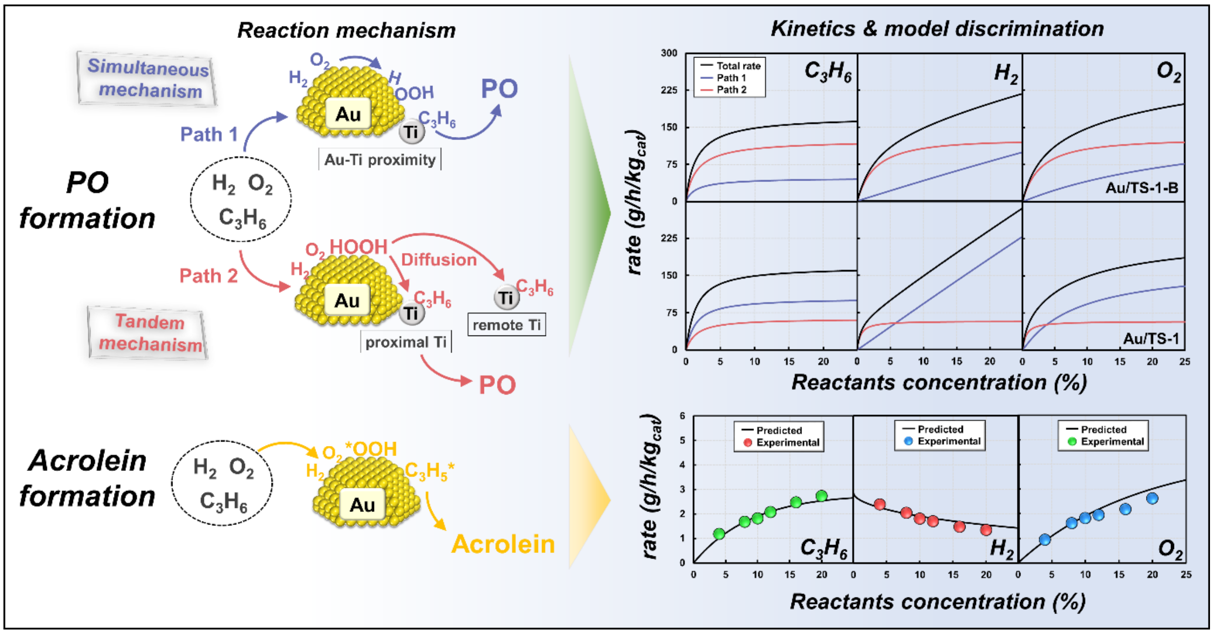

Fig. 2 PO and acrolein formation mechanism, and the formation rate of different paths calculated by reaction kinetics modelling.

Furthermore, the study also delved into the reaction mechanism of the primary byproduct, acrolein, using discrimination experiments and kinetic modeling. The kinetics model developed was able to accurately describe the experimental findings. This research sheds light on the role of remote Ti sites in PO formation and establishes a link between the kinetic behavior and Au location. These findings can guide the design of efficient tandem catalysts for the HOPO process, ultimately enhancing catalytic performance.

Acknowledges

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*Corresponding author: xgzhou@ecust.edu.cn

Theoretical Studies on Thermally Activated Delayed Fluorescence of Endohedral Fullerene

Xin-Xin Liu[1], Xin-Yi Guo[1], Wen-Kai Chen[2], Yuan-Jun Gao[1], Wei-Hai Fang[1], and Ganglong Cui[1,*]
[1] Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, Beijing Normal University, No. 19, Xinjiekouwai Street, Haidian District, Beijing, P. R. China
[2] College of Chemistry and Material Science, Hebei Normal University, No. 20, Road East. 2nd Ring South, Yuhua District, Shijiazhuang, P. R. China

Keywords

TADF, endohedral fullerene, TD-DFT.

Thermally activated delayed fluorescence (TADF) materials by virtue of making full use of both singlet and triplet state excitons, resulting in the internal quantum efficiency reach to 100% theoretically, has become one of the most promising luminescent materials. $Y_3N@C80$ with TADF phenomenon has a highly symmetrical carbon cage structure and delocalized π electron, showing unique luminescence properties, which also provide the possibility for fullerenes to be used as TADF materials in OLED and other fields. However, its microscopic luminescence mechanism remains elusive. Herein, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were applied to study the geometric and electronic structures, and spectral properties of $Y_3N@C80$. The calculation results show that the energy gap between S_1 and T_1 states is quite small, ca. 1.9 kcal/mol, which is easy to conduce to the open of intersystem crossing (ISC) and reverse intersystem crossing (rISC) channels. Meanwhile, appropriate spin-orbit coupling strength provides favorable condition for TADF. Subsequently, nonradiative (r)ISC rates, including all vibration modes and excluding one vibration mode, were calculated by the time correlation function method to explore the relationship between Huang-Rhys factor, vibration mode and rates. Our theoretical research reveals the TADF mechanism of $Y_3N@C80$ endohedral fullerene and establish important theoretical basis for designing new fullerene luminescent materials.

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*Corresponding author: e-mail address

Multi-Structural Torsional Anharmonicity Approximation for Thermodynamics and Kinetics Calculations of Complex Molecules with a Coupled Torsional Potential and Delocalized Torsions Using Redundant Internal Coordinates

Wenqi Chen[1], Pengchao Zhang[1], Donald, G. Truhlar[2], Jingjing Zheng[3,*], Xuefei Xu[1,*]
[1] Center for Combustion Energy, Department of Energy and Power Engineering, Tsinghua University, Beijing 100084, China
[2] Department of Chemistry, Chemical Theory Center, and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455
[3] Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 06492, USA

Keywords

Anharmonicity, Torsional potential, Multi-structures, Partition functions, Kinetics.

Single-structure harmonic approximation is often used for thermochemical and kinetic calculations. However, for complex molecules with multiple flexibly rotational single bonds, the potential anharmonicity of torsions and the multi-conformer anharmonicity caused by the internal rotations usually need to be considered for accurately calculations of partition function, thermodynamic functions, and/or kinetics based on transition-state-theory. It is very challenging to correct the multi-structural torsional anharmonicity because the torsions are usually strongly coupled with each other and/or with other non-torsional vibrational motions. Zheng and Truhlar (2013) developed a multi-structural method with torsional anharmonicity based on a reference coupled torsional potential (MS-T(C)) to properly correct torsional anharmonicity in both thermochemistry and kinetics calculations. The MS-T(C) has the advantage of balancing the computational costs and accuracy by including the couplings of normal modes without the calculations of the fully coupled many-dimensional torsional potential and the need for torsional assignments. One challenge in the MS-T(C) method is to define a set of well-chosen nonredundant internal coordinates to project coupled torsions for systems with a large number of conformers. Recently, based on the MS-T(C) method and the delocalized internal coordinates method developed by Baker et al. (1996), we proposed a new multi-structural method with torsional anharmonicity with a coupled potential and delocalized torsions (MS-T(CD)) in the redundant internal coordinate representation (Chen et al. 2022). The MS-T(CD) method can automatedly identify and separate the coupled torsions with a set of highly redundant primitive internal coordinates, and thus it circumvents the definition of nonredundant coordinates and simplifies greatly the MS-T calculations. More importantly, the MS-T(CD) method is conformer-independent so that it can give robust and consistent results. The MS-T(CD) method has been implemented in the *MSTor 2023* program calculating partition functions and thermodynamic functions of complex molecules with multiple torsions (Zheng et al. 2023).

*Corresponding author: xuxuefei@tsinghua.edu.cn

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*Corresponding author: xuxuefei@tsinghua.edu.cn

N-N bond fission dynamics of the N_2O^+ cation in the $C^2\Sigma^+$ state: competition between the NO^+ and N^+ fragment ion formation pathways

Yan Chen[1], Xiangkun Wu[2] and Xiaoguo Zhou[1,*]
[1] Department of Chemical Physics, University of Science and Technology of China, 96 Jinzhai Road, Hefei, P. R. China
[2] Paul Scherrer Institute, 232 Villigen, Switzerland

Keywords

Dissociation photoionization, TPEPICO, Velocity map image, N_2O.

The N-N bond fission is dominant for dissociation of N_2O^+ cation in the $C^2\Sigma^+$ state, producing two parallel fragmentation pathways of $NO^+(X^1\Sigma^+)+N(^2P)$ and $N^+(^3Pg)+NO(X^2\Pi)$. In addition to the well-studied former, the N^+ formation mechanism and dynamics remained unattended. Here we have performed a specific investigation on the N^++NO dissociation pathway from N_2O^+ cation in the $C^2\Sigma^+$ state using threshold photoelectron-photoion coincidence (TPEPICO) velocity map imaging, in comparison to our previous study of NO^++N channel. From the recorded N^+ images, the ro-vibrational populations of NO neutral fragments are derived for the different vibrational levels of $C^2\Sigma^+$, as well as the angular distributions. Unlike that only rotationally cold NO fragments are produced from the vibrationless $N_2O^+(C^2\Sigma^+)$ cations, some rotationally hot NO fragments are observed in dissociation of the vibrationally excited states like (1,0,0) and (0,0,1). With the aid of the calculated potential energy surfaces with the complete active space self-consistent field, the N^+ formation mechanism and ro-vibrational distributions of NO^+ fragment dissociated from the $N_2O^+(C^2\Sigma^+)$ cation are reasonably elucidated, and the influence of bending in the dissociation dynamics is considered.

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*Corresponding author: xzhou@ustc.edu.cn

Interfacial Charge-transfer Excitonic Insulator in a Two-dimensional Organic–inorganic Superlattice

Yang Liu[1,†], Hongen Zhu[1,†], Haifeng Lv[1,†], Yuqiao Guo[1,2,*], Yingcheng Zhao[1], Yue Lin[1], Xiaolin Tai[1], Jiyin Zhao[1], Bingkai Yuan[1,*], Yi Liu[2], Guobin Zhang[2], Zhe Sun[2], Xiaojun Wu[1], Yi Xie[1,2] and Changzheng Wu[1,2,*]
[1] University of Science and Technology of China, Hefei 230026, P. R. China.
[2] Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, P. R. China.

Keywords

organic–inorganic superlattice, excitonic insulator, charge density wave, metal-insulator transition.

Excitonic insulators are long-sought-after quantum materials predicted to spontaneously open a gap by the Bose condensation of bound electron-hole pairs, namely, excitons, in their ground state. Since the theoretical conjecture, extensive efforts have been devoted to pursuing excitonic insulator platforms for exploring macroscopic quantum phenomena in real materials. However, owing to the interference of intrinsic lattice instabilities, it is still debatable whether those features, such as charge density wave and gap opening, are primarily driven by the excitonic effect or by the lattice transition. Herein, we develop a novel charge-transfer excitonic insulator in organic–inorganic superlattice interfaces, which serves as an ideal platform to decouple the excitonic effect from the lattice effect. In this system, we observe the narrow excitonic gap, gap opening and the formation of a charge density wave without periodic lattice distortion, providing visualized evidence of exciton condensation occurring in thermal equilibrium. Our findings identify spontaneous interfacial charge transfer as a new strategy for developing novel excitonic insulators and investigating their correlated physics.

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Kinetic and mechanism studies of the gas-phase reaction of O_3 with diene

Chenyang Xue[1], Xuyang Yuan[2] and Yangang Ren[3,4,*]
[1] College of Marine and environmental Sciences, Tianjin University of Science & Technology, Tianjin, 300457, P. R. China
[2] Resources and Environment Innovation Research Institute, School of Municipal and Environmental Engineering, Shandong Jianzhu University, Ji'nan, 250101, P. R. China
[3] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences; Beijing, 100085, P. R. China
[4] University of Chinese Academy of Sciences; Beijing, 100049, P. R. China

Keywords

kinetic, mechanism, dienes, ozonolysis

Dienes, a fraction of non-methane hydrocarbons (NMHCs), are highly reactive because of their two carbon-carbon double bonds (C=C), which make them susceptible to participate in atmospheric reactions (Li et al., 2021 , Simayi et al., 2020 , Sharma et al., 2015). Ozonolysis is one of the important driving reactions to influence the fate of dienes in the atmosphere (Lewin et al., 2001 , Hua et al., 2008 , Khan et al., 2018). The ozonolysis of dienes would also inject a certain amount of carbonyl compounds, criegee intermediates, organic acids etc. into the troposphere, which lead to direct HO_x production and promote the secondary organic aerosol formation (Alam et al., 2013 , Hassan et al., 2021 , Ariya et al., 2000). In this work, the gas-phase reaction of ozone with a series of dienes including 1,4-hexadiene (1,4-HD), 3-methyl-1,3-pentdadiene (3M-1,3-PD), 3-methyl-1,2-butadiene (3M-1,2-BD), 1,2-pentadiene (1,2-PD) were studied at room temperature and atmospheric pressure. Firstly, their reaction rate constants were determined as 1,4-HD (106.18±0.53), 3M-1,3-PD (82.73±0.54); 3M-1,2-BD (3.88±0.23); 1,2-PD (2.10±0.22), in units of 10^{-18} cm^3 $molecule^{-1}$ s^{-1}, using absolute and relative method under 'OH-free' conditions. Then, their reaction mechanism was proposed based on the products investigation. This work will provide the first kinetic and mechanism studies of ozone reaction with 1,4-HD, 3M-1,3-PD, 3M-1,2-BD and 1,2-PD. The obtained data are discussed and evaluated to update the structure reactivity relationship of ozone reaction with alkenes.

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*Corresponding author: ygren@rcees.ac.cn

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*Corresponding author: ygren@rcees.ac.cn

Isotope effects in charge-transfer reactions: $Ar^{+}+H_2O/D_2O \rightarrow H_2O^{+}/D_2O^{+}+Ar$

Yaya Zhi[2], Qiang Guo[2], Jie Hu[1*] and Shanxi Tian[1,2*]
[1] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China
[2] Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China.

Keywords

Inverse kinetic isotope effect, Ion-molecule reaction, Ion velocity imaging, Charge transfer

Isotope effects is widely existed in the basic scientific researches of organic chemistry and astronomy chemistry, and also the applied fields of biomedicine and environmental monitoring, playing an important role in the substance evolution of these processes [1-3]. The H/D isotope effect is the key to reveal the origin of water in the earth [4]. Recently, we investigated the charge transfer reactions from Ar^{+} to H_2O/D_2O using our three-dimensional ion velocity map imaging apparatus. According to the product ion yields at different collision energies, the inverse kinetic isotope effect leading to the higher reaction rate of D_2O has been confirmed. The charge transfer products H_2O^{+}/D_2O^{+} is distributed at the forward energy resonance position, corresponding to the excited bending vibration of A^2A_1 state. By fitting the velocity distribution of H_2O and D_2O supersonic beams, it is found that D_2O has a lower rotation temperature, inducing more effective orientation during the approach process of Ar^{+} to water and more efficient excitation of the bending vibrational mode, leading to the higher reaction rate.

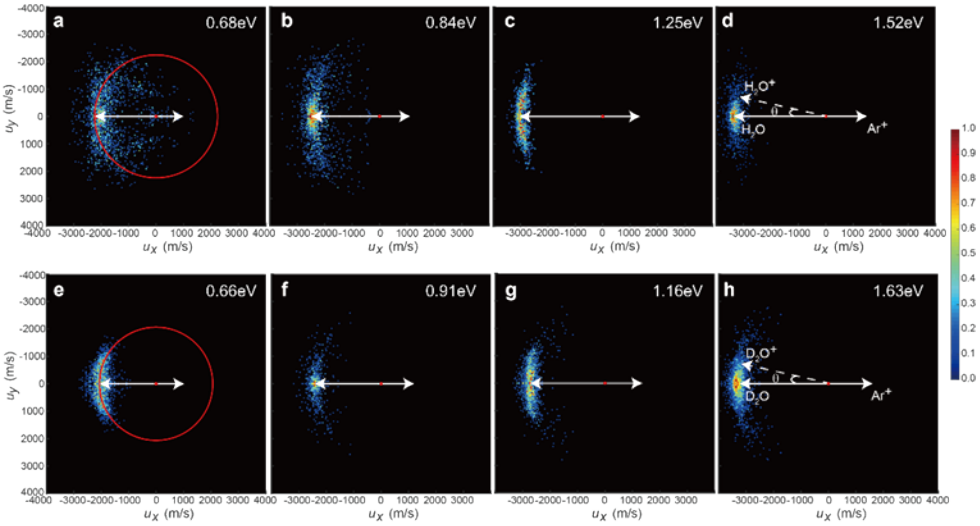

Figure 1: Ion velocity images of H_2O^{+}(upper half)/D_2O^{+}(bottom half) at different collision energies

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*Corresponding author: sxtian@ustc.edu.cn

High pressure real gas effects on predicting fundamental combustion properties of large hydrocarbon fuels

Yecheng Song[1], Wei Shen[1], Hangpeng Jiang[1], Kun Wang[1*]
[1]State Key Laboratory of Engines, Tianjin University,Tianjin 300350,China

Keywords

Supercritical combustion, Laminar flame speed, Real gas effects, Large hydrocarbon fuels.

To achieve high efficiency and low emissions, modern engines is being pushed to the high pressure near- or supercritical operating region. The combustion reaction of hydrocarbon fuels under high temperature and pressure conditions generates crucial real gas effects that alter basic combustion properties. To accurately simulate fuel combustion under high pressure, especially for large hydrocarbon fuels with higher critical temperature, it is critical to take the real gas effects into consideration. This study examines the impact of real gas effects on the fundamental combustion properties including ignition delay time and laminar flame speed, using two typical large hydrocarbon fuels, *n*-heptane and *n*-dodecane, as the examples, through accommodating thermodynamics and transport properties at high pressures. Implemented within the CANTERA kinetic modeling suite, the computational framework utilized in this study integrates real gas properties into a steady-state, freely propagating flame solver. The governing equations are closed using the cubic equation of state (EOS) to treat the thermodynamic data, which showed notable difference between the low- and high-pressure conditions. In high-pressure transport models, viscosity is described by the Lucas model, thermal conductivity is described by the Ely and Hanley model, and the binary diffusion coefficient is described by the Takahashi model. A comprehensive evaluation was conducted to reveal the real gas effects on fundamental combustion properties. Results indicate that real gas effect on ignition delay time is indeed correlated with pressure primarily through the change of thermodynamic data, and peaks in the negative temperature coefficient (NTC) region. Compared to ideal gas, the laminar flame speed decreases more rapidly with increasing pressure when the real gas equation of state (EOS) is employed, and this difference is largely attributed to the effect of high pressure on the specific heat of the mixture. Impact of transport properties on the laminar flame speed is primarily due to their influence on the flame's preheat zone rather than the reaction zone.

*Corresponding author: kwang5@tju.edu.cn

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*Corresponding author: kwang5@tju.edu.cn

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*Corresponding author: kwang5@tju.edu.cn

SPEEDING UP TURBULENT REACTIVE FLOW SIMULATION VIA DEEP ARTIFICIAL NEURAL NETWORK

Yi Ouyang [a], Laurien A. Vandewalle [a], Lin Chen [b], Pieter P. Plehiers [a], Maarten R. Dobbelaere [a], Geraldine J. Heynderickx [a], Guy B. Marin [a], Kevin M. Van Geem [a*]

[a] Ghent University, Laboratory for Chemical Technology, Technologiepark 125, 9052 Gent, Belgium
[b] AVGI, Technologiepark Zwijnaarde 122, 9052 Gent, Belgium

Keywords

Turbulent Reactive Flow Simulation, Artificial Neural Network, Lagrangian PDF Method, Turbulence-Chemistry Interaction, Sub-Grid Effect

Turbulent reactive flow simulation often requires accounting for turbulence-chemistry interactions and the sub-grid phenomena. Their complexity leads to a trade-off between computational efficiency on one hand and computational accuracy on the other. We attempt to bridge this gap by coupling the power of machine learning with the turbulent reactive flow simulation, specifically in the form of a deep artificial neural network. The Lagrangian Monte Carlo method is chosen as a demonstration case as it is one of the most accurate models for turbulent reactive flow simulation, but also one of the most time-consuming. The workflow consists of training data generation, deep neural network construction, and implementation in ANSYS-Fluent, followed by an evaluation of model accuracy and efficiency, which results in an order of magnitude faster simulation without loss of accuracy thanks to our data-driven deep neural network. This approach can be of universal relevance in speeding up time-consuming models in the field of reactive flow simulation.

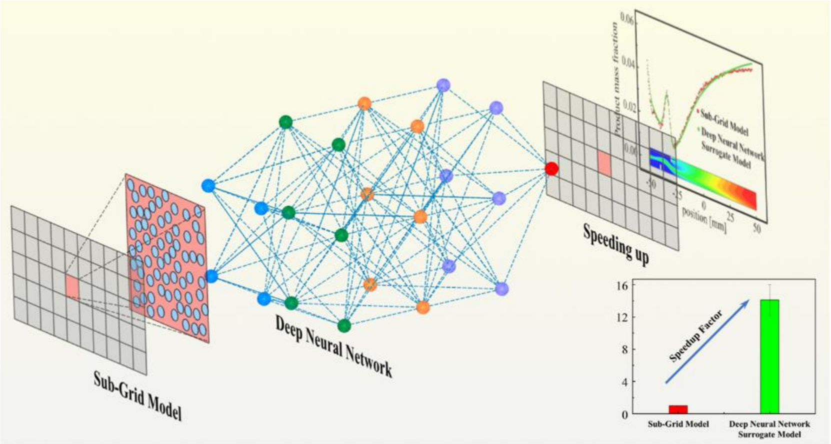

Figure 1: Framework of coupling Lagrangian PDF method and artificial neural network

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*Corresponding author: Kevin.VanGeem@UGent.be

Smart Modulation of Plasma Reactors with Physics Assisted Machine Learning Methods

Yifei ZHU*, Bo YIN and Yun WU
Xi'an Jiaotong University, Xi'an, China, P. R. China

Keywords

Plasma Chemistry, Plasma Modeling, Machine Learning

Smart modulation of the chemistry processes in low temperature plasmas is necessary to generate specific reactive species in an energy-efficient way. A physics corrected plasma + deep learning framework, the DeePlaskin, is proposed. This framework can be used for the nonequilibrium plasma systems that can be described by a global chemistry model (assuming global uniformity, e.g., in spark channels or the early afterglow of the fast ionization wave discharges). Knowing the kinetics scheme and the predefined temporal evolution of target species, we will be able to reconstruct the temporal profile of the reduced electric field E/N and all the other species. To generate the same concentration of O atom at the end of the discharge, the electric field profiles customized by the DeePlaskin differ significantly depending on the predefined evolution, resulting in different energy consumption. The combination of the deep learning method and plasma physics/chemistry model shows great potential in optimizing the design of plasma sources in practical applications. The DeePlaskin framework is further updated with the reinforced learning technique to make it easier for power source manufacturers to generate required voltage waveforms.

*Corresponding author: syjcoolr@163.com

Kinetics of light olefins production from municipal plastic waste using hierarchical HZSM-5: assessing deactivation by Cl

Yihan Wang, Mohammadhossein Havaei, Oğuzhan Akin, Parviz Yazdani, Robin John Varghese, Yi Ouyang*, and Kevin M. Van Geem*
Ghent University, Laboratory for Chemical Technology (LCT), Technologiepark 121, 9052 Gent, Belgium

Keywords

Municipal plastic waste, catalytic pyrolysis, intrinsic kinetics, hierarchical HZSM-5, chlorine.

Catalytic pyrolysis of municipal plastic waste for producing light olefins from municipal plastic wastes (MPW) is one of the most promising plastic recycling methods. However, large quantities of organic chlorine contained in MPW severely deteriorated the performance of catalysts. In this work, the Cl effects on catalytic product yield, intrinsic kinetics, and catalyst deactivation will be systematically discussed by conducting controlled experiments in a tandem micropyrolyzer and related characterization. The intrinsic kinetics of the catalytic reaction will be investigated by analyzing the reaction rate and activation energy using experimental data. With increasing Cl content, the yield of light olefins decreased, while the yields of aromatics and coke increased. The incorporation of Cl into the mesoporous-HZSM-5 framework led to a decrease in the ratio of strong/weak acid sites, resulting in a lower selectivity for light olefins. Based on this, a novel hierarchical HZSM-5 has been designed via the mesoporous introduction and surface functionalization to achieve higher catalytic activity and anti-poisoning properties. Ion exchange with noble metal Pt on HZSM-5 effectively improved the Cl-resistance, and meanwhile increased the light olefin yield. Further, the catalyst deactivation experiments revealed that mesoporous introduction and Pt ion exchange protected the acid sites and thereby decreased the coking yield. These findings offered a comprehensive understanding of the influence of Cl on intrinsic kinetics of plastic catalysis and provided a practical approach for the valorization of municipal plastic waste through innovative catalyst design.

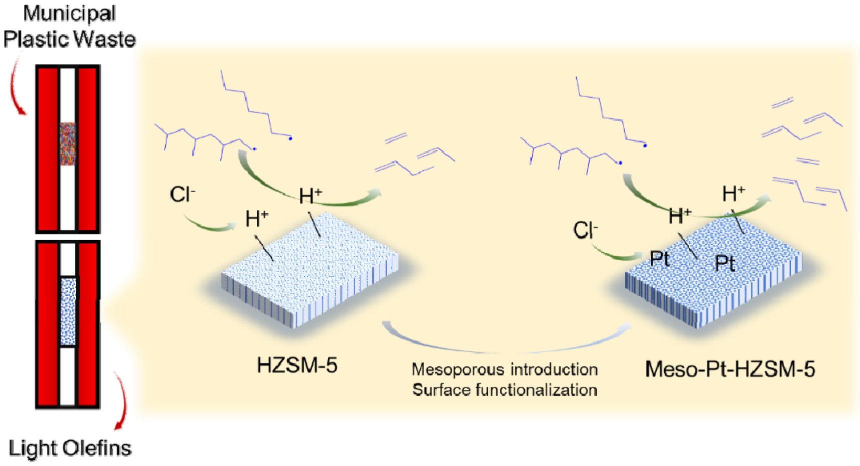

Figure 1: HZSM-5 modification for high-yield light olefins production from MPW

*Corresponding author: Yi. Ouyang@UGent.be, Kevin.VanGeem@UGent.be

Exemplar-based Clustering Algorithms for Experimental Datasets Using Affinity Propagation and Global Sensitivity Analysis

Yiru Wang[1,2], Keli Lin[1,2], Chenyue Tao[1,2], Chung K. Law[3] and Bin Yang[1,2,*]
[1] Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing, P. R. China
[2]Key Laboratory for Thermal Science and Power Engineering of MOE, International Joint Laboratory on Low Carbon Clean Energy Innovation, Tsinghua University, Beijing, P. R. China
[3] Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersy, 08544, USA

Keywords

Data clustering; Affinity propagation; Global sensitivity analysis; Uncertainty quantification.

The accuracy of combustion kinetics models is vital for investigating combustion phenomena and conducting numerical simulations in practical engineering problems. To diminish the uncertainty of model parameters, a significant factor affecting prediction accuracy, Bayesian methods are commonly employed for uncertainty constraints based on experimental data. However, with the rapid growth of experimental data, utilizing all data for optimization becomes redundant, time-consuming, and may result in data consistency issues. Consequently, this study introduces a novel method for clustering experimental datasets and selecting representative experimental conditions using affinity propagation [1] and global sensitivity analysis [2]. Initially, the global sensitivity coefficient is acquired through global sensitivity analysis to characterize the kinetic model's reactivity under various experimental conditions. The similarity coefficient, defined based on global sensitivity, is employed to indicate the similarity of model uncertainty sources between two experimental conditions. Through exchanging messages derived from similarity, affinity propagation allows the experimental dataset to be automatically clustered into several clusters without predefining the number of clusters. This method innovatively incorporates the consideration of model and experimental uncertainty under distinct conditions to achieve superior optimization results. The method's correctness and effectiveness are validated by clustering and optimizing a laminar flame speed dataset containing 288 conditions. The dataset is automatically clustered into 27 categories, with an exemplar provided for each category. These representative conditions reflect the dominant chemistry of their respective clusters while exhibiting larger model prediction uncertainty and smaller experimental uncertainty for improved Bayesian constraints. The uncertainty of model parameters is effectively constrained after Bayesian optimization, reducing the average uncertainty of model predictions across the dataset from 30% to 10% using only 27 exemplar conditions for optimization. In addition to selecting experimental data for model optimization, the clustering results offered by this method also aid in data classification and understanding the underlying chemical mechanisms.

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*Corresponding author: byang@tsinghua.edu.cn

Microkinetic analysis of the CO_2 effect on OCM over a La-Sr/CaO catalyst

Yonggang Cheng[1], Pedro S. F. Mendes[2], Parviz Yazdani[1] and Joris W. Thybaut[1,*]
[1] Laboratory for Chemical Technology, Ghent University, Ghent, Belgium
[2] Department of Chemical Engineering & Centro de Química Estrutural - IMS, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisbon, Portugal

Keywords

Heterogeneous catalysis, Mircokinetics, Oxidative coupling of methane, CO_2 effect.

La-Sr/CaO is a promising catalyst for oxidative coupling of methane (OCM) that offers a good trade-off between CH_4 conversion and C_2 selectivity. However, the catalyst is easily impacted by the presence of CO_2, which is believed to result in carbonates, negatively affecting the catalyst performance (Guan et al. 2021). In this work, the impact of CO_2 is analyzed by microkientic modeling, providing an in-depth and comprehensive understanding of the underlying mechanisms.

The microkinetic modeling is conducted employing an in-house developed code that has been demonstrated to perform adequately for a wide variety of OCM catalysts (Alexiadis et al. 2016). Experimental kinetics data have been acquired on a La-Sr/CaO catalyst both in the presence and in the absence of CO_2. Kinetic parameters, c.q., catalyst descriptors, have been determined for each of the two data sets, which are then compared and analyzed to understand the CO_2 impact on the catalyst and the corresponding mechanism.

The estimated values for the catalyst descriptors, which significantly differ in the presence or absence of CO_2, are summarized in Table 1, indicating CO_2 can exert pronounced effect on the catalyst properties. More specifically, in the presence of CO_2 in the feed, the active site density is decreased and so is the reaction enthalpy of H abstraction from CH_4. Simultaneously, the initial sticking probability of $CH_3\bullet$ on the active sites dramatically increases. I.e., all impacted values result in OCM becoming less favored/effective.

As pointed out by Choudhary and Rane, there are various types of active sites on the catalyst including acidic, amphoteric and basic sites. Among them, basic sites strongly interact with CO_2. As a consequence, strong CO_2 adsorption on these basic sites may render them unavailable for OCM reaction, thus, leading to the decrease in the density of active sites. At the same time, the catalyst reflects more acidic and amphoteric properties. Unsaturated hydrocarbons and/or radicals, such as $CH_3\bullet$, tend to strongly absorb on the active sites, which can be reflected in the significant increase in the initial sticking probability of $CH_3\bullet$. Additionally, the decrease in the reaction enthalpy of H abstraction from CH_4 suggests that the acidic sites on the catalyst induce a high activity in the continuous abstraction of H from hydrocarbons. However, it does not lead to the desired coupling products, as the acidic active sites typically promote the catalytic methane combustion instead of its oxidative coupling.

This work offers an insight into the impact of CO_2 from a microkinetics perspective and demonstrates the utility of microkinetics in understanding the underlying mechanism behind experimental observations. The La-Sr/CaO is impacted by the CO_2, leading the changes in catalyst properties, which can be reflected in the variations of the catalyst descriptors. Specifically, CO_2 easily adsorbs on the basic active sites that are responsible for C_2 production, making the OCM reaction less favored. The catalyst, therefore, mainly exhibits the properties of the remaining acidic sites which usually lead to full oxidation.

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* Corresponding author: Joris.Thybaut@UGent.be

Table 1: *Summary of the fitted kinetic parameters*

Kinetic parameters (unit)	without CO_2 co-feeding	with CO_2 co-feeding
Reaction enthalpy of H abstraction of CH_4 (kJ/mol)	18 ± 6	6 ± 2
Chemisorption enthalpy of O_2 (kJ/mol)	-371 ± 0	-371 ± 14
Chemisorption of CO (kJ/mol)	-303 (dropped)*	-142 ± 0
Chemisorption of CO_2 (kJ/mol)	-252 ± 14	-147 ± 17
Initial sticking probability of CH_3•	$(1.3 \pm 0.3)\times10^{-3}$	$(7 \pm 1)\times10^{-2}$
Density of active sites (mol/m^2)	11 ± 0	7 ± 2

*: The parameter is dropped because it induces rank deficiency. In the given context, a likely explanation is that the CO chemisorption is linearly correlated to CO_2 chemisorption.

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* Corresponding author: Joris.Thybaut@UGent.be

High accuracy and high efficiency rate coefficients calculations on high-fidelity PES: using Cl(^{2}P)+HCl→HCl + Cl(^{2}P) as an example

Yongle Li[1,*]
[1] Department of Physics, Shanghai University, 99 Shangda Road, Shanghai, 200444 P. R. China

Keywords
Reaction dynamics, PES, RPMD, rate coefficient.

We present a pair of ab initio globally accurate full-dimensional potential energy surfaces (PES) of Cl(2P)+HCl→HCl + Cl(2P) chemical reaction system based on MRCI-F12+Q/AVTZ level. One is fitted by permutation invariant polynomial neural network (PIP-NN) and another by embedded atomic neural network (EANN). The total root mean square errors (RMSE) are 0.043 kcal/mol and 0.056 kcal/mol respectively. Based on these high-fidelity PESs, the rate coefficients of the title reaction and two of its isotopic reactions, and corresponding kinetic isotope effects (KIE) are calculated by ring-polymer molecular dynamics with high efficiency Cayley propagator (Cayley-RPMD) and quantum dynamics (QD) using wave packet (WP) method, and compared with other theoretical and experimental results. Our computational results are in the best agreement with the experimental results, but as other theoretical results, the computational data deviate from the experimental ones at lower temperatures.

In this work, EANN is the first applied in gas-phase chemical reaction system. The method takes embedded atomic density as the input of neural network, and is expected to become one of the important ways for PES fitting of gas phase reaction systems in large systems. And a systematic thorough calculation of rate coefficients on both of new PESs is performed, confirming the kinetics of the title reaction.

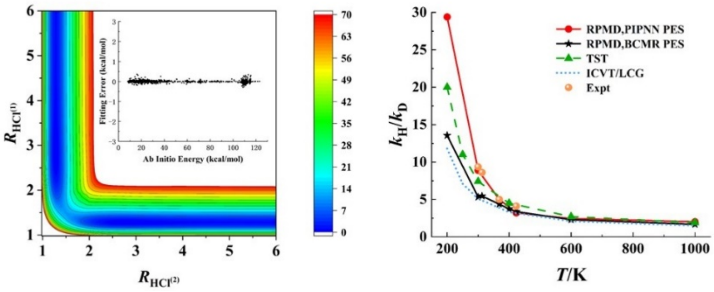

Figure 1: PES of the title reaction and KIE from RPMD compared with other theoretical methods and experimental result.

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*Corresponding author: yongleli@shu.edu.cn

Quantitative kinetics for the unimolecular reaction of several typical peroxy radicals

Yu Xia[1,2], Bo Long[3,*] Xiaofeng Tang[1,*] and Weijun Zhang[1]
[1] Anhui Institute of Optics and Fine Mechanics, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, Anhui, China
[2] Science Island Branch, Graduate School, University of Science and Technology of China, Hefei, 230026, Anhui, China
[3] College Materials Science and Engineering, Guizhou Minzu university, Guiyang, 550025, China

Keywords

Computation chemistry, Atmospheric chemistry, peroxy radicals, reaction kinetics

Organic peroxy radicals (RO_2) are of important intermediates in the atmospheric chemistry because their subsequent chemistry poses an influence on the cycling of the HO_x radicals, and the formation of ozone (O_3) and second organic aerosols (SOAs). The quantitative kinetics of organic peroxy radical are important for atmospheric modeling but still limited. Here, we use high-level theoretical methods to obtain quantitative rate constants for the unimolecular reaction of several typical peroxy radicals ($CH_3SCH_2O_2$, $HOCH_2CH_2O_2$, $CH_3CH_2O_2$, $CH_3C(O_2)O$ and CH_2O_2CHO). The high-pressure-limit rate constants have been calculated by using a dual-level strategy that combines high-level coupled-cluster theory with quasi-perturbative quadruple excitation's electronic structure for the conventional transition state theory calculations and canonical variational transition state theory with small-curvature tunneling based on a validated density functional. We aim to obtain quantitative kinetics of the unimolecular reaction of organic peroxy radicals and then try to find a general method to calculate other large size peroxy radical reaction.

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*Corresponding author: longbo@gzmuedu.cn, tangxf@aiofm.ac.cn

Application of a Heavy-atom Free Organic Fullerene Photosensitizer for Red-to-blue Light Fluorescence Upconversion

Yuanming Li[1], Jianhui Zhang[2], San-e Zhu[2,*], Shilin Liu[1], and Xiaoguo Zhou[1,*]
[1] Department of Chemical Physics, University of Science and Technology of China, 96 Jinzhai Road, Hefei, P. R. China;
[2] School of Energy, Materials and Chemical Engineering, Hefei University, 99 Jinxiu Avenue, Hefei, P. R. China.

Keywords

Photosensitizer, heavy-atom-free, triplet-triplet annihilation upconversion.

Pure organic heavy-atom free photosensitizers are essential for triplet-triplet annihilation (TTA) fluorescence upconversion, but few examples have been reported of successful red-to-blue implementation. Herein, we constructed a new TTA upconversion system using C_{70}-bodipy-triphenylamine triad (**C_{70}-BDP-T**) as a heavy-atom free photosensitizer with perylene as an acceptor and investigated its photophysical and photochemical properties utilizing steady-state and transient absorption spectroscopy. The experimental results show that the C_{70} group and the bodipy group can generate triplet state of photosensitizer (Φ_Δ = 78%) through an efficient charge transfer and recombination mechanism and eventually achieve a red-to-blue TTA upconversion with a quantum yield up to 10.4%. Notably, this is the highest yield to date for the application of heavy-atom free photosensitizers to achieve red-to-blue TTA upconversion.

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*Corresponding author: xzhou@ustc.edu.cn (X.G. Zhou)， zhuse@hfuu.edu.cn (S.E. Zhu)

Automated kinetics extraction and network generation for *n*-octane oxidation by ReaxFF molecular dynamics simulations

Xiao Yuanyuan[1,2], Zheng Mo[1,2,*], Li Xiaoxia[1,2,*]
[1]State Key Laboratory of Multiphase Complex Systems Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China,
[2]University of Chinese Academy of Sciences, No.19A Yuquan Road, Beijing, 100049

Keywords

ReaxFF MD, Reaction rate constants, skeletal network, reaction mechanism, hydrocarbon fuel pyrolysis and oxidation

N-octane is a major component for gasoline, and can be used as a model fuel for gasoline and diesel. Detailed research of the oxidation behavior is essential to improve the efficiency of current combustors and reduce the pollution species production. Large-scale ReaxFF molecular dynamics (MD) simulation is a promising method to reveal comprehensive reaction mechanisms for hydrocarbon fuels with reasonable accuracy and efficiency, which can be used to get an in-depth understanding of *n*-octane oxidation. However, obtaining kinetic parameters for each elementary reactions and generating the skeleton reaction network from the simulation results remain challenges for complex systems with a huge number of elementary reactions and species, which is necessary for getting the chemical kinetic model for numerical simulation of reactor. In this work, we aim to develop a strategy to extract the kinetics for elementary reactions of n-octane oxidation obtained from ReaxFF MD simulations of ~6000 atoms and construct a skeletal reaction network based on kinetic parameters, which cannot be accessible manually.

The approach consists of two major steps: (1) Calculating reaction rate constants automatically for each elementary reaction from n-octane oxidation system containing 10,000+ reactions; (2) Simplifying the comprehensive reaction pathways into a skeletal reaction network on basis of kinetic parameters. The relatively skeletal reaction network for *n*-octane oxidation with detailed kinetic parameters was obtained and shown in Fig.1. Particularly, the approach has the capability to reveal the time-dependent net reaction rate for all reactions during the whole simulation process, which provides new insight into the reactions and kinetics not included in the mechanism library or reported in literature. The findings of this study demonstrate the potential of the computational method of ReaxFF MD in obtaining kinetic data and advancing the understanding of reaction kinetics in fuel oxidation.

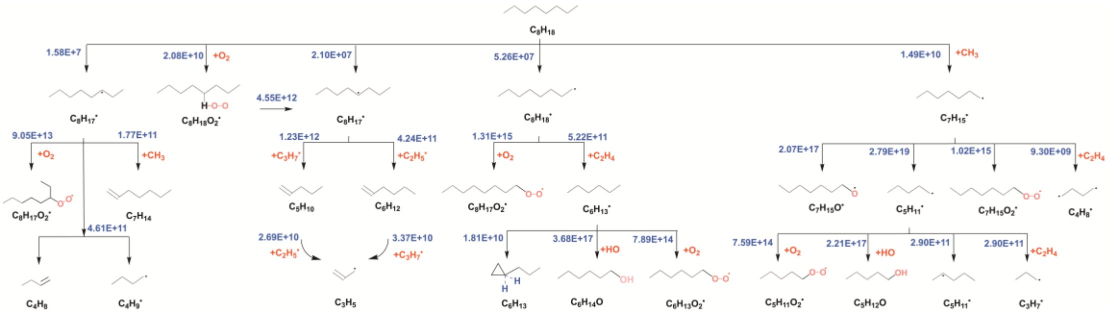

Fig. 1 A skeletal reaction network with rate constant parameters for the *n*-octane oxidation processes obtained from ReaxFF MD simulation at 2000 K and the develop strategy in this work (cm^3-mol-s-cal Units).

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The Catalytic Cracking of Methylcyclohexane over ZSM-5 Catalysts: A ReaxFF molecular dynamics

Yuyue Gao1, Quan Zhu1, 2*and Haisheng Ren1, 2*
1 School of Chemical Engineering, Sichuan University, Chengdu, 610065, P. R. China
2 Engineering Research Center of Combustion and Cooling for Aerospace Power, Ministry of Education, Sichuan University, Chengdu, Sichuan 610065, China;

Keywords

endothermic hydrocarbon fuel, catalytic cracking, ZSM-5.

Cracking of endothermic hydrocarbon fuel is an effective strategy to solve the thermal management of hypersonic aircraft, while catalytic cracking can promote fuel low-temperature cracking, improve fuel conversion and increase fuel heat sink[1,2]. In this work, methylcyclohexane(MCH) as a typical component of aviation fuel was adopted to learn the catalytic cracking reaction mechanism over zeolites catalyst models (i.e., ZSM-5, the hydrated ZSM-5 and the hydrated Al/ZSM-5). It was found that the MCH conversion was significantly improved compared with the participation of zeolite catalysts. Especially, the hydrated Al/ZSM-5 model exhibited the greatest catalytic activity and stability for the catalytic cracking of MCH molecules. Moreover, the hydrated Al/ZSM-5 model had a best product selectivity of C2H4 and C3H6. According to the analysis of reaction mechanism, the important reaction over the hydrated Al/ZSM-5 catalyst belonged to protonation, resulting in the generation of carbenium ions. Based on the theoretical calculation, the hydrated Al/ZSM-5 with the Bronsted acid sites can make the initial reaction stage more favorable for ring-opening of MCH through protonation than direct ring-opening. We hope that this work can provide a great significance for understanding the cracking process of hydrocarbon fuels and the selection of target products.

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*Corresponding author: e-mail address

Ab Initio Molecular Dynamics Simulations of the Structural Evolution of Cu Clusters Confined in (17,0) Carbon Nanotubes

Han Yurui[1], Fu Qiang[2, *] and Yang Jinlong[1, 2, *]
[1] University of Science and Technology of China, Key Laboratory of Precision and Intelligent Chemistry, 96 Jinzhai Road, Hefei, P. R. China
[2] University of Science and Technology of China, Hefei National Laboratory for Physical Sciences at the Microscale, 96 Jinzhai Road, Hefei, P. R. China

Keywords

Nano confinement effect, Copper cluster, Structural dynamic evolution, Ab initio molecular dynamics.

The nano confinement effect can alter the morphology and size of the catalyst by external spatial constraint, thereby achieving effective modulation of catalyst structure and properties at the microscopic level. A dynamic perspective on the structural changes of metal cluster catalysts in a nano-confined environment, especially when the clusters are at high local concentrations of reactant molecules, will help to improve the understanding of the microscopic processes and mechanisms of confined area catalysis. Copper (Cu) is a kind of metal catalyst for the deep reduction of CO molecules and has important application prospects. Based on density functional theory (DFT) calculations, we investigated the effect of the (17, 0) carbon nanotube confined space on the structure and CO adsorption properties of Cu_{18} clusters and compared the corresponding results with those of the graphene open space. We also have investigated the dynamic evolution behaviors of Cu_{18} clusters in the presence of high concentration of CO molecules by ab initio molecular dynamics simulations (AIMD). It was found that, in contrast to the weakened adsorption of reactant molecules caused by the nano-confined environment in the static perspective, the dynamic evolution reveals that the Cu_{18} clusters in the confined space exhibit a degree of enhanced adsorption of CO molecules instead. This change results from the further reconstruction of the Cu_{18} clusters triggered by the driven effect of CO molecules in the confined environment: CO tends to be adsorbed on only part of the Cu sites, leading to a significant increase in CO coverage in local regions of the cluster surface, which further enhances the reconstruction of the Cu_{18} clusters and their interaction with CO. However, a similar phenomenon does not occur in the open environment of graphene. We further investigated the application of the above effect to the C-C coupling reaction and found that it helps to facilitate the coupling step between CHO and CHO. This work has confirmed that the nano-confined effect can be used to modulate the structure and properties of metal cluster catalysts, and also provides some guidance for the theoretical design of CO reduction catalysts.

*Corresponding author: qfu3@ustc.edu.cn, jlyang@ustc.edu.cn

Research on Clean Efficient Ammonia Combustion Driven by Chemical Kinetics

Yuyang Li*
Institute of Aerospace Propulsion, School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China

Keywords

Ammonia, Combustion enhancement, Pollutant control, Kinetic model, Regulation strategy.

Ammonia, also called the other hydrogen, is well recognized as a promising carbon-zero fuel for a variety of energy and power devices, such as gas turbines, marine engines, industry furnaces, and boilers. However, the low combustion intensity and strong pollutant formation trend of ammonia greatly limits its practical applications. Here we reported our recent efforts to pursue clean efficient ammonia combustion with the help of combustion chemical kinetics. Oxygen enrichment (Mei et al., 2019), fuel co-firing (Mei et al., 2020), and fuel pre-cracking (Mei et al., 2021a) strategies were proposed to enhance the combustion intensity of ammonia, which greatly increased the laminar burning velocity of ammonia. Kinetic models were developed to either reproduce the combustion characteristics of ammonia or capture the enhancement performance. The modified fictitious diluent gas method was proposed to solve the challenges in quantifying the contributions of thermal effects and chemical effects to ammonia combustion enhancement. Besides, the pressure dependency of ammonia and ammonia/hydrogen flames was also found to be dramatically different from that of other low-carbon fuels, such as hydrogen and methane (Zhang et al., 2022). Fuel-NOx interaction was also explored with our recently proposed oxygen-free laminar flame propagation method (Mei et al., 2021b), which provides an extraordinarily sensitive reaction circumstance into specific kinetics involving fuel radicals and NOx under high-temperature combustion conditions. Further strategies were proposed to extend the stable combustion window and low emission window simultaneously. A gas turbine model combustor was adopted to verify the performance of proposed strategies. Future development in clean efficient ammonia combustion research is also suggested.

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*Corresponding author: yuygli@sjtu.edu.cn

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*Corresponding author: yuygli@sjtu.edu.cn

Quantification of hydroperoxides in the low-temperature oxidation of alkanes

Zhandong Wang
National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China
State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Abstract

Hydroperoxides are formed in the atmospheric oxidation of volatile organic compounds, in the combustion autoxidation of fuel, in the cold environment of the interstellar medium, and also in some catalytic reactions. They play crucial roles in the formation and aging of secondary organic aerosols and in fuel autoignition. In this report, the recent progress on the quantification of hydroperoxides in the low-temperature oxidation of alkanes is discussed.

Advanced synchrotron vacuum ultraviolet radiation photoionization mass spectrometry (SVUV-PIMS) is widely used for *in-situ* analysis of H_2O_2 and organic hydroperoxides formed in low-temperature oxidation. However, considerable uncertainty has been observed in the quantification of H_2O_2 by SVUV-PIMS, and the concentration of organic hydroperoxides is seldom measured, and typical estimates have large uncertainties.

This work first improves the quantification of H_2O_2 by re-evaluating its photoionization cross section (PICS). Spray vaporization, combined with a low pressure flow reactor, was used to minimize decomposition and wall loss of H_2O_2 in the PICS measurement. It was found that the PICS of H_2O_2 obtained here was lower than that reported in the literature by a factor of two. Adopting this newly obtained PICS significantly improved quantification of H_2O_2.

Furthermore, we developed a mild and environmentally friendly method for the synthesis of alkyl hydroperoxides (ROOH) with various structures, and we systematically measured the absolute PICSs of the ROOHs using SVUV-PIMS. A chemical titration method was combined with an SVUV-PIMS measurement to obtain the PICS of 4-hydroperoxy-2-pentanone, a typical molecule for combustion and atmospheric autoxidation ketohydroperoxides (KHPs). We found that organic hydroperoxide cations are largely dissociated by loss of OOH. This fingerprint was used for the identification and accurate quantification of the organic peroxides. This work will prove valuable in evaluating the reaction kinetics of H_2O_2 and organic hydroperoxides and the development of combustion and atmospheric autoxidation models.

Zhandong Wang (zhdwang@ustc.edu.cn)

INVESTIGATION OF THE OXIDATION AND DECOMPOSITION OF NITRATES AND NITRITES IN AN RCM

Zhaohan Chu[1], Wanxiong Liao[1], Zhongkai Liu[1] and Bin Yang[1,*]
[1] Center for Combustion Energy and Department of Energy and Power Engineering, Tsinghua University, Beijing, 100084, P. R. China

Keywords

Nitrates, Nitrites, Gas phase kinetics, RCM.

Nitrates and nitrites, which are two typical nitrogen-containing fuels, have been considered as potential propellants and additives for internal combustion engines. A comprehensive experimental and kinetic study was conducted to investigate the oxidation and decomposition of nitrates and nitrites. Ignition delay times and pressure profiles were measured using a rapid compression machine (RCM) under 5-8 bar at temperatures ranging from 550 to 600 K and varying concentrations of O_2. Time-resolved species profiles were recorded during the auto-ignition process and decomposition process using a fast sampling system combined with a gas chromatograph (GC). The results revealed that both nitrates and nitrites exhibit three-stage heat release behavior under specific conditions, with an auto-ignition phenomenon observed only during the nitrate fuel decomposition process. To better compare nitrates and nitrites, ignition delay times of amyl nitrate and amyl nitrite were measured, under 5-8 bar at temperatures from 580 to 600 K. Nitrates fuels are generally more active than nitrites. A detailed kinetic mechanism was constructed to predict the pyrolysis and oxidation behaviors of these fuels. The incomplete combustion has an impact on the total heat release. Nitrogen-containing intermediates participate in the combustion process, resulting in the three-stage heat release in oxygen-rich conditions. The "$NO – NO_2$ loop" is the primary pathway for OH formation in the studied conditions, which is mainly responsible for the first heat release phenomenon during the ignition period. Auto-ignition is caused by NO_2 acting as an oxidant during the decomposition process, which is unique to nitrate fuels. Small hydrocarbon molecules generated in the process of pyrolysis produce CO_2 through the oxidation reactions involving NO_2, $CH_3CO + NO_2 = CH_3 + NO + CO_2$, $HCO + NO_2 = H + NO + CO_2$. Compared with nitrites, nitrates fuels produce OH radicals more quickly through $H + NO_2 = NO + OH$, $HO_2 + NO = NO_2 + OH$.

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*Corresponding author: byang@tsinghua.edu.cn

Toward accurate and efficient microkinetic modeling in heterogeneous catalysis

Zheng Chen[1*] and Xin Xu[1,2*]
[1] Fudan University, Department of Chemistry, 2005 Songhu Road, Shanghai, P. R. China
[2] Hefei National Laboratory, 96 Jinzhai Road, Hefei, P. R. China

Keywords

microkinetics, KMC, time-scale separation, lateral interactions, syngas conversion

As a key part of the multiscale approach, microkinetic models are required to bridge the gap between atomic scale properties and macroscopic performance. However, an accurate and efficient microkinetic method is still lacking. On the one hand, the efficient and widely used mean-field microkinetics cannot accurately describe the intrinsic inhomogeneity of heterogeneous catalysis arising from adsorbate-adsorbate lateral interactions and nonuniform reaction sites. On the other hand, while Kinetic Monte Carlo (KMC) on the explicit lattice can account for such inhomogeneity, the disparity in time scales of various processes usually makes brute force KMC simulations impractical.

Recently, we have proposed a method, namely XPK, to extend the phenomenological kinetics (PK) for an accurate and efficient microkinetic modeling of heterogeneous catalysis. XPK is achieved through a hybrid between the diffusion-only KMC on an explicit lattice to evaluate the reaction propensities and later an implicit lattice KMC in the PK form to evolve the coverages and calculate the final rates.

XPK has been successfully applied to various important systems, including syngas conversion on the Rh(111) surface. Using this catalytic system as a representative, we show that it is the dynamic and intermediate-specific local coverage that controls the activity and selectivity instead of the average coverage, while a static and uniform model is unable to predict the selectivity under high pressure even qualitatively.

We conclude that XPK is a powerful tool for understanding catalytic phenomena and rationally designing catalysts.

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*Corresponding author: zhengchen13@fudan.edu.cn; xxchem@fudan.edu.cn

Toward accurate and efficient dynamic computational strategy for surface catalysis

Zhe-Ning Chen*, and Jun Chen*
State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P. R. China

Keywords: Dynamic strategy, Temperature-dependent thermodynamics and kinetics, Statistical sampling, Neural networks potential energy surface.

Computational tools on top of first principle calculations have played an indispensable role in revealing the molecular details, thermodynamics, and kinetics in catalytic reactions. Here we proposed a highly efficient dynamic strategy for the calculation of thermodynamic and kinetic properties in surface catalysis on the basis of efficient potential energy surface (PES) and MD simulations. Taking CO adsorbate on Ru(0001) surface as the illustrative model system, we demonstrated the PES-based MD can efficiently generate reliable two-dimensional potential-of-mean-force (PMF) surfaces in a wide range of temperatures, and thus temperature-dependent thermodynamic and kinetic properties can be obtained in a comprehensive investigation on the whole PMF surface. Moreover, MD offers an effective way to describe the surface kinetics such as adsorbate on-surface movement, which goes beyond the most popular static approach based on free energy barrier and transition state theory (TST). We further revealed that the dynamic strategy significantly improves the predictions of both thermodynamic and kinetic properties as compared to the popular ideal statistic mechanics approaches such as harmonic analysis and TST. It is expected that this accurate yet efficient dynamic strategy can be powerful in understanding mechanisms and reactivity of a catalytic surface system, and further guides the rational design of surface catalysts.

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*Corresponding author: znchen@fjirsm.ac.cn; chenjun@fjirsm.ac.cn

Simplification of mechanism and verification of combustion characteristics of Dimethyl ether at high pressure based on the DRGEPSA method

Lin Teng[a,b], Zhiwei Shan[a], Xigui Li[a] , Lijun Liao[a], Pengbo Yin[a,b,*]

[a] *College of Chemical Engineering, Fuzhou University, Fuzhou, 350116, China*

[b]*Qingyuan Innovation Laboratory (QYIL, Fujian Innovation Laboratory of Chemical Engineering), Quanzhou, PR China*
[*]*Corresponding author email: yinpengbo@fzu.edu.cn*

Abstract

In recent years, Dimethyl ether (DME) has been considered a promising alternative fuel for internal combustion engines and gas turbines owing to its unique physicochemical properties. However, the research on the combustion of dimethyl ether is not mature. There are still significant gaps, especially in the research on the combustion mechanism at high pressure. It is essential to develop a simple and accurate chemical kinetic mechanism to predict DME in familiar combustion environments such as gas turbines. In this study, the existing detailed mechanism of DME is simplified by using the method of DRGEPSA in the CHEMIKIN program. The reactions that strongly influence the combustion characteristics are then identified by sensitivity analysis, and the optimal skeleton mechanism is achieved by continuously adjusting the pre-finger factor. In the end, the data predicted by the simplified mechanism, such as ignition delay time (IDT) and laminar flame velocity, are compared with experimentation and detailed chemical kinetic models. A simplified kinetic model (Mech_191) was studied, and it turned out that it can favorably match the detailed mechanism and experiments (includes a wide range of operating conditions and environments for gas turbines and fast compressors T = 600-1650 K, p = 11-30 atm, φ = 0.3-2.0) with no more than 10% error rate. The ability of the simplified mechanism obtained by us to describe the combustion characteristics at high-pressure conditions is fully verified.

Keywords:

DRGEPSA; ignition delay time; laminar flame speed; sensitivity analysis

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Quantum Chemical Study on the Mechanism of Enzymatic (De)carboxylation of 2-Furanic Acid to 2,5-Furandicarboxylic Acid

Ziwei Liu[1], Xiang Sheng[1*]
[1] Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Keywords

Biocatalysis, 2,5-furandicarboxylic acid, prFMN, Reaction mechanism, decarboxylase, Quantum chemistry.

2,5-Furandicarboxylic acid (FDCA) is considered as a promising chemical for the synthesis of biodegradable polyester PEF. It can replace polyethylene terephthalate (PET), which is widely used at present. HmfF belongs to the UbiD family and can catalyze the (de)carboxylation of 2-furanic acid to FDCA. The mechanism of this reaction is still unclear. In this study, the quantum chemical cluster approach is used to reveal the detailed mechanism of HmfF reaction. The calculations showed that the substrate binds to the active site by the polar interaction with E259, H296 and Arg304, and also carbonyl oxygen of H296 interaction with H_2O. The reaction is proposed to occur via a 1,3-dipolar cycloaddition mechanism involving the formation of two C-C bonds between the substrate and the prFMN cofactor, rather than the nucleophilic attack mechanism involving the formation only of one C-C bond.

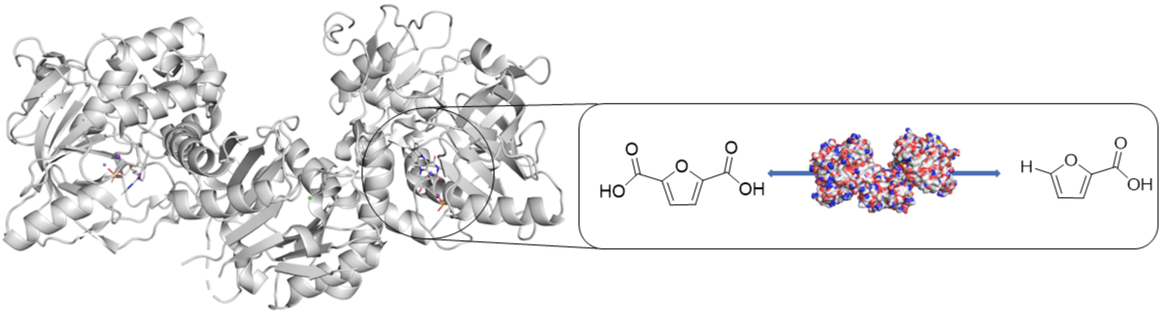

Figure. *Enzymatic Decarboxylation of 2,5-Furandicarboxylic Acid (FDCA) Yields 2 -Furoic Acid.*

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*Corresponding author: shengx@tib.cas.cn

Electron-Induced Synthesis of Dimethyl Ether in the Liquid−Vapor Interface of Methanol

Ziyuan Li[1] and Shan Xi Tian[1, *]
[1] Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, 96 Jinzhai Road, Hefei, P. R. China

Keywords

Alcohols, Chemical reactions, Interfaces, Ions, Liquids.

Reaction dynamics in the liquid–vapor interface is one of the crucial physical sciences but is still starving for in-depth exploration. It is challenging to selectively detect the interfacial species or the yields of chemical reaction therein. Using a liquid microjet (Chen et al., 2018; Chen et al., 2020) in combination with a pulsed electron beam, a linear time-of-flight mass spectrometer, and a quadrupole mass filter, we recently innovated time-delayed mass spectrometry (TDMS) for investigations of chemical reactions in the liquid–vapor interface (Li et al., 2022).

Using this apparatus, it is found that the dimethyl ether is spontaneously synthesized in the liquid-vapor interface of pure methanol though protonation after electron irradiation (Li et al., 2022). Figure 1(a) shows the two-dimensional (Δt–TOF) time-delayed mass spectra of the liquid beam of methanol, $(CH_3)_2OH^+$ (the protonated dimethyl ether) yields at TOF $\approx 40\ \mu s$ and the hydrogen-bonded cluster $[CH_3OH \cdots (CH_3)_2OH^+]$ around a TOF of 55–62 μs is identified. Two different processes for producing $[CH_3OH \cdots (CH_3)_2OH^+]$ were proposed: one is the methyl transfer reaction of the protonated trimer in the outermost layer, as described in Figure 1(b), and the other is a similar reaction in the inner region (i.e., the subsurface).

It is well known that ether can be synthesized from two alcohol molecules by acid-catalyzed dehydration (Azizi et al., 2014) .According our study, the dimethyl ether can be produced due to local interfacial acidification by electron impacts. With further research, the molecular level mechanism of chemical reactions in the liquid–vapor interface can be gradually established.

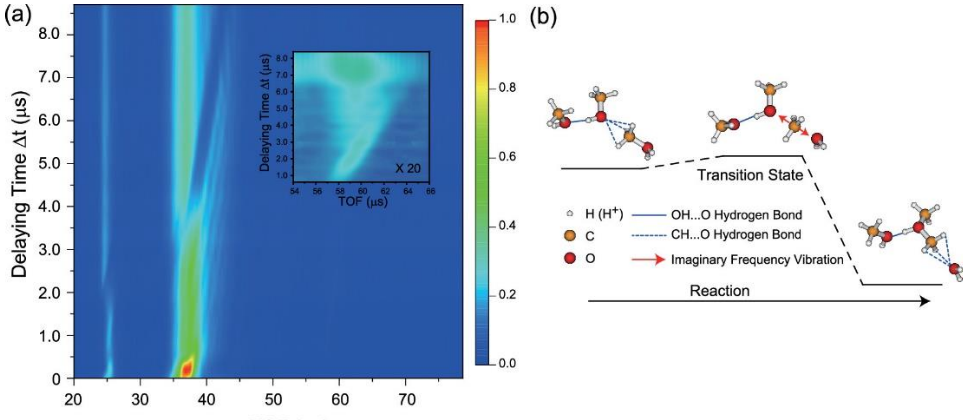

Figure 1. (a) Two-dimensional time-of-flight mass spectra of the liquid beam of methanol obtained at an electron energy of 22 eV and (b) an energy diagram of the interfacial reaction of the protonated trimer.

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*Corresponding author: sxtian@ustc.edu.cn

Chemical kinetic modeling of nitric oxide reduction in the presence of methane and other hydrocarbons

Á. Veres-Ravai, I. Gy. Zsély* and T. Turányi
Institute of Chemistry, ELTE Eötvös Loránd University, Budapest, Hungary

Keywords: NOx reburning; detailed mechanisms; mechanism testing; mechanism development.

Nowadays, conversion of nitrogen oxides to species that are unharmful for the environment has become particularly important due to increasing industrial activities. One elimination technique of NO_x is the well-known NO_x reburning process (Wendt *et al.*, 1973). The reduction process includes the conversion of nitric oxide to HCN by hydrocarbon fuel injection leading the conversion of nitrogen to N_2 through several intermediates. This complex reaction involves a large number of elementary reactions. The long-term goal of our research is to create a more accurate, optimized reaction mechanism by describing the conversions of nitrogen compounds better. The first part of this work is the quantitative comparison of existing reaction mechanisms using experimental data. In our research, the performances of 7 recently developed reaction mechanisms including hydrocarbon and reburning chemistry were compared. For this purpose, a great amount of experimental data was collected from the literature focusing on publications in which methane, ethane, natural gas, ethene, acetylene, propane or their mixtures were used as reburning fuel. The experiments cover species concentration measurements in jet-stirred reactor (JSR), flow reactor (FR) and burner-stabilized flames in wide ranges of equivalence ratio and temperature. The published data were encoded in ReSpecTh Kinetic Data format (Varga *et al.*, 2022) XML files. At the conditions of all these experiments, chemical kinetic simulations were performed using the 7 reaction mechanisms with program Optima++ (developed by our research group) (Papp *et al.*, 2022) and solver OpenSmoke++ (Cuoci *et al.*, 2015). Performances of the models on reproducing experimental data were analyzed according to experiment types and conditions using quantitative measures. Models could describe burner-stabilized flame measurements very well, jet-stirred reactor measurements also well for most cases, but the reproduction of experimental data for several flow reactor measurements was quite bad. The simulation results for JSR and FR measurements can be sensitive to the temperature used in the calculations, so the effect of experimental temperature uncertainty on mechanism performance was also analyzed in detail. As a result of this work, the POLIMI-2019 mechanism (Song *et al.*, 2019) showed the best-performance. Local sensitivity analysis was carried out with this model on the pre-exponential factors and the most important reactions were identified. The results were compared with the few sensitivity analysis results found in the literature.

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*Corresponding author: e-mail address